

Thermodynamic Origins of the Solvent-Dependent Stability of Lithium Polysulfides from First Principles

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Supplementary Materials

Tables

Table S1: Standard molar entropy (J/mol/K/molecule) of reference systems. We compare the results of our FPMD simulations to classical simulations employing the GAFF¹ and OPLS² force fields, and to experimental measurements where available.

	Expt	FPMD	GAFF	OPLS
alpha-S ₈ (s)	256 ^a	177.94 ± 2.1	259.87 ± 2.85	
Li ₂ S(s)	63	43.32 ± 1.46	29.390	
DGM(l)	352.7 ^b	300.92 ± 5.23	242.840 ± 3.82	289.22 ± 4.12
DMF(l)		195.55 ± 3.45	175.63 ± 2.14	

^a Reference³

^b Reference⁴

Table S2: Average atomic distances (Å) of dissolved polysulfides obtained from pair distribution functions during equilibrium FPMD simulations. Distances are indicated with respect to both bound (Li+) and unbound (LiSx-) lithium ions (in parentheses) in the lithium polysulfide dianion ion pairs.

	DMF			diglyme		
	Li - Li	Li - S	Li - O	Li - Li	Li - S	Li - O
Li ₂ S ₂	3.53	2.45 (2.50)	1.95 (1.92)	3.89	2.51 (2.48)	2.07 (2.05)
Li ₂ S ₃	3.25	2.44 (2.46)	1.93 (1.95)	3.75	2.42 (2.44)	2.05 (2.07)
Li ₂ S ₄	3.15	2.50 (2.54)	1.97 (1.96)	2.83	2.46 (3.24)	2.01 (2.10)
Li ₂ S ₅	3.21	2.43 (2.62)	1.95 (1.94)	2.94	2.39 (3.42)	1.99 (2.21)
Li ₂ S ₆	3.27	2.45 (2.52)	1.91 (1.95)	3.03	2.37 (3.30)	2.02 (2.20)
Li ₂ S ₇	3.29	2.49 (2.64)	1.90 (1.99)	2.99	2.39 (3.21)	2.00 (2.25)
Li ₂ S ₈	3.35	2.50 (2.75)	1.91 (1.97)	3.00	2.47 (3.39)	2.03 (2.17)
LiS ₂	-	2.71	1.85	-	2.82	2.11
LiS ₃	-	2.60	1.88	-	2.84	2.10
LiS ₄	-	2.50	1.90	-	2.85	2.07
LiS ₅	-	2.54	1.89	-	2.83	2.09
LiS ₆	-	2.56	1.91	-	2.85	2.07
LiS ₇	-	2.55	1.92	-	2.83	2.05
LiS ₈	-	2.52	1.89	-	2.84	1.96

Table S3: Average coordination number of various lithium polysulfides in DMF and diglyme. For the dianions, both the unbound (Li^{u}) and bound (Li^{b}) lithium ions are shown.

	DMF				diglyme			
	$\text{Li}^{\text{u}} - \text{O}$	$\text{Li}^{\text{b}} - \text{O}$	$\text{Li}^{\text{u}} - \text{S}$	$\text{Li}^{\text{b}} - \text{S}$	$\text{Li}^{\text{u}} - \text{O}$	$\text{Li}^{\text{b}} - \text{O}$	$\text{Li}^{\text{u}} - \text{S}$	$\text{Li}^{\text{b}} - \text{S}$
Li_2S_2	1.99	1.95	2.96	2.56	3.19	2.04	1.63	1.73
Li_2S_3	1.99	1.98	1.42	1.68	2.86	1.98	0.95	1.37
Li_2S_4	2.26	1.85	0.88	1.36	3.01	1.84	0.87	1.51
Li_2S_5	2.86	1.18	0.68	2.20	3.36	1.95	0.38	1.57
Li_2S_6	2.98	1.14	0.54	2.42	3.12	2.06	0.53	1.76
Li_2S_7	3.00	1.18	0.50	2.48	3.01	2.06	0.61	1.42
Li_2S_8	3.00	0.99	0.50	2.58	3.06	2.10	0.76	1.74
LiS_2	2.53		2.68		3.07		2.16	
LiS_3	2.37		1.44		2.89		1.12	
LiS_4	2.54		1.96		2.83		0.96	
LiS_5	2.36		1.96		2.85		1.00	
LiS_6	2.42		1.92		2.73		0.96	
LiS_7	2.48		1.96		2.64		1.16	
LiS_8	2.55		2.04		2.59		0.96	

