Supplementary Material

Force-field Bonding Parameters

Table 1 - Bond angles, lengths and their associated force constants for 2,4-DNEB

angle label	angle (°)	angle force constant kcal mol^{-1}	bond label	bond length (Å)	bond force constant kcal mol^{-1}
C1-C2-C3	118.3	45.845	C1-C2	1.381	396.060
C1-C2-H1	120.9	17.794	C1-C6	1.389	309.486
C1-C6-C5	118.7	47.814	C1-N2	1.475	147.446
C1-C6-H2	119.7	17.048	C2-C3	1.388	315.792
C1-N2-O1	117.3	46.273	C2-H1	1.077	350.855
C1-N2-O2	117.6	44.336	C3-C4	1.402	321.522
C2-C1-C6	121.4	43.961	C3-N1	1.479	110.392
C2-C1-N2	119.0	37.416	C4-C5	1.402	358.459
C2-C3-C4	122.9	47.000	C4-C7	1.510	193.014
C2-C3-N1	115.4	48.531	C5-C6	1.384	338.068
C3-C2-H1	120.8	17.266	C5-H6	1.081	339.334
C3-C4-C5	116.0	39.872	C6-H2	1.079	349.463
C3-C4-C7	125.8	37.907	C7-C8	1.538	113.742
C3-N1-O3	117.8	54.335	C7-H3	1.089	307.316
C3-N1-O4	117.2	37.037	C8-H4	1.089	320.433
C4-C3-N1	121.6	45.817	C8-H5	1.090	103.472
C4-C5-C6	122.6	54.708	N1-O3	1.225	505.821
C4-C5-H6	118.3	17.569	N1-O4	1.223	524.178
C4-C7-C8	112.9	37.238	N2-O1	1.225	518.364
C4-C7-H3	109.1	37.504	N2-O2	1.223	522.263
C5-C4-C7	118.2	35.121			
C5-C6-H2	121.6	20.554			
C6-C1-N2	119.5	46.621			
C6-C5-H6	119.1	17.672			
C7-C8-H4	111.0	23.433			
C7-C8-H5	109.9	19.696			
C8-C7-H3	109.2	22.692			
H3-C7-H3	107.3	37.665			
H4-C8-H5	108.1	20.954			
H4-C8-H4	108.5	24.058			
O1-N2-O2	125.0	39.169			
O3-N1-O4	125.0	49.379			

Force-field Bonding Parameters

Table 2 - Bond angles, lengths and their associated force constants for 2,4,6-TNEB

angle label	angle (°)	angle force constant kcal mol^{-1}	bond label	bond length (Å)	bond force constant kcal mol^{-1}
C1-C2-C1	121.2	53.330	C1-C2	1.381	305.549
C1-C2-N1	119.4	43.139	C1-C3	1.385	343.552
C1-C3-C4	124.2	49.689	C1-H1	1.078	352.237
C1-C3-N2	114.6	50.765	C2-N1	1.477	128.720
C2-C1-C3	118.3	47.652	C3-C4	1.407	289.481
C2-C1-H1	120.8	16.581	C3-N2	1.484	151.191
C2-N1-O3	117.2	36.035	C4-C5	1.513	189.968
C3-C1-H1	120.9	67.881	C5-C6	1.541	128.785
C3-C4-C3	113.7	36.888	C5-H2	1.089	120.522
C3-C4-C5	123.1	41.074	C6-H3	1.086	134.596
C3-N2-O1	118.1	61.941	C6-H4	1.089	317.571
C3-N2-O2	116.4	57.002	N1-O3	1.222	526.127
C4-C3-N2	121.2	45.755	N2-O1	1.221	410.589
C4-C5-C6	114.2	37.247	N2-O2	1.222	325.988
C4-C5-H2	108.7	36.312			
C5-C6-H3	111.0	45.107			
C5-C6-H4	108.9	27.020			
C6-C5-H2	109.0	44.783			
H2-C5-H2	107.0	56.359			
H3-C6-H4	108.2	24.611			
H3-C6-H3	109.5	51.985			
O1-N2-O2	125.5	69.733			
O3-N1-O3	125.6	36.558			

