

Thermodynamics of liquids: Standard molar entropies and heat capacities of common solvents from 2PT Molecular Dynamics

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Supplementary Materials

Appendix I. Description of forcefield potential functions

The molecules are represented explicitly (including hydrogen atoms) by interaction sites located on each nucleus. The potential energy is expressed as a sum of valence (or bonded) interactions and nonbonded interactions:

$$E_{total} = E_{valence} + E_{nonbond}$$
 (A.I.1)

The valence interactions consist of diagonal terms namely, bond stretching (E_b), bond angle bending (E_a), dihedral angle torsion (E_t), and inversion (E_v):

$$E_{valence} = E_{bond} + E_{angle} + E_{torsion} + E_{inversion}$$
 (A.I.2)

The nonbonded interactions consist of van der Waals (E_{vdw}), electrostatic (E_{Coul}) and the case of the Dreiding forcefield, hydrogen bond (E_{hb}) terms.

$$E_{nonbond} = E_{vdw} + E_{coulomb} + E_{hbond}$$
 (A.I.3)

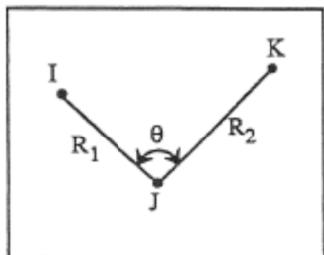
A.I.1. E_{bond}

The two-body bond stretch is a function of the bond equilibrium distance R_0 and the force constant K_b , described with a harmonic function:

$$E_b = \frac{1}{2} K_b(R - R_0)^2$$
 (A.I.4)

A.I.2. E_{angle}

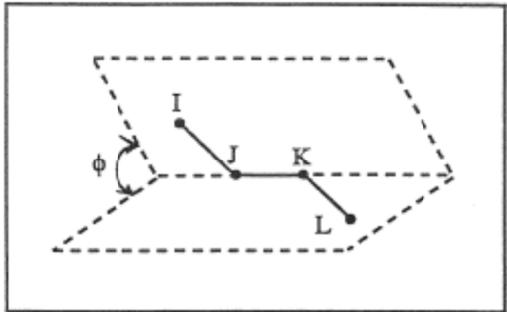
Given any two bonds to a common atom, the bond angle interaction is a function of the angle θ between them and the K_θ force constant, described with a harmonic function: Dreiding should use the cosine form



$$E_a = \frac{1}{2} K_\theta(\theta - \theta_0)^2$$
 (A.I.5)

A.I.3. $E_{torsion}$

Given any two bonds IJ and KL attached to a common bond JK, the dihedral angle ϕ is defined as the angle between the JKL plane and the IJK plane:

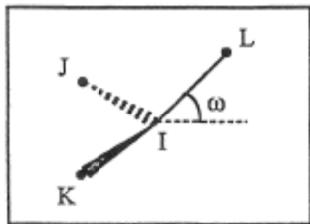


$$E_t = \sum_{n=1}^p \frac{1}{2} K_{\theta,n} [1 - d \cos(n\varphi)] \quad (\text{A.I.6})$$

A positive angle is clockwise when looking from J toward K. $\varphi=0^\circ$ for the cis configuration and $\varphi = 180^\circ$ for the trans configuration. The torsional energy is summed over all available torsions, where each $K_{\theta,n}$ is one-half the rotational barrier, $n = 1,2,3\dots 6$ is the periodicity of the potential and $d = \pm 1$ is the phase factor ($d = +1$ when the cis conformation is the minimum while $d = -1$ when the trans conformation is minimum).

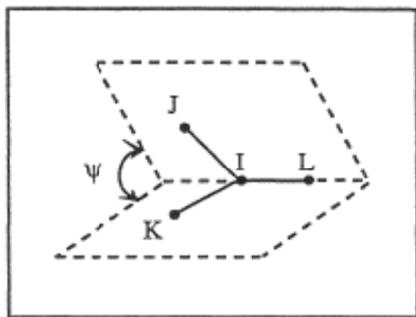
A.I.4. $E_{inversion}$

Given an atom I having exactly three distinct bonds IJ, IK, and IL (e.g. NH₃), the inversion potential is used to keep all the atoms in the same plane. For Dreiding, this potential is described using an Umbrella inversion term, where ω_0 is the angle between the IL axis and the IJK plane:



$$\begin{aligned} E_n &= \frac{1}{2} C [\cos(\omega) - \cos(\omega_0)] \text{ for } \omega_0 \neq 0^\circ \\ &\text{where } K_\omega = C \sin^2 \omega_0 \text{ is the force} \\ &\text{constant} \\ E_n &= K_\omega [1 - \cos(\omega)] \text{ otherwise} \end{aligned} \quad (\text{A.I.7})$$

