Supporting Information

Comparison of Biomolecular Force Fields for Alkanethiol Self-Assembled Monolayer Simulations

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Section I. Setup of Model Systems

Table S1. Alkanethiol SAM ligands and their thicknesses in fully-extended all-trans conformations.

Name	Chemical Formula	Chain length (n)	Thickness (Å)
1-Decanethiol	SH-$(CH_2)_9$-CH_3	10	13.90
1-Dodecanethiol	SH-$(CH_2)_{11}$-CH_3	12	16.42
1-Tetradecanethiol	SH-$(CH_2)_{13}$-CH_3	14	18.93
1-Hexadecanethiol	SH-$(CH_2)_{15}$-CH_3	16	21.30
1-Octadecanethiol	SH-$(CH_2)_{17}$-CH_3	18	23.75

Table S2. Atom types of SAM ligand atoms in each force field.

Force Field	Atoms		
	Carbon (C)	**Hydrogen (H)**	**Sulfur (S)**
Lipid14	cD	Hl	SH
Slipids	CTL3 (CH_3); CTL2 (CH_2)	HAL3 (CH_3); HAL2 (CH_2)	SH
GAFF*	c3	HC; H1 ($\underline{CH_2}$-S)	SH
CHARMM36	CTL3 (CH_3); CTL2 (CH_2)	HAL3 (CH_3); HAL2 (CH_2)	S
L-OPLS	opls_135 (CH_3); opls_136 (CH_2)	opls_970 (CH_3); opls_140 (CH_2)	opls_200
GROMOS54a7	CH_3(CH_3); CH_2 (CH_2)	-	S

*The Antechamber software from Amber16 was used to generate GAFF topologies and subsequently converted into GROMACS format using the ACPYPE script[1].

[1.] Sousa da Silva, A. W.; Vranken, W. F., ACPYPE - AnteChamber PYthon Parser interfacE. *BMC Res Notes* **2012**, **5**, 367.

Table S3. Non-bonded cut-off parameters used for each force field.

Force Field	**$R_{Coulomb}$ (nm)**	**vdW modifier**	**R_{vdW} (nm)**	**$R_{vdW\text{-}switch}$ (nm)**
Lipid14[1]	1.0	-	1.0	
Slipids[1]	1.5	Potential-switch	1.5	1.4
GAFF[1]	1.0	-	1.0	
CHARMM36[1]	1.2	Potential-switch	1.2	0.8
L-OPLS[2]	1.0	-	1.0	1.0
GROMOS54a7[1]	1.4	-	1.4	

For all force fields, the cut-off scheme was *Verlet* (particle-based cut-off), the vdw-type was *cut-off*.

The optimized parameters were referenced from:

[1] Pluhackova, K.; Kirsch, S. A.; Han, J.; Sun, L.; Jiang, Z.; Unruh, T.; Bockmann, R. A., A Critical Comparison of Biomembrane Force Fields: Structure and Dynamics of Model DMPC, POPC, and POPE Bilayers. J. Phys. Chem. B 2016, 120 (16), 3888-903.

[2] Modified based on *Siu, S. W.; Pluhackova, K.; Bockmann, R. A., Optimization of the OPLS-AA Force Field for Long Hydrocarbons. J Chem Theory Comput 2012, 8 (4), 1459-70.*