Table S4: Dissolution thermodynamics (kJ/mol) of various lithium polysulfides in DMF. This data was plotted in figure 2.

species	ΔG	\pm	ΔH	\pm	$T\Delta S$	\pm
Li ₂ S	62.21	1.23	64.32	1.57	2.11	0.96
S ₈	-34.77	1.56	-118.74	3.99	-83.98	2.82
Li ₂ S ₂	28.81	1.86	-70.99	2.46	-99.80	1.39
Li ₂ S ₃	-35.74	1.93	-19.81	1.53	15.93	1.59
Li ₂ S ₄	-47.19	1.47	-38.31	2.77	8.88	1.42
Li ₂ S ₅	-46.76	2.00	-57.73	1.58	-10.96	1.69
Li ₂ S ₆	-50.29	1.72	-105.33	1.77	-55.03	1.06
Li ₂ S ₇	-49.70	2.00	-130.80	1.68	-81.10	1.67
Li ₂ S ₈	-48.74	1.46	-139.53	1.73	-90.79	1.79
LiS ₂	26.74	2.54	-11.63	3.16	-38.37	1.93
LiS ₃	-35.10	2.26	-121.78	2.25	-86.68	1.79
LiS ₄	-33.63	2.46	-124.21	2.46	-90.58	1.21
LiS ₅	-32.68	2.96	-124.65	2.56	-91.97	1.60
LiS ₆	-33.03	2.72	-125.32	3.01	-92.29	2.19
LiS ₇	-31.45	3.39	-120.00	3.79	-88.55	1.49
LiS ₈	-32.44	3.04	-119.40	3.35	-86.96	1.87

Table S5: Dissolution thermodynamics (kJ/mol) of various lithium polysulfides in diglyme

species	ΔG	\pm	ΔH	\pm	$T\Delta S$	\pm
Li ₂ S	45.24	3.42	48.72	3.05	3.48	2.02
S ₈	-35.93	4.14	-238.06	1.99	-202.12	1.00
Li ₂ S ₂	80.71	2.69	-117.70	1.59	-198.41	0.59
Li ₂ S ₃	7.05	1.74	-196.27	1.21	-203.32	0.71
Li ₂ S ₄	-19.04	1.11	-224.46	1.22	-205.42	1.00
Li ₂ S ₅	-22.62	1.78	-229.41	2.03	-206.79	0.78
Li ₂ S ₆	-30.39	1.16	-305.35	1.43	-274.96	0.88
Li ₂ S ₇	-33.96	1.27	-308.28	1.30	-274.32	0.89
Li ₂ S ₈	-31.59	1.56	-295.79	1.11	-264.20	1.03
LiS ₂	78.18	2.06	-168.27	1.40	-246.45	0.36
LiS ₃	29.41	2.58	-239.90	3.39	-269.31	1.15
LiS ₄	26.96	2.80	-245.17	3.31	-272.12	0.99
LiS ₅	31.86	2.72	-253.08	4.56	-284.94	1.38
LiS ₆	32.94	2.54	-272.71	2.61	-305.66	1.35
LiS ₇	31.89	2.76	-265.78	4.69	-297.67	0.98
LiS ₈	32.77	2.40	-276.82	2.57	-309.59	1.14