For the AMBER 2003/GAFF and OPLS AA/L forcefields, the inversion term is defined as if it were a torsion (improper torsion JILK) where K_ψ is the rotational barrier and n is the periodicity:



$$E_n = \frac{1}{2} K_\psi \cos [n(\psi - \psi_0)] \quad (\text{A.I.8})$$

A.I.5. E_{vdw}

The vdW interactions between atoms i and j are represented by the analytic Lennard-Jones 12-6 (LJ12-6) potential, with interaction energy ϵ , equilibrium distance R_0 and r being the distance between the atoms. A switching function $S(r)$ is applied that ramps the energy and force smoothly to zero between an inner (r_{inner}) and outer (r_{outer}) cutoffs:

$$E_{vdw} = \begin{cases} \epsilon \left[\left(\frac{R_0}{r} \right)^{12} - 2 \left(\frac{R_0}{r} \right)^6 \right] & r < r_{inner} \\ \epsilon \left[\left(\frac{R_0}{r} \right)^{12} - 2 \left(\frac{R_0}{r} \right)^6 \right] \times S_{vdw} & r_{inner} < r < r_{outer} \\ 0 & r > r_{outer} \end{cases} \quad (\text{A.I.9})$$

$$S_{vdw} = \frac{\left[r_{outer}^2 - r^2 \right]^2 \left[r_{outer}^2 + 2r^2 - 3r_{inner}^2 \right]}{\left[r_{outer}^2 - r_{inner}^2 \right]^3}$$

vdW interactions with 1-2 and 1-3 bonded neighbors are ignored while the interactions between 1-4 bonded neighbors (atoms in a torsion) are scaled by 0.5 for the AMBER 2003/GAFF and OPLS AA/L forcefields and 1.0 for Dreiding.

A.I.6. E_{Coul}

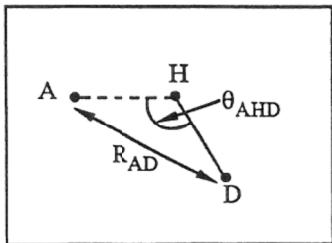
The electrostatic interactions between atoms i and j are separated into a long range contribution calculated by the PPPM¹ method and a real space contribution calculated from the Coulombic formula:

$$E_{coul} = \frac{q_i q_j}{\epsilon_0 r} \quad (\text{A.I.10})$$

where $(1/\epsilon_0) = 332.056$ converts units so that energy is in kcal/mol, the charge is in electron units, and r is the distance in Å between the atoms. Electrostatic interactions with 1-2 and 1-3 bonded neighbors are ignored while the interactions between 1-4 bonded neighbors are scaled by 0.833 for AMBER 2003/GAFF, 0.5 for OPLS AA/L and 1.0 (no scaling) for Dreiding.

A.I.7. E_{hb}

The Dreiding force field has an explicit term describing atoms involved in a hydrogen bond. Here, R_{AD} is the radial distance between the donor (D) and acceptor (A) atoms and θ_{AHD} the bond angle between the acceptor (A), the hydrogen (H) and the donor (D). The hydrogen bond is then described as:



$$E_{hb} = D_0 \left[5 \left(\frac{R_0}{R_{AD}} \right)^{12} - 6 \left(\frac{R_0}{R_{AD}} \right)^{10} \right] \cos^4(\theta_{AHD}) \quad (\text{A.I.11})$$

with equilibrium distance R_0 and interaction energy D_0 . We have added the Dreiding hbond potential to the open source LAMMPS² MD package.