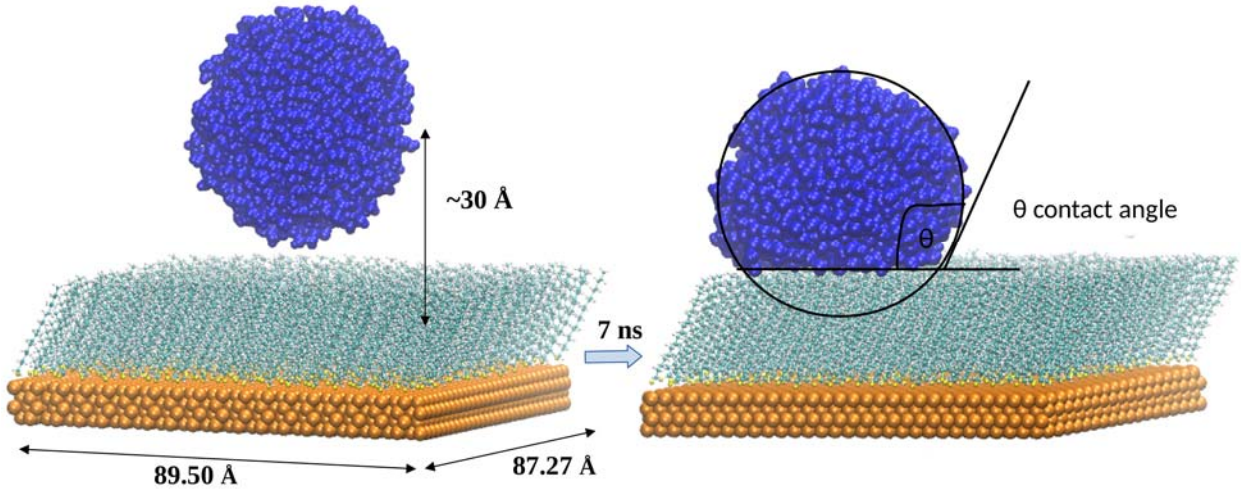


Figure S1. Snapshots of a droplet-SAM system with 1-Octadecanethiol ligands: Initial structure (left) and equilibrated structure after 7 ns of simulation time (right). The water droplet sat on the monolayer surface and stabilized with a contact angle (θ).

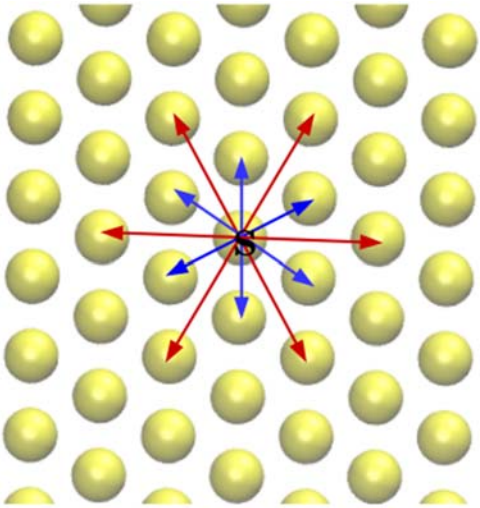


Figure S2. The hexagonal arrangement of Sulfur atoms (yellow) on the Au layer (omitted for clarity). For each S atom, the next nearest neighbour (NNN, red arrow) S atoms are at ±0°, ±60°, ±120°, ±180° directions; the nearest neighbour (NN, blue arrow) S atoms are at ±30°, ±90° and ±150° directions.

Section II. Contact Angle Calculation

The contact angle (θ) of a water droplet can be estimated using a simple geometric method proposed by Fan *et al.* (Fan1995):

$$cos\theta = 1 - \frac{h}{R}$$

$$R = \frac{h}{2} + \frac{S}{2\pi h}$$

$$S = \pi r^2$$

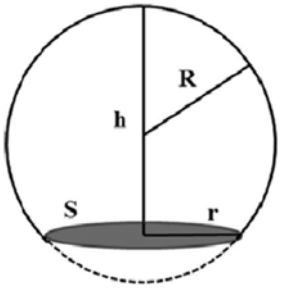


Figure S3. A geometric method to estimate droplet contact angle.

where *h* is the height of the droplet, *R* is the radius of the sphere, *r* is the radius of the intersection circle and *S* (dark grey surface) is the interfacial area as illustrated in Figure S3. In above figure circle with solid line represent the shape of droplet on YZ plane. Hence, this simple geometric method requires two parameters, i.e. the height and the surface-intersection radius of the droplet to estimate the droplet contact angle.

Calculation of the height of the droplet (h): Suppose the droplet is placed on a surface that is perpendicular to the *Z* axis, then the height of the droplet can be determined from the location of the Gibbs dividing surface at the top of the droplet. To find the Gibbs dividing surface, we calculated the density profile of water in the cylinder passing through the center of the droplet as a function of *Z*. Radius of this cylinder was taken to be 5 Å and slab width was 0.5Å.

The density profile *f(z, ρ)* is fitted to the hyperbolic tangent function:

$$f(z,\rho) = \frac{\rho}{2} - \frac{\rho}{2} tanh((z-h)/d)$$

where *d* is the thickness of the interface, *h* is the height of the droplet, *ρ* is density of water and z is the distance in z direction. Fitting of the two coefficients *h* and *d* were done by the curve fitting tool in MATLAB software. A typical fit is shown in the figure below. The height of the droplet (h) is estimated from the middle point of the descending slope.