Figures

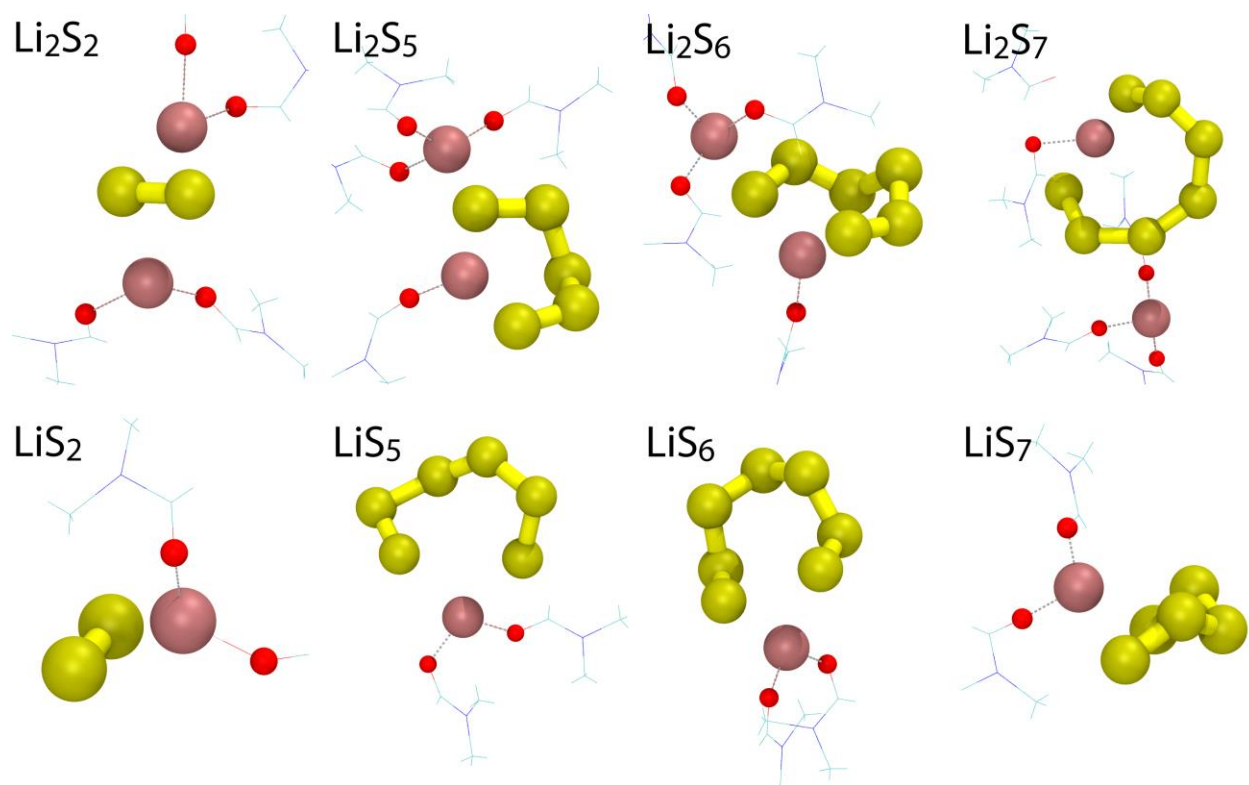


Figure S1: Representative equilibrium configurations of Li_xS_2 , Li_xS_5 , Li_xS_6 and Li_xS_7 polysulfide dianions ($x = 2$, top row) and radicals ($x = 1$, bottom row) in DMF from 298K FPMD simulations. The lithium (pink), sulfur (yellow) and DMF oxygen (red) atoms are emphasized.