Appendix II. Calculation of physical properties from MD

A.II.1. Bulk Density ρ

The average bulk density $\langle \rho \rangle$ (g/cm^3) is a test of the R_0 of the van der Waals parameters in the forcefield and is calculated³ from 5 1ns windows over the entire production dynamics from the window averaged volume $\langle V \rangle$ according to

$$\langle \rho \rangle = \frac{512 \times M_{\text{liquid}}}{N_a \times \langle V \rangle} = \frac{512 \times M_{\text{liquid}}}{0.6023 \times \langle V \rangle} \quad (\text{A.II.1a})$$

The fluctuation in the density is then obtained from the variance:

$$\delta \langle \rho \rangle = \langle \rho \rangle \frac{\delta \langle V \rangle}{\langle V \rangle} \quad (\text{A.II.1b})$$

A.II.2. Self-diffusion constant D

The self-diffusion constant D was obtained using two complementary approaches:

1. From the center of mass (COM) mean squared displacement r^2 (Einstein's relation⁴):

$$\langle r^2 \rangle = 6Dt \quad (\text{A.II.2a})$$

2. From the Green-Kubo VAC formulism⁴ in linear response theory:

$$D = \frac{1}{N} \sum_1^N \int_0^\infty \langle v_i(t) \cdot v_i(0) \rangle dt \quad (\text{A.II.2b})$$

where t is time, v_i is the axial COM velocity of molecule i and the brackets denote an autocorrelation that is summed over all molecules.

Self diffusion constants are calculated by 5 additional runs of 100 ps, using the NVT ensemble, with the atomic coordinates saved every 1ps.

A.II.3. Static dielectric constant ϵ_0

For isotropic systems in the canonical ensemble, the frequency dependent dielectric constant is given by^{5, 6}

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = 1 - i\omega \int_0^\infty e^{-i\omega t} \Phi(t) dt \quad (\text{A.II.3a})$$

where

$$\Phi(t) = \frac{(\langle \vec{M}(t) \cdot \vec{M}(0) \rangle - \langle \vec{M} \rangle^2)}{\langle \Delta M \rangle^2} \quad (\text{A.II.3b})$$

is the dielectric decay function and

$$\Delta M = (\langle M \rangle^2 - \langle \vec{M} \rangle^2) \quad (\text{A.II.3c})$$

is the total dipole moment fluctuations.

The static dielectric constant is a test of the accuracy in the atomic charges used in the forcefield and defined in linear response theory to be

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi\langle\Delta M^2\rangle}{3V k_B T} \quad (\text{A.II.4a})$$

Under Ewald boundary conditions, Neumann and Steinhauser⁶ showed that the equation A.II.4a has to be modified to

$$\epsilon_0^{\text{correct}} = \frac{(Q+2)(\epsilon_0 - 1) + 3}{(Q-1)(\epsilon_0 - 1) + 3} \quad (\text{A.II.4b})$$

where Q is determined from the real space Ewald cutoff r_c and the Ewald parameter η

$$Q = \int_0^{\frac{r_c}{2}} 4\pi r^2 dr \left(\frac{\eta}{\sqrt{\pi}}\right)^3 e^{-\eta^2 r^2} = \text{erf}(\eta r_c) - \frac{2}{\sqrt{\pi}} r_c e^{-\eta^2 r_c^2} \quad (\text{A.II.4c})$$

In our calculations, $Q = 0.9994$, leading to a negligible change in ϵ_0 . We note that effects due to charge polarization are neglected, as none of the forcefields considered here are polarizable.

A.II.4. Isothermal compressibility κ_T

Under isothermal conditions, the relative volume change in response to pressure is the compressibility. This is a test of the curvature of the van der Waals parameters. From classical statistic mechanics, it is defined to be:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (\text{A.II.5a})$$

This quantity can be obtained during MD by the volume fluctuation formula³:

$$\kappa_T = \frac{\langle V^2 \rangle - \langle V \rangle^2}{k_B \langle T \rangle \langle V \rangle} \quad (\text{A.II.5b})$$

A.II.5. Coefficient of thermal expansion α_p

The coefficient of thermal expansion α_p is a test of the balance between the electrostatic and van der Waals nonbond parameters and is defined as

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{A.II.6a})$$

It can be calculated from MD simulations by the enthalpy-volume fluctuation formula

$$\alpha_p = \frac{\langle VH \rangle - \langle V \rangle \langle H \rangle}{k_B \langle T \rangle^2 \langle V \rangle} \quad (\text{A.II.6b})$$

Tables

Table S1: Forcefield Parameters (forcefield types – FFtype and atomic charges) for each liquid

