Refined OPLS All-Atom Force Field Parameters for n-Pentadecane, Methyl Acetate, and Dimethyl Phosphate

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Supporting Information

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Construction and preliminary thermal equilibration of model molecular systems

Condensed phase homogeneous liquids of dimethyl phosphate (DMPH) and n-pentadecane (nPD) were created with `genbox` program[1] with the simple cubic lattice symmetry enforced while setting initial dimensions of simulation boxes. The molecules were placed uniformly on a rectangular grid and the 50-ps MD simulation in the canonical ensemble was carried out at 37°C. The pre-equilibrated model liquids were then submitted to the 15-ns MD simulation in the isothermal-isobaric ensemble at 10°C below the experimentally determined boiling point, which for DMPH and nPD is, respectively, 160°C and 270°C. High temperature MD simulations allowed to diminish artificial ordering of molecules characterizing their initial arrangement.

The initial configuration of 512 DMPH molecules filled a cubic box of edge length 4.31 nm what corresponds to density of 1338 kg/m^3. In case of nPD, the initial configuration of 162 molecules occupied a cubic box of edge length 5.01 nm and the initial density of the system was 455 kg/m^3. The initial configuration of 1000 methyl acetate (MAc) molecules was taken from `virtualchemistry.org` web site[2]. In that case, box dimension and density were, respectively, 5.06 nm and 947 kg/m^3.

Determination of the melting point temperature of n-pentadecane

The main protocol of determination of the melting point temperature (T_m) of n-pentadecane (nPD) involved carrying out two MD simulations at temperatures slightly below (8°C) and above (12°C) the experimental value of T_m (approx. 10°C). The number of nPD molecules in simulation boxes was 162 and in the initial configuration a large fraction of nPD molecules was in an extended conformation, however, they were not collectively aligned (see Results for further details).

The application of the new OPLS/AA force field parameters for nPD led to a gel-like

phase at 8°C and the liquid phase at 12°C indicating that T_m is likely in the range 8–12°C. To confirm the proper reproduction of T_m for nPD we performed additional MD simulations at temperatures 8°C, 10°C, 12°C, 14°C, and 16°C. The melting point temperature was determined in such a series of MD simulations as the highest temperature at which coexistence of the liquid and gel phases was seen. Three series of such MD simulations were performed to address uncertainty resulting from inadequate sampling of configuration space during transitions between liquid and gel phases. The simulated systems were made of 486 nPD molecules, which is three times larger than in the initial simulations performed while refining nPD force field parameters. Each of 15 simulations was 100 ns long; however, it should be noted that the careful choice of the starting configuration allowed to reach the thermal equilibrium in all MD simulations just within initial 40 ns. The melting point temperature averaged over three replicated MD simulations is 10°C with standard deviation of 2°C.

The determined value of melting point temperature is shown in Table 1. Below, we provide additional details concerning the way of obtaining the initial configuration used in three replicated MD simulations.

The initial configuration of the nPD simulation box was built by immersing a gel-like phase obtained earlier in the 8°C simulation in a box of liquid nPD thermally equilibrated at 12°C. In a subsequent series of eight 10 to 40-ps equilibration MD simulations, the gel fraction of nPD molecules was constrained to preserve their extended conformation and collective alignment while the box dimensions were allowed to shrink so that unconstrained nPD molecules could closely fill the empty space around the gel phase. The final 40-ps equilibration MD run was performed using the simulation protocol described in detail in Methods (section: Molecular modelling protocols and force field parameters). The final configuration contained approx. 17% nPD molecules in an extended conformation forming a phase which was considered a seed necessary to trigger transition of the remaining nPD molecules into gel phase at the relevant temperature.

