Electronic Supporting Information for: Enhanced Sampling Simulation Analysis of the Structure of Lignin in the THF-Water Miscibility Gap

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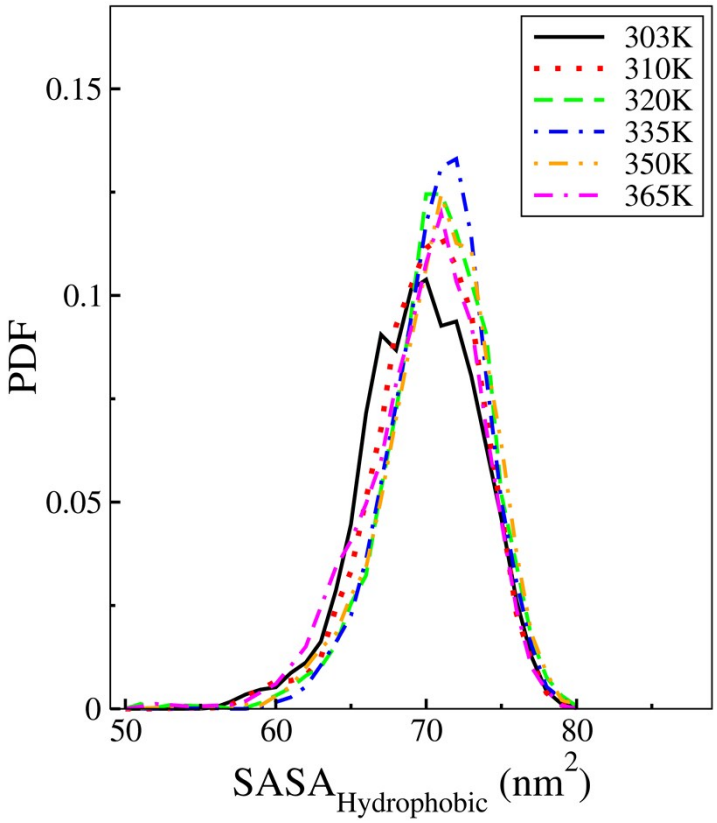
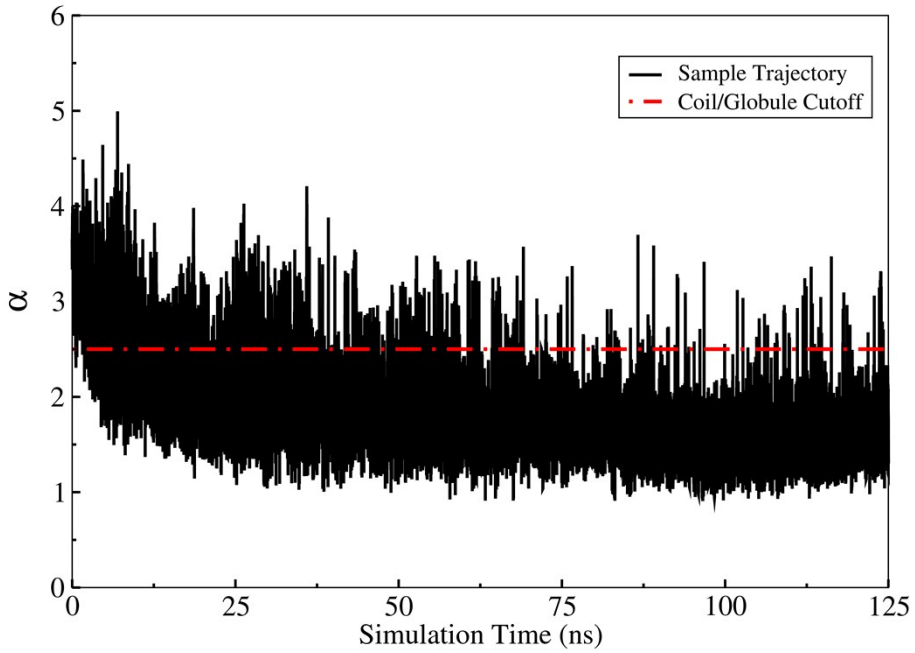
Organization and layout of this section