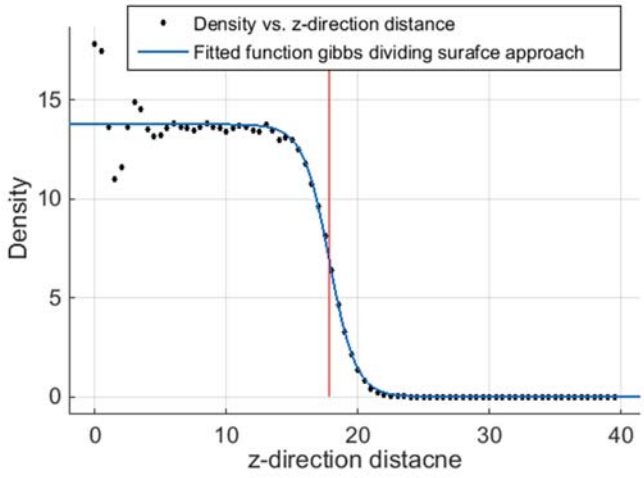


Figure S4. The hyperbolic tangent function (blue solid line) fitted to the water density profile (black dots). The Z location at the middle of the water-vapor interface is taken to be the height of the droplet.

Calculation of the surface-intersection radius of the droplet (r): First, all water molecules at the first hydration layer (i.e. 4 Å distance from surface) were identified. Then, we projected them on the XY-plane and binned into 2 Å × 2 Å grids. The number of water molecules presented at each grid was calculated. If the number of water molecules within one grid was less than a

threshold, then all water molecules of that grid were classified as boundary water. Finally, the positions of the boundary water were fitted to the circle function:

$$f(x, y) = (x - x_c)^2 + (y - y_c)^2 - r^2$$

where (x_c, y_c) is the center of the circle and r is the estimated surface-intersection radius of the droplet.

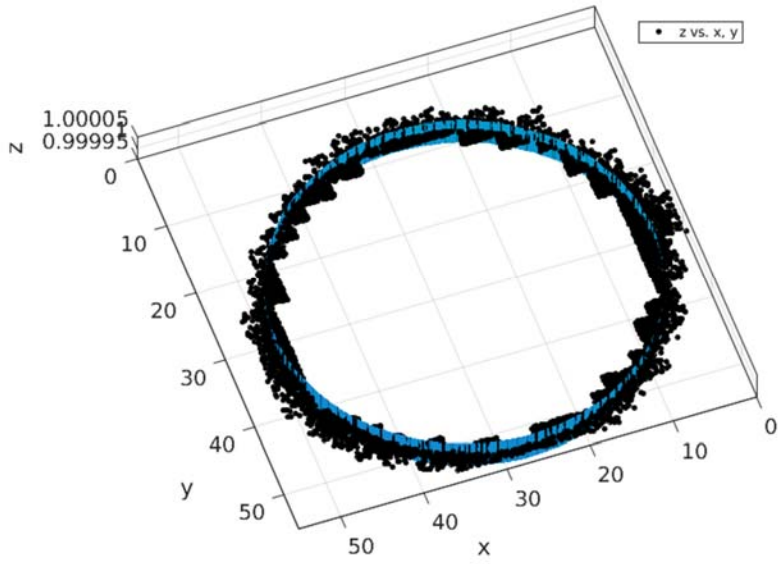


Figure S5. The interfacial water molecules at droplet boundary (black dots) were fitted to a circle (blue hollow cylinder).

Section III. Changes of the *Gauche* Defect Percentage in Simulated Annealing Simulations by Different Force Fields