Force-field Non-Bonding Parameters

Table 3 Dihedral angles for 2,4-DNEB and 2,4,6-TNEB

Dihedral Angle	Number of paths [c]	$V_n/2$ [d]	γ [e]	n [f]
$C_{ar} - C_{ar} - C_{ar} - C_{ar}$	1	14.5	180.0	2.0
$C_{ar} - C_{ar} - C_{ar} - C_{al}$	1	1.10	180.0	2.0
$C_{ar} - C_{ar} - C_{ar} - N$	1	6.14	180.0	2.0
$C_{ar} - C_{ar} - C_{ar} - H$	1	1.10	180.0	2.0
$C_{ar} - C_{ar} - N - O$	4	3.68	180.0	2.0
C_{ar} - C_{ar} - C_{al} - C_{al}	1	0.00	0.000	2.0
H - C_{al} - C_{al} - H	1	0.15	0.000	3.0
$C_{ar} - O - N - O$ (improper)	-	7.28	180.0	2.0

a – $_{ar}$ = aromatic carbon atoms, b – $_{al}$ = aliphatic carbon atoms, c – number of bond paths that total V_n must be divided by, d – magnitude of the torsion in kcal mol^{-1}, e – phase angle in degrees, f – periodicity of the torsion

Table 4 Lennard-Jones parameters for 2,4-DNEB and 2,4,6-TNEB

	R_{min} [a]	ε [b]
C_{ar}	1.9920	0.0700
C_{al}	1.9080	0.1094
H_{ar}	1.3580	0.0300
H_{al}	1.4870	0.0157
N	1.8240	0.1200
O	1.6610	0.1700

a - the distance where the potential reaches a minimum in Angstroms ($\sigma \times 2^{1/6}$), b - the potential well depth in kcal mol^{-1}

Simulation Boxes for simulations at 298 K

Method for 2,4,6-TNEB

Based on monoclinic TNT unit cell reported at 100 K[44]

The lattice parameters, a = 14.9113 Å, b = 6.0340 Å, c = 20.8815 Å

The volume of the unit cell was used to calculate how many TNT molecules would fit in a 40 Å × 40 Å × 40 Å cubic box.

14.9113 Å × 6.0340 Å × 20.8815 Å = 1879 $Å^3$, the unit cell of this volume contains 8 TNT molecules

40 Å × 40 Å × 40 Å = 64000 $Å^3$, a simulation box of this size can hold 272 TNT molecules

TNT = 21 atoms 2,4,6-TNEB = 24 atoms

Number of atoms in 40 Å × 40 Å × 40 Å cubic box of TNT molecules is 272 × 21 = 5712 atoms

Estimate of the number of 2,4,6-TNEB molecules in 40 Å × 40 Å × 40 Å cubic box
5712 ÷ 24 = **238 molecules**

Method for 2,4-DNEB

Based on monoclinic 2,4-DNT unit cell reported at 173 K[45]

The lattice parameters, a = 8.0057 Å, b = 15.1273 Å, c = 12.8853 Å

The volume of the unit cell was used to calculate how many 2,4-DNT cells would fit in a 40 Å × 40 Å × 40 Å cubic box.