Liquid	Atom #	Amber 2003/GAFF	Dreiding	OPLS AA/L ^c			
acetic acid	1 2 – 4 5 6 7 8	FFtype CT/c3 HC/hc C/c O/o OH/oh HO/ho	q(e) ^a -0.414320 0.127940 0.869200 -0.617290 -0.668320 0.456910	FFtype C_3 H_ C_R O_R O_2 H__A	q(e) ^b -0.517430 0.186320 0.452040 -0.402940 -0.464690 0.374060	FFtype CT HC C O OH HO	q(e) ^c -0.180000 0.060000 0.520000 -0.440000 -0.530000 0.450000
acetone	1 2 – 4 5 6 7 8 – 10	CT/c3 HC/hc C/c O/o CT/c3 HC/hc	-0.294100 0.077200 0.682500 -0.557800 -0.293800 0.077200	C_3 H_ C_2 O_2 C_3 H_	-0.479140 0.170510 0.362770 -0.427550 -0.479140 0.170510	CT HC CO4 O CT HC	-0.180000 0.060000 0.470000 -0.470000 -0.180000 0.060000
acetonitrile	1 2 – 4 5 6	CT/c2 HC/hc CY/c1 NY/n1	-0.236658 0.114711 0.382240 -0.489715	C_3 H_ C_1 N_1	-0.530570 0.227860 0.302060 -0.455070	CT HC CZ NZ	-0.080000 0.060000 0.460000 -0.560000
benzene	1 – 6 7 – 12	CA/ca HA/ha	-0.129400 0.129400	C_R H_	-0.130430 0.130430	CA HA	-0.115000 0.115000
chloroform	1 2 3 – 5	CT/c3 H3/h3 Cl/cl	-0.384700 0.265900 0.039600	C_3 H_ Cl ⁻	-0.446920 0.272260 0.058220	CT HC Cl	-0.333600 0.297600 0.012000

1,4 dioxane		1, 8 2, 5, 9, 12 3, 4, 6, 7, 10, 11, 13, 14	OS/os CT/c3 H1/h1	-0.424600 0.103300 0.054500	O_3 C_3 H_-	-0.348680 -0.107365 0.140853	OS CT HC	-0.400000 0.140000 0.030000
DMSO		1, 7 2 - 4 8 - 10 5 6	CT/c3 H1/h1 S/s4 O/O	-0.262450 0.125527 0.307524 -0.517786	C_3 H_- S_3 O_2	-0.601566 0.189727 0.768190 -0.703420	CT HC SZ OZ	-0.035000 0.060000 0.170000 -0.460000
ethanol		1 2 - 4 5 6, 7 8 9	CT/c3 HC/hc CT/c3 H1/h1 OH/oh HO/ho	-0.086100 0.024600 0.413200 -0.060600 -0.695100 0.415400	C_3 H_- C_3 H_- O_3 H_A	-0.495100 0.157400 -0.088920 0.126010 -0.499380 0.359180	CT HC CT HC OH HO	-0.180000 0.060000 0.145000 0.060000 -0.683000 0.418000
ethylene glycol		1, 9 2, 10 3, 6 4, 5, 7, 8	OH/oh HO/ho CT/c3 H1/h1	-0.710400 0.432600 0.221000 0.028400	O_3 H_A C_3 H_-	-0.507110 0.359080 -0.147670 0.147850	OH HO CT HC	-0.683000 0.418000 0.145000 0.060000
furan		1 2, 8 3, 9 4, 6 5, 7	OS/os CA/cc H4/h4 C*/cd HA/ha	-0.176000 -0.033600 0.159100 -0.195700 0.158200	O_R C_R H_- C_R H_-	-0.279120 0.072480 0.150090 -0.196380 0.113370	OA C5A HA C5BC HA	-0.190000 -0.019000 0.142000 -0.154000 0.126000