(a) Lipid14

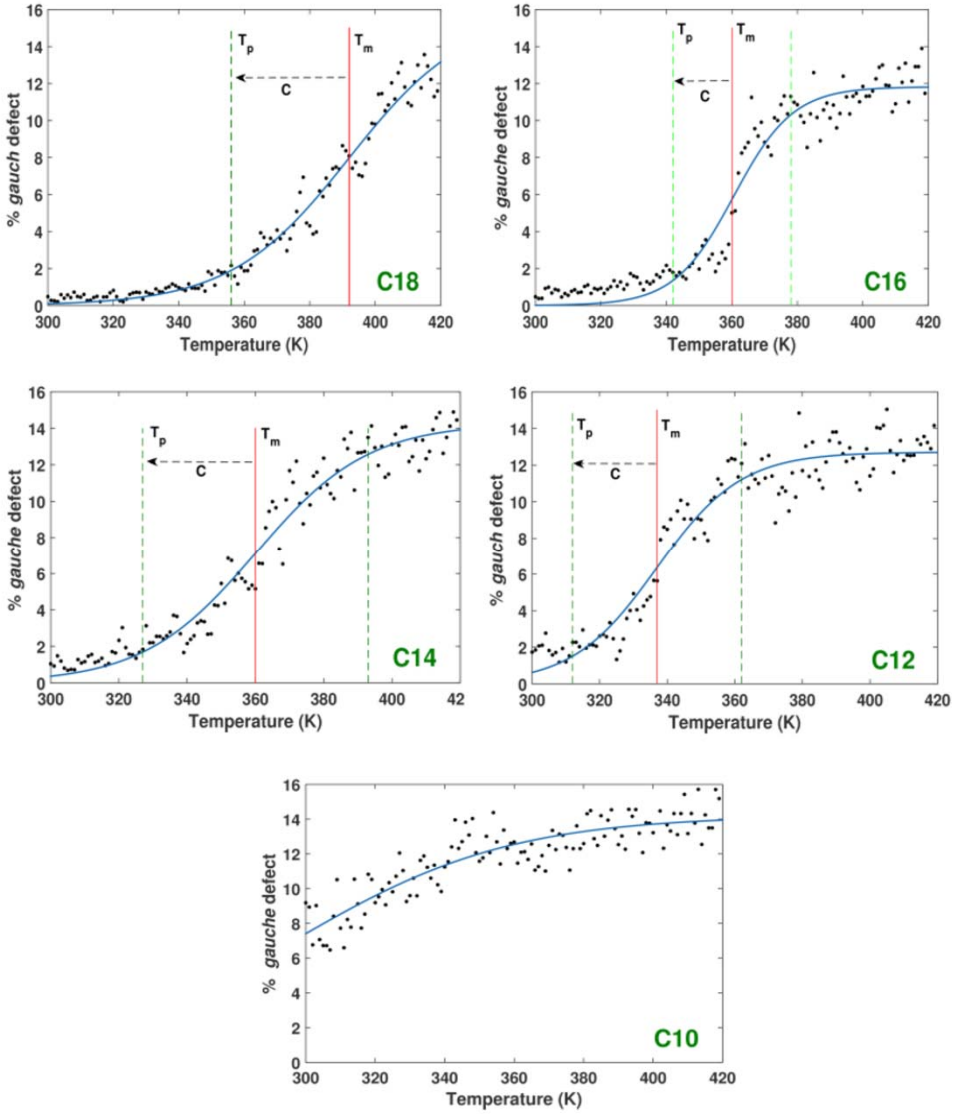