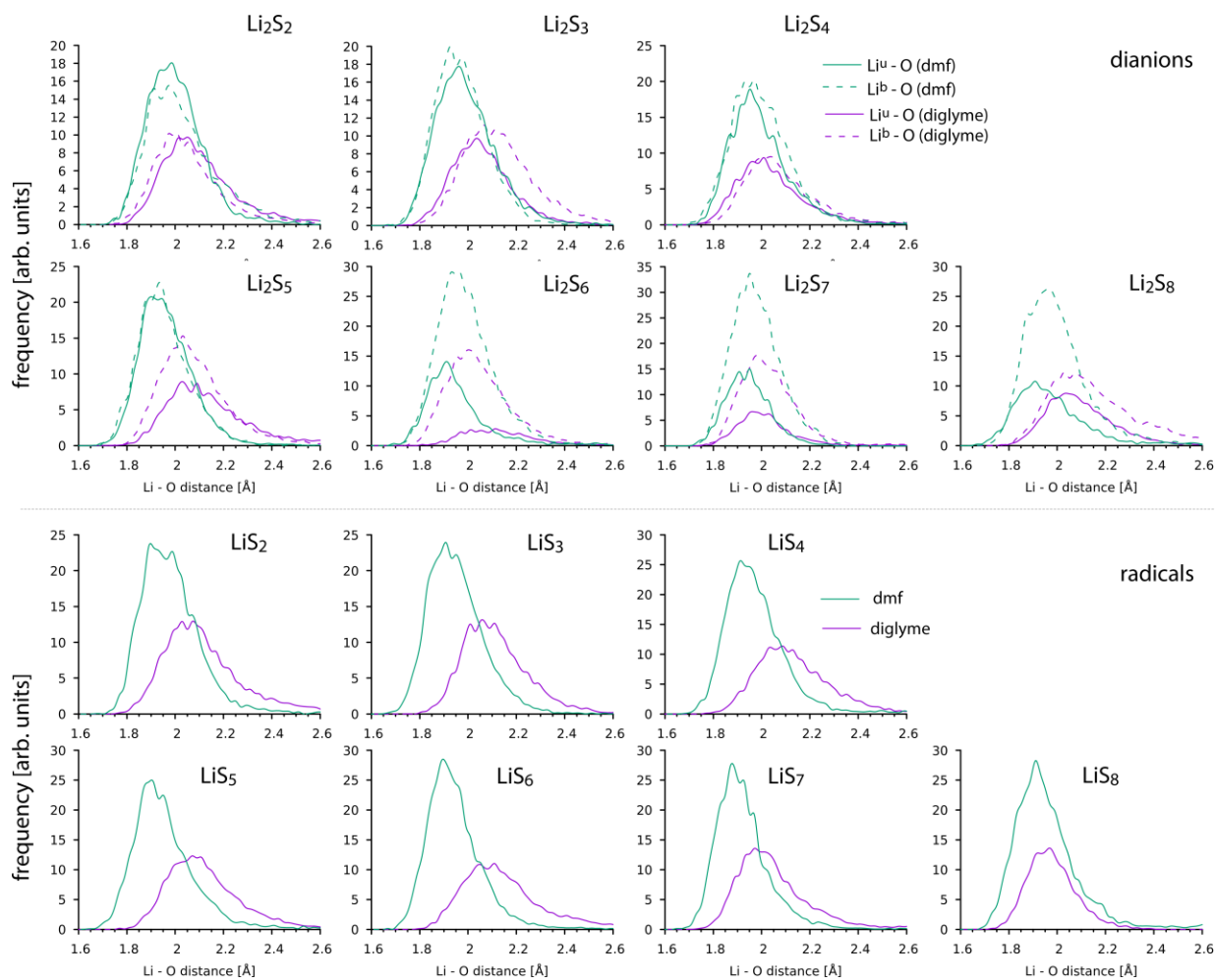


Figure S2: Distribution of lithium–oxygen distances in the various polysulfides in diglyme (green) and DMF (magenta). Upper panel: dianions; lower-panel: radicals. For the dianions, both the unbound (Li^u – solid lines) and bound (Li^b – dashed lines) lithium ions are presented.