methanol		1, 3, 4	H1/h1	0.037200	H _—	0.144520	HC	0.040000
		2	CT/c3	0.116600	C _— 3	-0.273960	CT	0.145000
		5	OH/oh	-0.649700	O _— 3	-0.506980	OH	-0.683000
		6	HO/ho	0.421500	H _— A	0.347380	HO	0.418000
NMA		1, 3, 4	HC/hc	0.017300	H _—	0.170560	HC	0.060000
		2	CT/c3	-0.041100	C _— 3	-0.533770	CT	-0.180000
		5	C/c	0.586900	C _— R	0.421960	C	0.500000
		6	O/o	-0.591100	O _— 2	-0.529550	O	-0.500000
		7	N/n	-0.419200	N _— R	-0.338550	N	-0.500000
		8	H/hn	0.282300	H _— A	0.317470	H	0.300000
		9	CT/c3	-0.207800	C _— 3	-0.360920	CT	0.020000
		10 - 12	H1/h1	0.112700	H _—	0.170560	HC	0.060000
THF		1, 2	CT/c3	-0.017180	C _— 3	-0.368460	CT	-0.120000
		3, 5	CT/c3	0.294740	C _— 3	0.019710	CT	0.140000
		4	OS/os	-0.607000	O _— 3	-0.718900	OS	-0.400000
		6 - 9	HC/hc	0.012880	H _—	0.182695	HC	0.060000
		10 - 13	H1/h1	0.000090	H _—	0.171405	HC	0.030000
Toluene		1	CT/c2	-0.241400	C _— 3	-0.494260	CT	-0.065000
		2 - 4	HC/hc	0.075700	H _—	0.159540	HC	0.060000
		5	CA/ca	0.115700	C _— R	0.073590	CA	-0.115000
		6, 14	CA/ca	-0.147800	C _— R	-0.137468	CA	-0.115000
		8, 12	CA/ca	-0.191000	C _— R	-0.137468	CA	-0.115000
		10	CA/ca	-0.092200	C _— R	-0.137468	CA	-0.115000
		7, 15	HA/ha	0.127400	H _—	0.125878	HA	0.115000
		9, 13	HA/ha	0.145300	H _—	0.125878	HA	0.115000
		11	HA/ha	0.123000	H _—	0.125878	HA	0.115000
TFE		1	CT/c3	0.503100	C _— 3	0.855690	CT	0.532300
		2 - 4	F/f	-0.179000	F _—	-0.302700	F	-0.205700
		5	CT/c3	0.047700	C _— 3	-0.164910	CT3	0.126300
		6, 7	H1/h1	0.071000	H _—	0.169580	HC	0.082500
		8	OH/oh	-0.586800	O _— 3	-0.493350	OH	-0.635100
		9	HO/ho	0.431000	H _— A	0.371710	HO	0.428600

^a RESP⁷ Charge scheme for HF/6-31G* geometry optimization

^b Mulliken⁸ population analysis from HF/6-31G* geometry optimization

^c As determined by the Macromodel 7.0 program

Table S2: Comparison of calculated heat of vaporization ΔH_{vap} (kcal/mol) for all 15 liquids and 4 forcefields

	Exp^a	AMBER 2003		Dreiding		GAFF		OPLS AA/L	
acetic acid	12.49			5.6 ± 0.10				11.66	± 0.01
acetone	7.39	7.37	± 0.01	6.71	± 0.02	7.28	± 0.01	6.70	± 0.01
acetonitrile	7.86	7.60	± 0.01	7.69	± 0.01	7.20	± 0.01	6.37	± 0.00
benzene	8.09	6.67	± 0.02	7.13	± 0.02	6.27	± 0.04	7.13	± 0.02
chloroform	7.46	6.02	± 0.01	6.24	± 0.02	6.29	± 0.01	6.69	± 0.02
dioxane	9.23	10.90	± 0.01	7.98	± 0.01	10.84	± 0.02	8.27	± 0.02
DMSO	11.26	12.29	± 0.03	11.18	± 0.12	12.11	± 0.02	13.05	± 0.01
ethanol	10.11	10.23	± 0.01	11.50	± 0.03	11.03	± 0.02	9.87	± 0.01
ethylene glycol	15.27	19.99	± 0.01	26.86	± 0.04	20.90	± 0.02	20.72	± 0.04
furan	6.56	6.51	± 0.02	6.22	± 0.01	6.66	± 0.02	6.46	± 0.03
methanol	8.95	9.33	± 0.01	16.43	± 0.07	10.04	± 0.01	8.85	± 0.00
NMA	13.30 ^b	14.54	± 0.01	17.17	± 0.08	14.30	± 0.02	13.88	± 0.02
THF	7.65	9.06	± 0.02	10.10	± 0.05	8.96	± 0.01	5.77	± 0.02
toluene	9.08	7.45	± 0.01	7.83	± 0.03	7.51	± 0.02	8.21	± 0.01
TFE	10.51 ^c	10.87	± 0.04	11.10	± 0.02	11.81	± 0.02	12.44	± 0.02