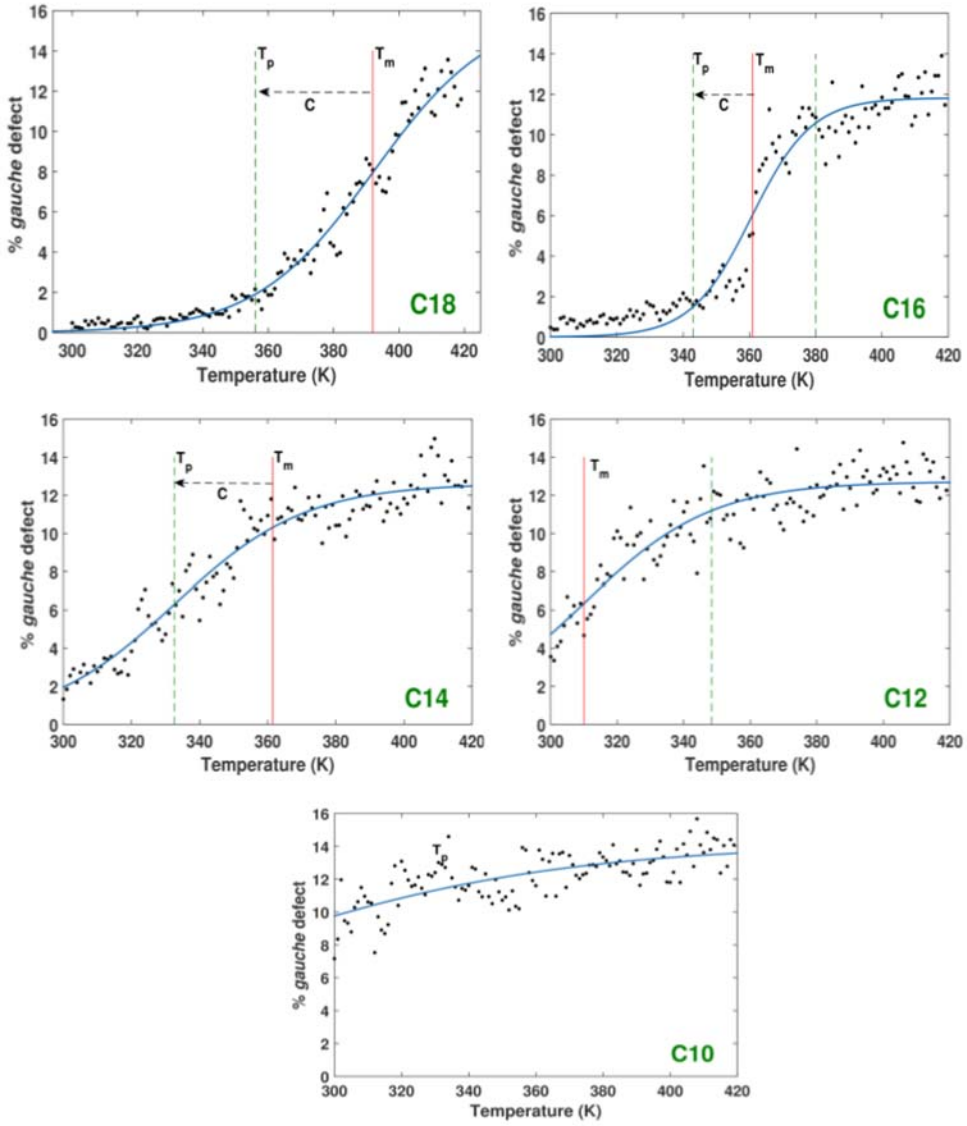
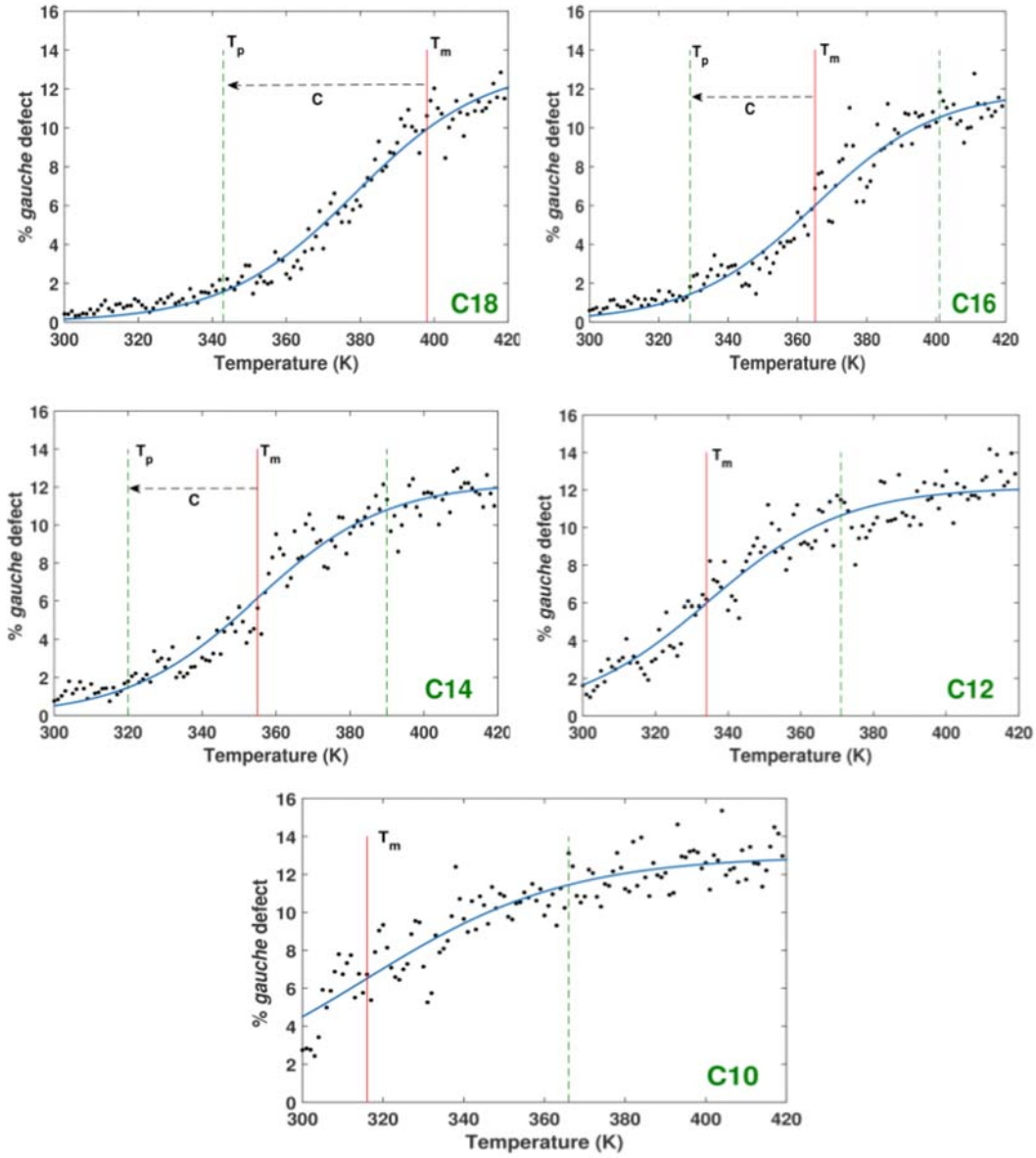