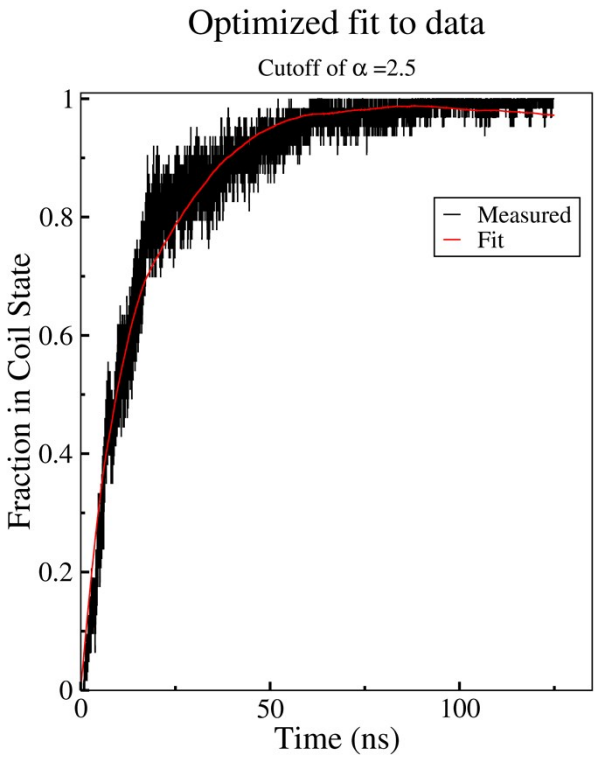
This section contains the SASA distribution mentioned in the text, a sample fractal dimension trajectory (also mentioned in the text), and sampled kinetic fit, along with the complete tables of our kinetic fits. This second ends with a list of the replica temperatures and a figure concerning the effectiveness of the temperature sampling. These figures and tables are provided with no additional discussion (aside from figure captions).



SI Figure 1) Hydrophobic Solvent Accessible Surface Area (SASA) Distributions. Generated using the last 75ns of simulation at each noted temperature window. Note that, as with the fractal-dimension and free-energy projections from the main text, there are only minor modifications with temperature.



SI Figure 2) Sample fractal dimension (α) trajectory. The dashed line indicates the location of the optimal cutoff obtained from the kinetic fits for the two state model.



SI Figure 3) Example of a fit to the two-state kinetics model. This fit was generated with a cutoff of a fractal-dimension of 2.5.

SI Table 1) Kinetic constants for "one"-state model evaluated at 298K. Highlighted rows are the best fits for this model

α cutoff	Kinetic (K_c) $(ns)^{-1}$	χ^2
1.7	6.59E-05	3.97E-01
1.8	8.07E-05	3.96E-01
1.9	1.06E-04	3.45E-01
2	1.11E-04	2.80E-01
2.2	1.69E-04	1.90E-01
2.4	2.20E-04	1.84E-01
2.5	2.50E-04	2.07E-01

SI Table 2) Kinetic constants and thermodynamics for two-state model evaluated at 298K. Highlighted rows are the best fits for this model

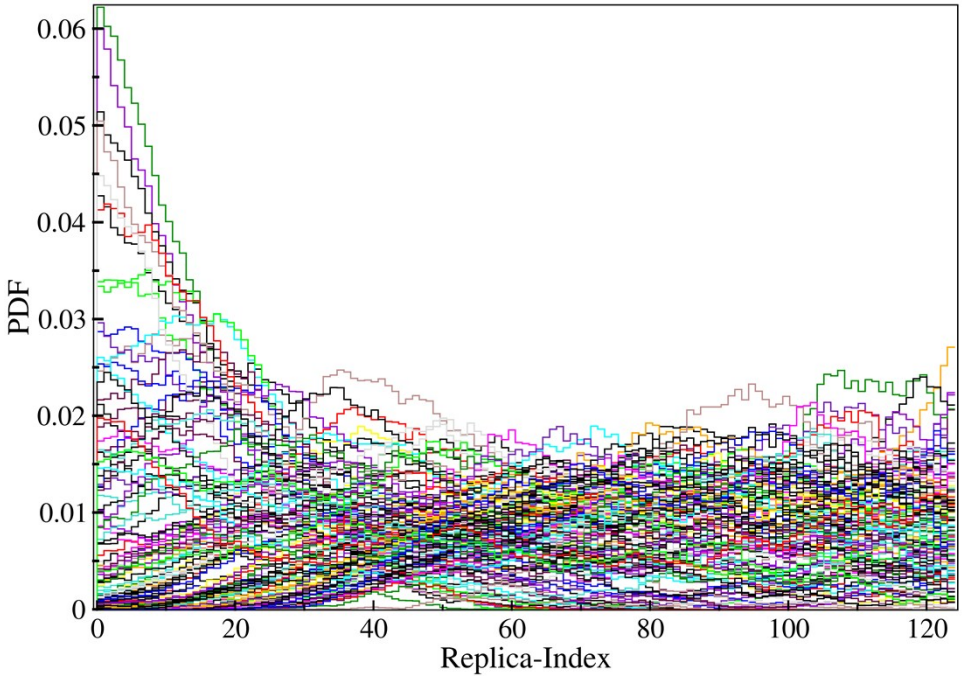
α cutoff	Kinetic (Kc, Kg) $(ns)^{-1}$		ΔG (kJ/mol)	ΔH (kJ/mol)	TΔS (kJ/mol)	χ^2
1.9	1.40E-04	1.27E-05	-5.96	-2.12	3.86	2.13E-01
2	1.76E-04	9.41E-06	-7.28	-4.35	2.95	1.72E-01
2.2	2.62E-04	6.51Ee-06	-9.19	-4.54	4.68	1.46E-01
2.4	3.92E-04	6.54E-06	-10.19	-6.89	3.33	9.04E-02
2.5	4.57E-04	7.99E-06	-10.06	-4.15	5.95	8.64E-02
2.6	5.50E-04	7.91E-06	-10.47	-6.63	3.84	8.83E-02
2.7	6.66E-04	7.73E-03	-10.76	-7.65	2.8	1.12E-01