8.0057 Å × 15.1273 Å × 12.8853 Å = 1561 $Å^3$, the unit cell of this volume contains 8 2,4-DNT molecules

40 Å × 40 Å × 40 Å = 64000 $Å^3$, a simulation box of this size can hold 328 2,4-DNT molecules

2,4-DNT = 19 atoms 2,4-DNEB = 22 atoms

Number of atoms in 40 Å × 40 Å × 40 Å cubic box of 2,4-DNT molecules is 328 × 19 = 6231.9 atoms

Estimate of number of 2,4-DNEB molecules in 40 Å × 40 Å × 40 Å cubic box
6231.9 ÷ 22 = **283 molecules**

Calculation of diffusion coefficients

$$6D = \lim_{t \to \infty} \frac{MSD}{t}$$

To calculate the diffusion coefficients, D the gradient was divided by 6, according to the equation below where *n* the number of dimensions is 3,

To calculate the standard error of D the standard error of the gradient was divided by 6.

Table 5 - Table displaying the data used to calculate the self-diffusion coefficients of 2,4-DNEB and 2,4,6-TNEB and the diffusion coefficients of 2,4-DNEB and 2,4,6-TNEB in K10 and R8002 in $m^2\ s^{-1}$.

	slope (Å²/ps)	std. error of slope (Å²/ps)	D (Å²/ps)	D (m^2/s)	D std. error (Å²/ps)	D std. error (m^2/s)
2,4-DNEB self-diffusion coefficient	0.04961	0.0003246	0.008268333	$8.26833\ 10^{-11}$	0.0000541	$5.41\ 10^{-13}$
2,4,6-TNEB self-diffusion coefficient	0.003492	0.00003313	0.000582	$5.82\ 10^{-12}$	$5.52167\ 10^{-06}$	$5.52167\ 10^{-14}$
2,4,6-TNEB in K10	0.006111	0.00006787	0.0010185	$1.0185\ 10^{-11}$	1.1311710^{-05}	$1.13117\ 10^{-13}$
2,4-DNEB in K10	0.008513	0.00003632	0.001418833	$1.41883\ 10^{-11}$	$6.05333\ 10^{-06}$	$6.05333\ 10^{-14}$
2,4,6-TNEB in R8002	0.002719	0.00003724	0.000453167	$4.53167\ 10^{-12}$	$6.20667\ 10^{-06}$	$6.20667\ 10^{-14}$
2,4-DNEB in R8002	0.004767	0.0000737	0.0007945	$7.945\ 10^{-12}$	$1.22833\ 10^{-05}$	$1.22833\ 10^{-13}$

Table 6 - Table displaying the data used to calculate the diffusion coeffcients, D in $m^2\ s^{-1}$ for SPC/E water in 2,4-DNEB, 2,4,6-TNEB, K10 and R8002 respectively.

	slope ($Å^2$/ps)	std. error of slope ($Å^2$/ps)	D ($Å^2$/ps)	D (m^2/s)	D std. error ($Å^2$/ps)	D std. error (m^2/s)
DNEB 298 K	0.2648	0.001554	0.044133333	$4.41333\ 10^{-10}$	0.000259	$2.59\ 10^{-12}$
DNEB 338 K	0.4956	0.001313	0.0826	$8.26\ 10^{-10}$	0.000218833	$2.18833\ 10^{-12}$
TNEB 298 K	0.05138	0.000247	0.008563333	$8.56333\ 10^{-11}$	$4.11667\ 10^{-5}$	$4.11667\ 10^{-13}$
TNEB 338 K	0.06202	0.0008206	0.010336667	$1.03367\ 10^{-10}$	0.000136767	$1.36767\ 10^{-12}$
K10 298 K	0.1305	0.0005878	0.02175	$2.175\ 10^{-10}$	$9.79667\ 10^{-5}$	$9.79667\ 10^{-13}$
K10 338 K	0.2221	0.0007505	0.037016667	$3.70167\ 10^{-10}$	0.000125083	$1.25083\ 10^{-12}$
R8002 298 K	0.1231	0.0006572	0.020516667	$2.05167\ 10^{-10}$	0.000109533	$1.09533\ 10^{-12}$
R8002 338 K	0.3312	0.003311	0.0552	$5.52\ 10^{-10}$	0.000551833	$5.51833\ 10^{-12}$

