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1.1 Determination of ε and r_0 parameters of V_{nel}

Extending to the Improved Lennard Jones formulation some guidelines described in Refs. 29 and 30 of the manuscript (see also F. Pirani et al., Int. Rev. Phys. Chem. 2006 **25** 165-199), the C_6 coefficient (in meV Å^6) for a given A-B pair interaction can be calculated through the following semiempirical equation,

$$C_6 = 11300 \frac{\alpha_A \alpha_B}{\left(\frac{\alpha_A}{N_{eff_A}}\right)^{1/2} + \left(\frac{\alpha_B}{N_{eff_B}}\right)^{1/2}} \quad (1)$$

where α_A and α_B (in Å^3) are the effective polarizabilities associated to the interaction groups, whose values are compatible with the total molecular polarizability. In our study, α_{CH_3}=2.21, α_{OH}=0.98 and α_{H_2O}=1.47 have been used. N_{eff_A} and N_{eff_B} are the number of electrons participating to the polarization of groups A and B, respectively. In our study, values of N_{eff} equal to 7.35, 5.0 and 6.0 for CH_3, OH and H_2O, respectively, have been adopted as proper values.

ε (in meV) is related with C_6 through the following equation,

$$\varepsilon = \frac{C_6}{r_0^6} \quad (2)$$

The r_0 parameter is calculated taking into account many body contributions to the balance of repulsion and attraction, operative between interacting neighbour groups in polyatomic molecules (as for instance CH_3 and OH in the methanol molecule). For such reason we use polarizability components representing an effective size increase of each partner (α'). Accordingly, r_0 (in Å) is expressed by,

$$r_0 = 1.767 \frac{(\alpha'_A)^{1/3} + (\alpha'_B)^{1/3}}{(\alpha'_A \alpha'_B)^{0.097}} \quad (3)$$

In our study, for CH_3OH, the values of α'_{CH_3}=2.60 Å^3 and α'_{OH}=1.30 Å^3 taking into account the many body contributions to the repulsion, have been considered, while for the smaller H_2O, for which only one interaction center has been considered, $\alpha'_{H_2O} = \alpha_{H_2O}$=1.47 Å^3 is the simple global molecular polarizanbility.

Table 1 Cartesian coordinates (Å) and punctual charges (a.u.) calculated in vacuo and in solvent.

Atoms	x	y	z	$q_{invacuo}$	$q_{insolvent}$
C	-0.045624	0.653500	0.0	0.238935	0.261339
O	-0.045624	-0.744428	0.0	-0.692643	-0.768162
H	-1.076814	0.975862	0.0	0.048408	0.040016
H	0.439103	1.060649	0.882635	-0.010685	0.000654
H	0.439103	1.060649	-0.882635	-0.010685	0.000654
H	0.837346	-1.064238	0.0	0.426670	0.46452

On the top panel of the figure, where the evolution of the distance from the O atom of water and the H atom of the OH group of methanol is represented along the trajectory, it can be observed that at the beginning of the simulation, methanol acts as a H-donor. Earlier, after about 0.2 ns from the beginning of the simulation, frequent isomerizations are observed. Such dynamical behavior can be also interpreted from the middle and lower panels of the Figure. In fact, the middle panel of the figure shows that the distance from the O atom of methanol and one of the H atoms of water, oscillates from values lower than 2.0 Å to values higher than 4.0 Å, indicating that, along the trajectory, water acts as a H-donor and as H-acceptor. Such behavior is also reflected in the lower panel of the figure where the angle γ takes values in the 0°-180° range.

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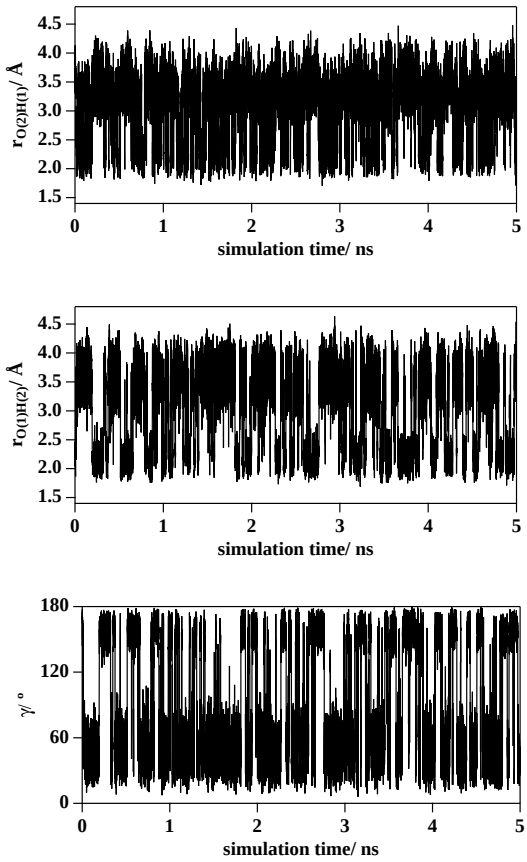

Figure 1 Evolution of the distance from the O atom of water and the H atom of the OH group of methanol (top panel), of the distance from the O atom of methanol and one of the H atoms of water (middle panel) and of the angle involving the OH bond of methanol and the O atom of water, represented by γ (lower panel) along a MD simulation performed at T= 185 K.

Table 2 Number of molecules of CH_3OH (N_{CH_3OH}) and of H_2O (N_{H_2O}) and fraction molar of methanol (x_{CH_3OH})

N_{CH_3OH}	279	578	861	1144	1405	1661	1936	2209	2472
N_{H_2O}	2465	2166	1883	1600	1339	1083	808	535	272
x_{CH_3OH}	0.102	0.211	0.314	0.417	0,512	0.605	0.705	0.805	0.901