^a Reference⁹

^b Reference¹⁰

^c Reference¹¹

Table S3: Comparison of calculated coefficients of thermal expansion α_p ($\times 10^4$ K $^{-1}$) for all 15 liquids and 4 forcefields

	AMBER 2003		Dreiding		GAFF		OPLS AA/L	
acetic acid			5.440 ± 0.880				7.000	± 0.918
acetone	15.241	± 0.837	16.743	± 3.286	15.332	± 1.759	12.703	± 1.303
acetonitrile	17.813	± 1.953	15.105	± 1.057	17.953	± 1.244	31.648	± 4.758
benzene	14.729	± 2.929	10.788	± 4.202	19.717	± 1.976	10.740	± 0.537
chloroform	16.310	± 0.966	12.099	± 1.959	15.464	± 0.571	16.146	± 2.376
1,4 dioxane	10.098	± 1.682	11.572	± 2.771	10.917	± 1.340	13.565	± 1.025
DMSO	12.065	± 0.607	10.066	± 0.733	9.355	± 1.443	10.751	± 0.801
ethanol	15.372	± 1.900	26.081	± 4.856	17.386	± 2.995	11.898	± 1.911
ethylene glycol	6.332	± 0.468	3.689	± 1.665	4.650	± 1.753	9.041	± 1.754
furan	12.000	± 1.030	11.511	± 1.135	10.634	± 0.998	14.011	± 1.077
methanol	12.803	± 1.146	16.938	± 4.128	11.029	± 1.139	13.629	± 1.333
NMA	8.515	± 1.028	11.156	± 1.207	10.229	± 1.154	9.069	± 0.620
THF	13.164	± 2.593	9.399	± 1.003	11.277	± 2.310	19.680	± 1.379
toluene	13.297	± 1.188	9.258	± 1.009	11.928	± 0.712	13.273	± 0.973
TFE	15.698	± 2.074	12.695	± 2.731	11.602	± 1.570	17.269	± 1.492

Table S4: Comparison of calculated isothermal compressibilities κ_T ($\times 10^6$ atm $^{-1}$) for all 15 liquids and 4 forcefields

	AMBER 2003		Dreiding		GAFF		OPLS AA/L	
acetic acid			51.20	± 5.01			55.60	± 5.34
acetone	119.00	± 5.54	186.00	± 22.40	124.00	± 11.20	130.00	± 8.71
acetonitrile	133.00	± 6.90	118.00	± 10.40	144.00	± 11.60	398.00	± 51.00
benzene	123.00	± 22.90	81.10	± 32.00	164.00	± 29.80	79.70	± 5.76
chloroform	169.00	± 7.29	132.00	± 12.50	154.00	± 4.11	139.00	± 27.30
1,4 dioxane	47.20	± 6.60	98.00	± 15.70	61.70	± 7.93	87.30	± 6.67
DMSO	58.30	± 1.87	57.60	± 5.38	52.10	± 5.97	47.20	± 3.12
ethanol	121.00	± 4.86	319.00	± 50.40	146.00	± 20.50	97.40	± 3.98
ethylene glycol	23.40	± 0.87	53.90	± 13.00	31.70	± 9.22	44.10	± 4.85
furan	106.00	± 10.10	100.00	± 9.02	81.50	± 5.00	104.00	± 12.00
methanol	105.00	± 7.20	265.00	± 38.80	91.30	± 5.08	119.00	± 10.40
NMA	52.50	± 5.17	104.00	± 13.50	55.80	± 3.76	58.40	± 2.89
TFE	145.00	± 10.60	87.90	± 14.90	93.50	± 8.24	165.00	± 14.80
THF	79.30	± 12.80	56.70	± 4.15	60.40	± 14.30	202.00	± 23.10
toluene	121.00	± 13.20	80.40	± 4.52	105.00	± 10.30	110.00	± 8.50

Table S5: ΔC_v (cal/mol/K) corrections to C_v to obtain C_p according to equation (1)