MSD (Å^2) versus time (ps) graphs for the self-diffusion of 2,4,6-TNEB and 2,4-DNEB and for SPC/E water in 2,4,6-TNEB and 2,4-DNEB, respectively at 298 K

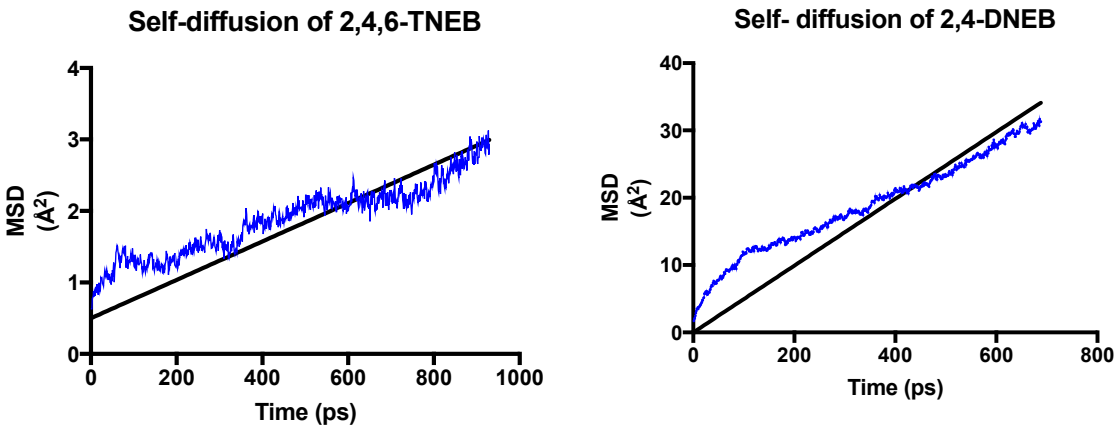

Figure 1 Graphs displaying the MSD (Å^2) vs time (ps) at 298 K of 2,4,6-TNEB in 2,4,6-TNEB and 2,4-DNEB in 2,4-DNEB respectively.

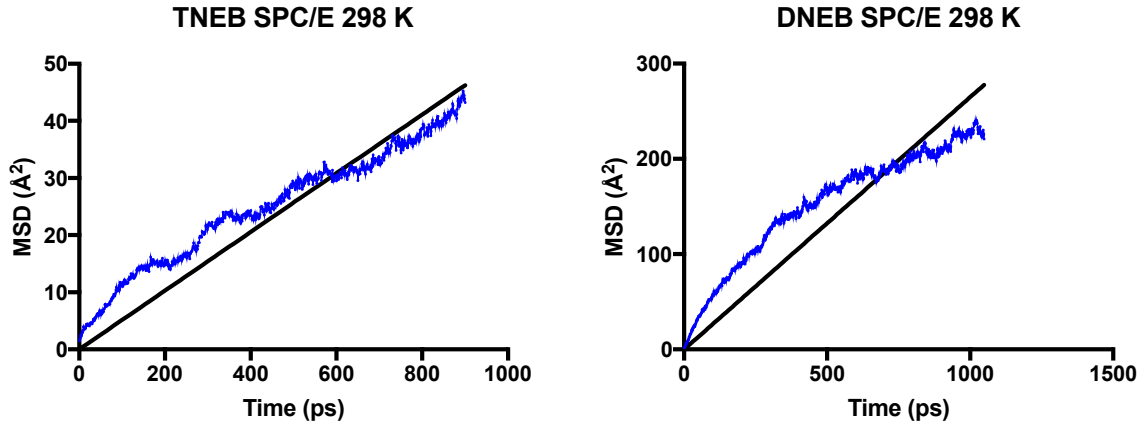

Figure 2 Graphs displaying the MSD (Å^2) vs time (ps) at 298 K of SPC/E water in 2,4,6-TNEB and SPC/E water in 2,4-DNEB respectively.