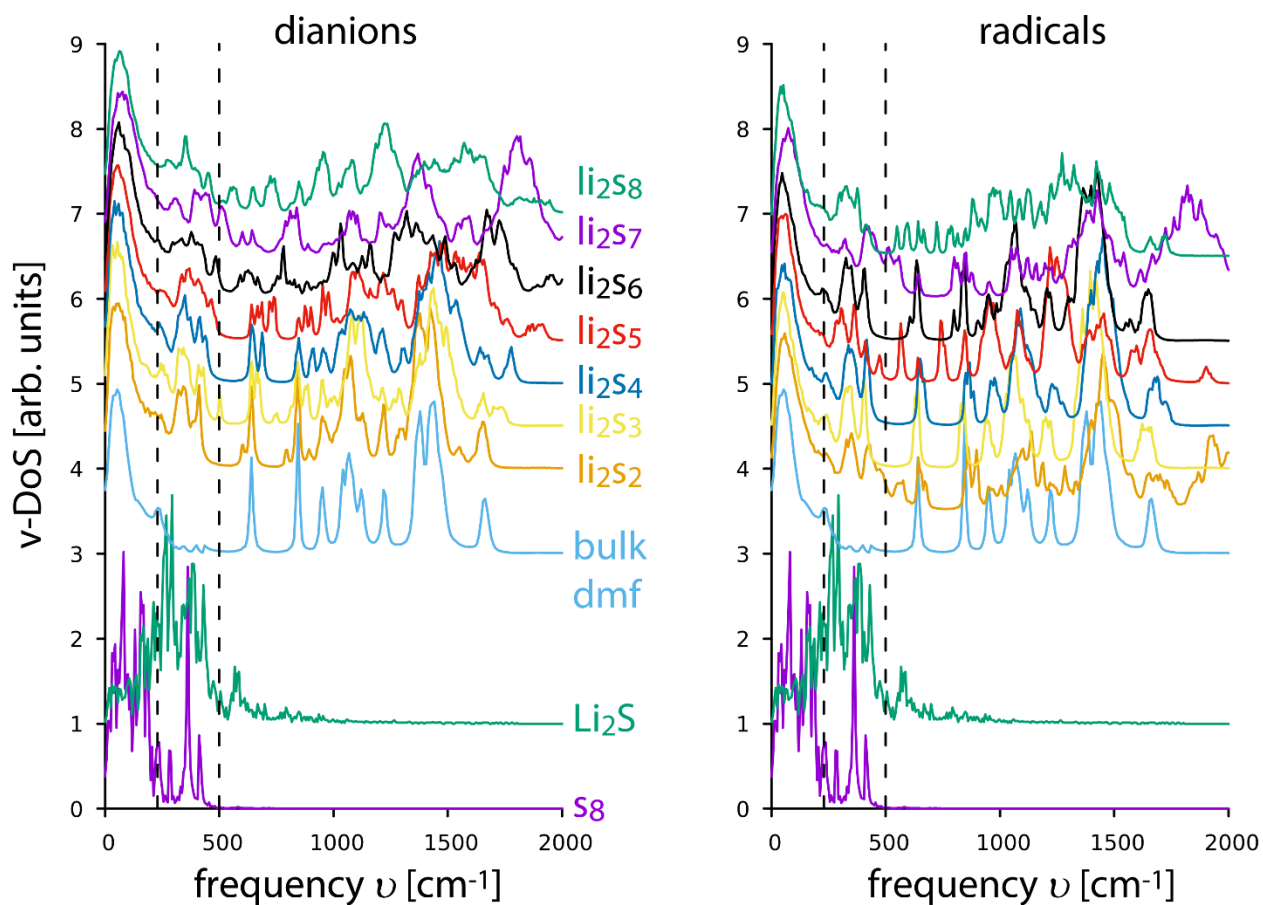


Figure S3: Vibrational density of states (v-DoS) of the DMF molecules in the pure solvent (light blue) and in various lithium polysulfide solutions. The v-DoS for the dissolved octa-sulfur S_8 (purple) and Li_2S (green) are provided as reference (at the bottom of each graph). Individual v-DoS are offset vertically for clarity. The dashed vertical lines represent the 230 – 500 cm^{-1} region that are present in the polysulfide systems but absent in bulk DMF.

Computational Methods

Obtaining condensed phase thermodynamics using The Two-Phase Thermodynamics (2PT) Method

All methods of obtaining the free energy from molecular simulations ultimately reduce to descriptions of the canonical partition function Q . In the 2PT method, Q is approximated from the vibrational density of states $DoS(\nu)$ (also referred to as the power spectrum or spectral density). In practice, we obtain the system thermodynamics from $DoS(\nu)$, by performing a Fourier Transform of the velocity autocorrelation function $C(t)$ ⁵:

$$C(t) = \sum_{j=1}^N \sum_{k=1}^3 m_j \left[\lim_{t \rightarrow \infty} \frac{1}{2\tau} \int_{-\tau}^{\tau} v_j^k(t'+t) v_j^k(t') dt' \right] \quad (2)$$

$$DoS(\nu) = \lim_{t \rightarrow \infty} \frac{1}{2kT} \int_{-\tau}^{\tau} C(t) e^{-2\pi\nu t} dt \quad (3)$$

The total $DoS(\nu)$ is then partitioned into a contribution arising from pure diffusion in the liquid [$DoS_{diffuse}(\nu)$] and a contribution arising from solid like vibrations [$DoS_{solid}(\nu)$], as proposed by Eyring and Ree⁶:

$$DoS(\nu) = f * DoS_{diffuse}(\nu) + (1-f) * DoS_{solid}(\nu) \quad (4)$$

where f is the “fluidicity factor”: the fraction of the modes of the system that are diffusional. This f factor is function of the system properties (self-diffusion, density and temperature) and is solved self consistently from the MD trajectory. The total system thermodynamics is then recovered by integrating the individual power spectrum with the appropriate weighting factors, obtained from the Carnahan-Sterling (CS) equation of state (EOS) of hard-spheres⁷ in the case of $DoS_{diffuse}(\nu)$ and from Debye theory of a vibrating crystal⁸ in the case of $DoS_{solid}(\nu)$.

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