The Thole Linear (TL) and Thole-Amoeba-like (TA) Dipole Interaction Models

For a collection of N point polarizable dipoles placed in a homogeneous electric field E, the induced dipole moment at point p (μ_p) is calculated by Eq. 1, where α_p is the atomic polarizability and T_{pq} is the dipole field tensor which is calculated with Eq. 2.

$$\mu_p = \alpha_p[E_p - \sum_{q \neq p}^{N} T_{pq}\mu_q] \qquad (1)$$

$$T_{pq} = \frac{f_e}{r_{pq}^3}I - \frac{3f_t}{r_{pq}^5}\begin{bmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z_2 \end{bmatrix} \qquad (2)$$

Where I is a unit matrix and f_e and f_t are the distance-dependent screening functions introduced by Thole to avoid the "polarization catastrophe" when two inducible dipoles approach to each other.[1,2]

For the TL model, f_e and f_t take a linear functional form:

$$v = r_{pq} / \left[k(\alpha_p\alpha_q)^{1/6} \right]$$
$$if(v >= 1) f_e = 1.0, f_t = 1.0 \qquad (3)$$
$$if(v < 1) f_e = 4v^3 - 3v^4, f_t = v^4$$

In the TA model, f_e and f_t take an exponential form:

$$v = r_{pq} / \left[k(\alpha_p\alpha_q)^{1/6} \right]$$
$$f_e = 1 - \exp(-v^3) \qquad (4)$$
$$f_t = 1 - (v^3 + 1)\exp(-v^3)$$

Where α_p, α_q are the atomic polarizabilities of atoms p and q, respectively; k is the screening factor, and r_{pq} is the distance between atoms p and q. The TA model is used in Amoeba force field.[3,4] Please note that the formula in Eq. 4 differs from those in Thole and Ren and Ponder's works. In our case we obtained $k = 1.6209$ for the TA model by fitting to the high-level QM data in our earlier work.[5] This is equivalent to 0.2348 when the formula is converted to those in Thole and Ren and Ponder's works and is smaller than 0.572 in Thole's work and 0.39

in Ren and Ponder's work, respectively. For TL model, our screening factor $k = 2.5874$, larger than 1.662 obtained by Thole.
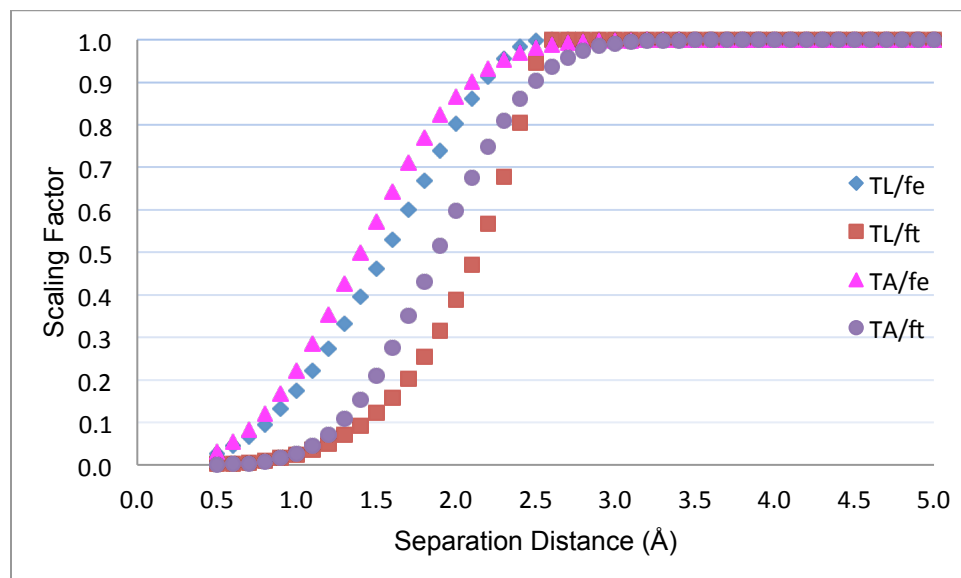

Figure S1. Screening effect of two Thole polarizable models for atomic pairs C_{sp3}-C_{sp3} as a function of separation distance. The screening functions, fe and ft for the two polarizability models (TL and TA) are defined in the supporting material. When two atoms approach to each other, to avoid "polarization catastrophe" the dipole interaction between two is scaled down. The smaller the scaling factor, the larger the screening effect is. It is demonstrated that when the separation distance is smaller than 2.5 Å, TL model has larger screening effect than the TA model.

References

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