Figure S6. The percentage of *gauche* defects as a function of temperature in simulated annealing simulations by (a) Lipid14, (b) Slipids, (c) CHARMM36, (d) L-OPLS, (e) GROMOS54a6, and (f) GAFF. Each black point is the computed average at a particular temperature during the simulated annealing process. The blue line is the fitted curve to the data points using a hyperbolic tangent function (Eq (1) in the main text). The red line indicates the middle temperature (T_m) of the phase transition and the two green dashed lines indicate the onset (the phase transition temperature, T_p) and the offset of the transition. One-half of the phase transition period is denoted as C (the black dashed line).

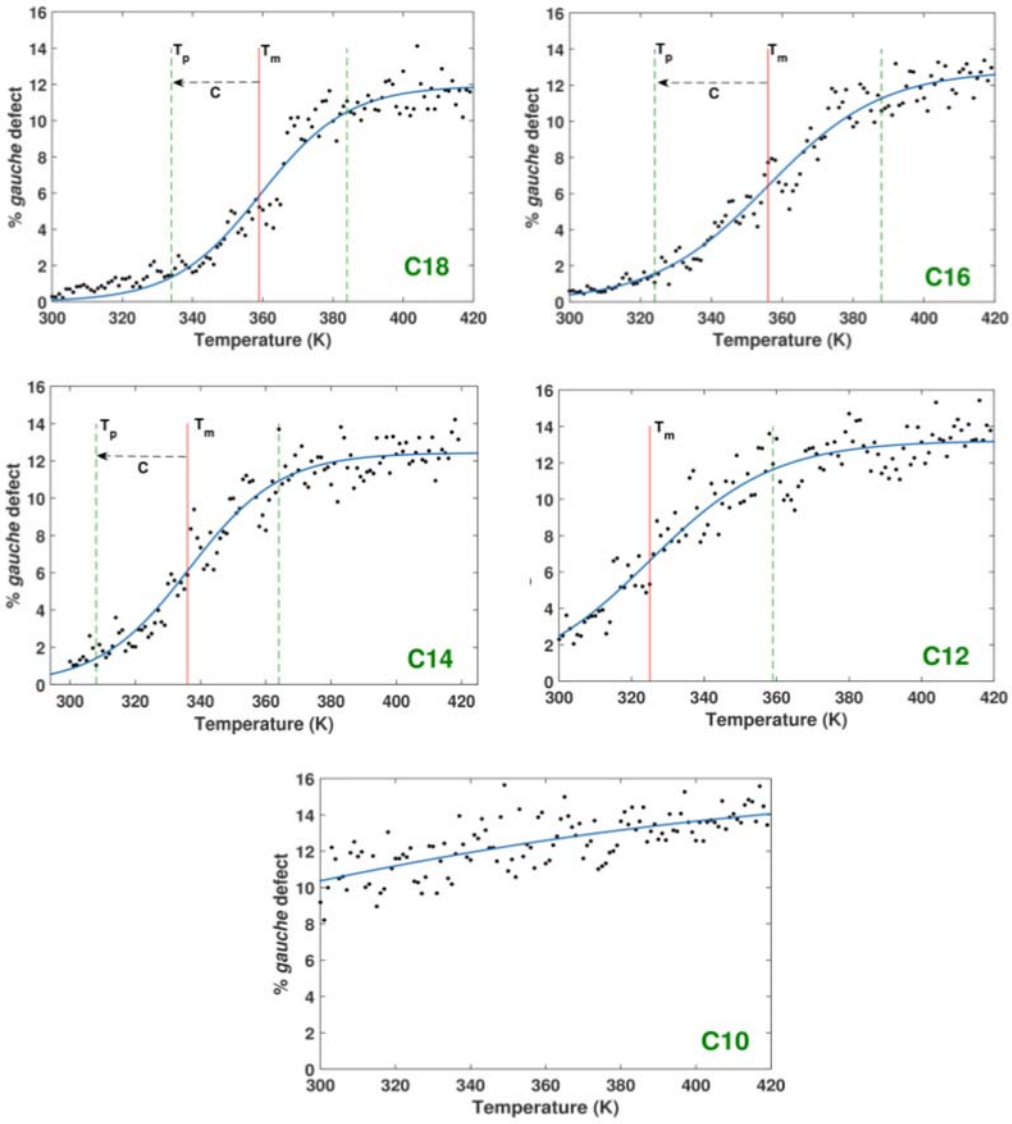
(b) Slipids



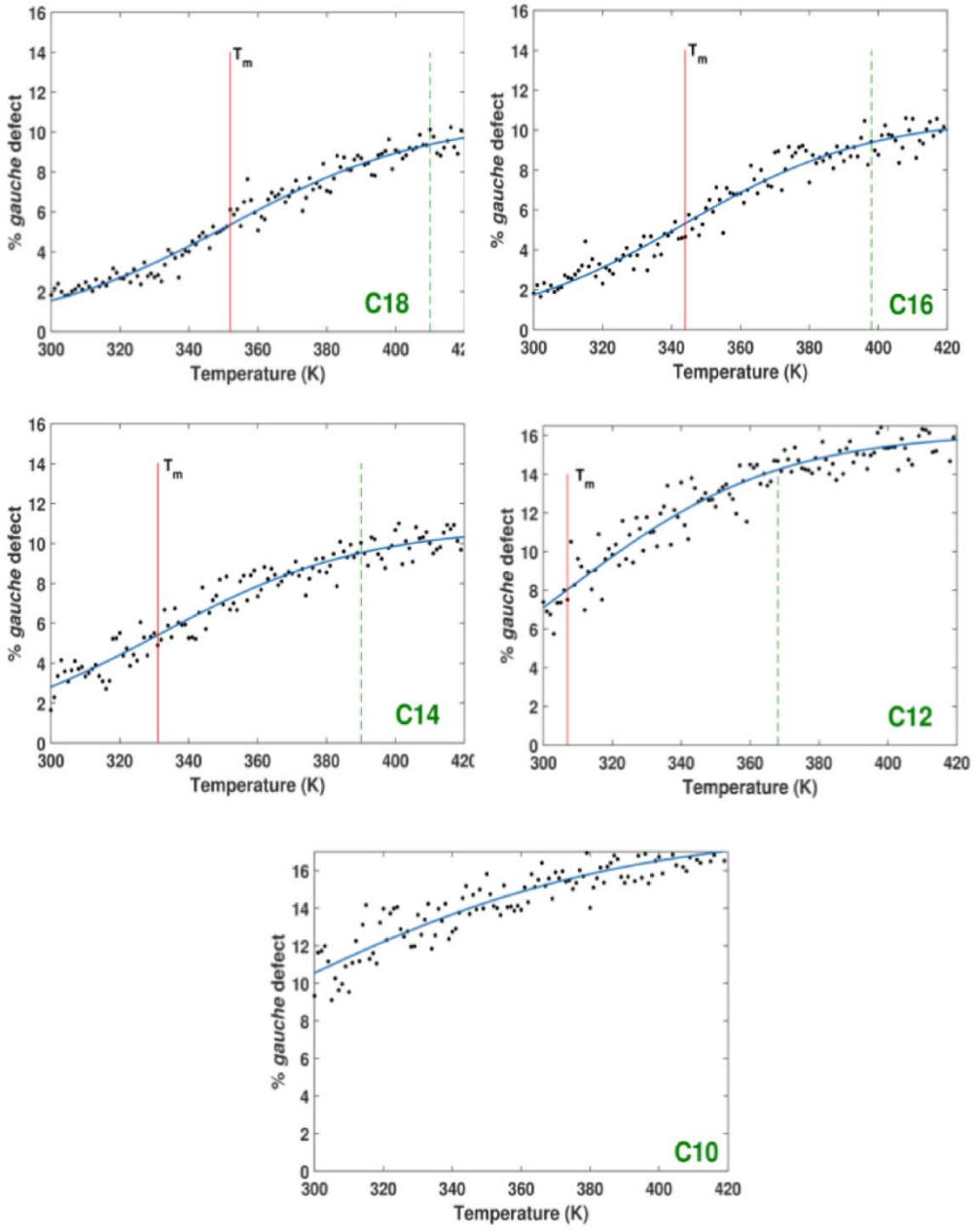
(c) CHARMM36



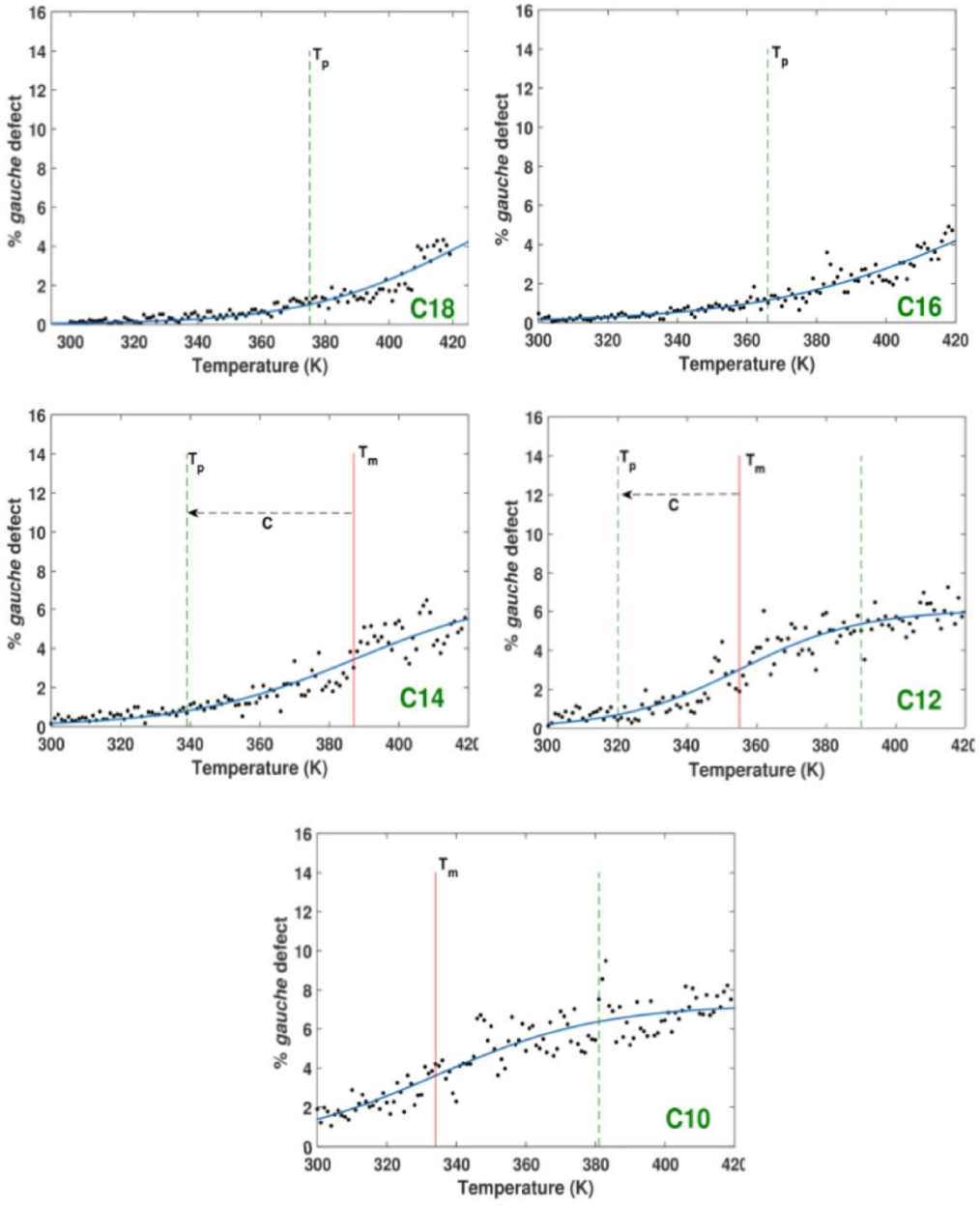
(d) L-OPLS



(e) GROMOS54a6



(f) GAFF



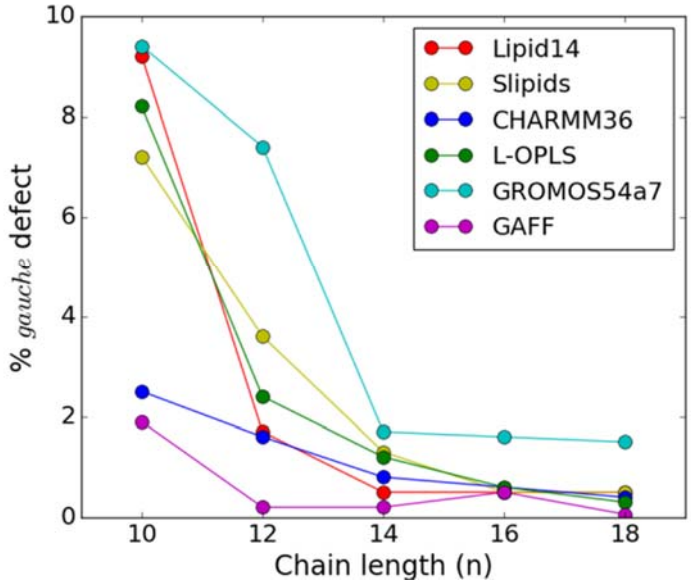


Figure S7. The percentage of *gauche* defects as a function of chain length at temperature 300 K.