SI Table 3) Kinetics constants and thermodynamics for three-state model evaluated at 298K. Highlighted rows are the best fits for this model

α Coil	α Inter	Kinetic (Kci, Kic_i,Kig, Kgi) $(ns)^{-1}$				ΔG (kJ/mol)	ΔH (kJ/ mol)	TΔS (kJ/mol)	χ^2
1.7	2.4	2.11E-04	7.44E-10	7.13E-12	-5.10E-05	-31.31	-28.98	2.54	19.55
1.8	2	9.65E-05	8.85E-09	3.34E-07	2.04E-08	-23.18	-21.79	1.39	2.75
1.8	2.4	2.36E-04	1.33E-08	1.53E-08	1.95E-02	-24.37	-19	5.4	12.23
1.8	2.7	5.06E-04	2.33E-09	5.09E-06	1.54E-08	-30.68	-33.57	-2.92	17.92
1.9	2.4	2.94E-04	3.56E-08	1.86E-06	0.02	-22.48	-21.09	1.4	7.41
2	2.2	2.53E-04	4.13E-10	1.50E-09	1.98E-05	-33.16	-33.42	-0.25	1.58
2	2.5	3.95E-04	3.77E-11	5.27E-10	7.12E-08	-41.24	-39.04	2.2	5.54
2.2	2.5	4.50E-04	1.70E-10	1.28E-10	4.05E-15	-37.25	-35.36	1.89	1.43
2.2	2.7	5.26E-04	5.86E-09	2.25E-05	2.28E-05	-28.42	-21.79	1.38	3.1

Replica Details:

List of temperatures used:
305, 305.282, 305.567, 305.854, 306.143, 306.434, 306.728, 307.024, 307.322, 307.623, 307.927, 308.232, 308.541, 308.851, 309.165, 309.48, 309.798, 310.119, 310.443, 310.769, 311.097, 311.428, 311.762, 312.099, 312.438, 312.78, 313.125, 313.472, 313.823, 314.176, 314.532, 314.891, 315.252, 315.617, 315.984, 316.355, 316.728, 317.105, 317.484, 317.867, 318.252, 318.641, 319.033, 319.428, 319.826, 320.227, 320.632, 321.04, 321.451, 321.865, 322.283, 322.704, 323.128, 323.556, 323.987, 324.422, 324.86, 325.302, 325.748, 326.196, 326.649, 327.105, 327.565, 328.028, 328.496, 328.967, 329.441, 329.92, 330.402, 330.889, 331.379, 331.873, 332.371, 332.873, 333.379, 333.889, 334.404, 334.922, 335.445, 335.971, 336.503, 337.038, 337.577, 338.121 ,338.67, 339.222 ,339.779, 340.341, 340.907, 341.478, 342.053, 342.633, 343.217, 343.807, 344.401, 344.999, 345.603, 346.211, 346.824, 347.443, 348.066, 348.694, 349.327, 349.965, 350.609, 351.257, 351.911, 352.57, 353.235, 353.904, 354.579, 355.26, 355.946, 356.637, 357.334, 358.037, 358.745, 359.459, 360.179, 360.904, 361.635, 362.372, 363.116, 363.865, 364.62



SI Figure 3) Histograms (probability distribution functions) of the walks through between replica-indices (traversal of temperature space). Each curve corresponds to a replica beginning at a different temperature.