	AMBER 2003	Dreiding	GAFF	OPLS
acetic acid		0.10		0.08
acetone	0.23	0.19	0.22	0.14
acetonitrile	0.20	0.16	0.20	0.22
benzene	0.25	0.21	0.35	0.20
chloroform	0.21	0.21	0.20	0.23
dioxane	0.27	0.21	0.24	0.29
DMSO	0.27	0.19	0.18	0.27
ethanol	0.17	0.23	0.18	0.13
ethylene glycol	0.14	0.02	0.06	0.16
furan	0.13	0.16	0.15	0.21
methanol	0.09	0.08	0.08	0.10
NMA	0.16	0.16	0.22	0.16
TFE	0.20	0.21	0.17	0.20
THF	0.26	0.21	0.26	0.27
toluene	0.25	0.19	0.23	0.26

Figures

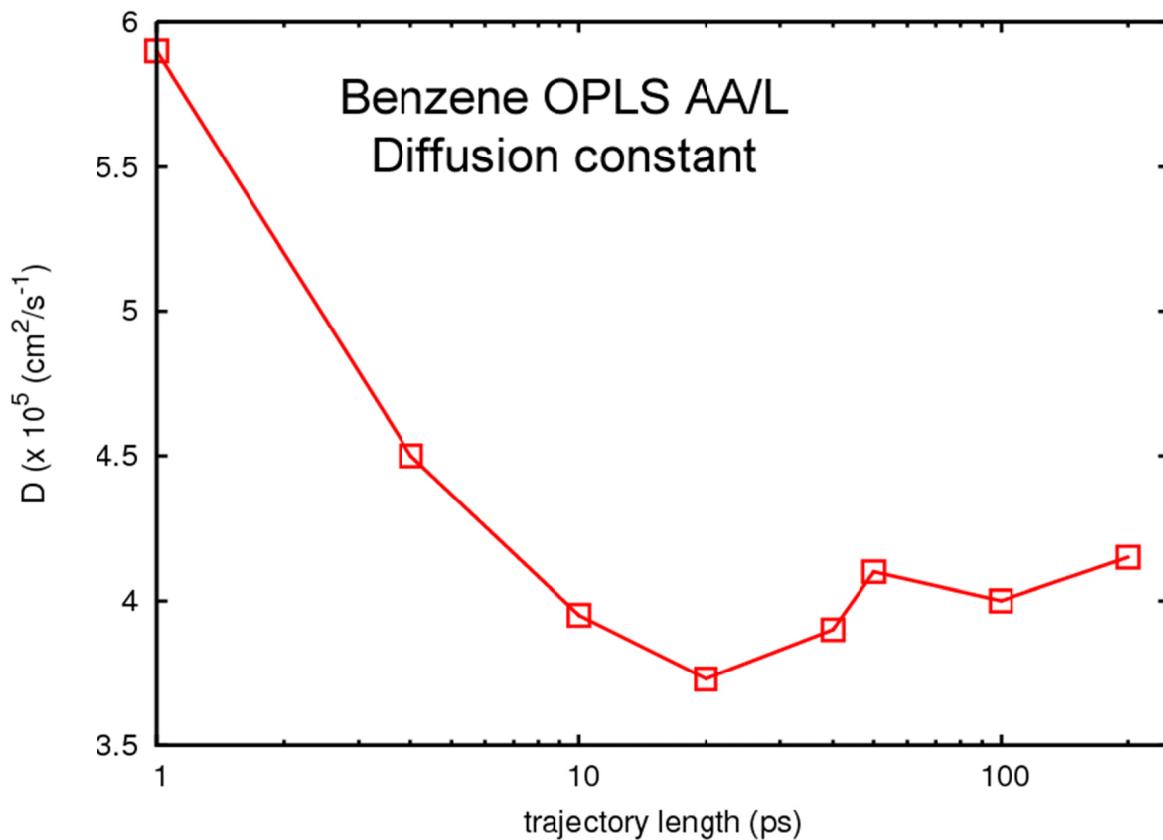


Figure S1: Convergence of the self-diffusion constant D ($\times 10^5 \text{ cm}^2/\text{s}^{-1}$) of benzene using the OPLS AA/L forcefield, calculated with the 2PT method and the Green-Kubo VACF approach. Convergence is observed after 50ps.

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