Three series of five MD simulations started from the configuration described above but

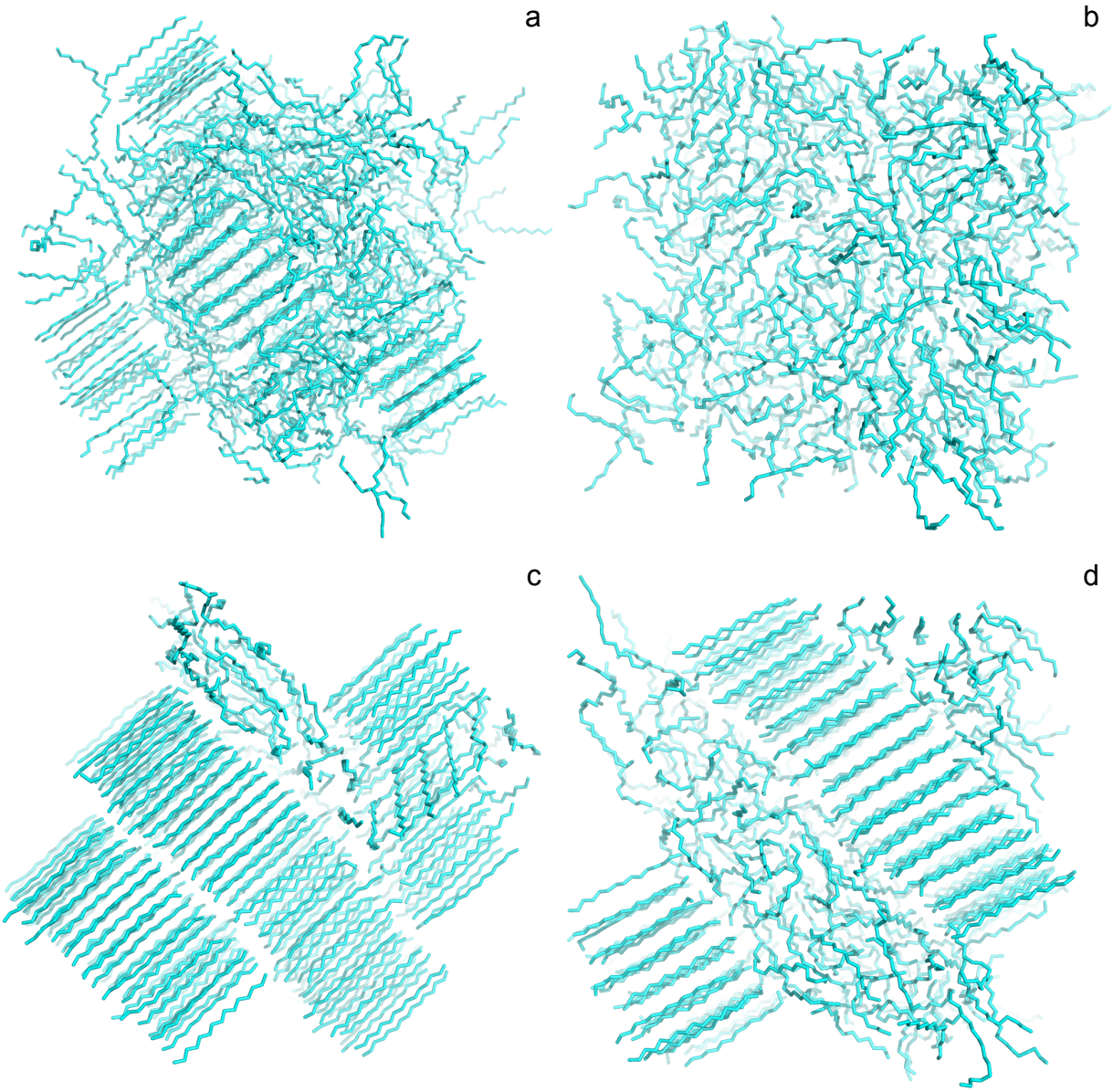

Figure S1: (a) The initial configuration of 486 nPD molecules, which was used in determination of the melting point temperature of n-pentadecane. (b-d) The final configurations of 486 nPD molecules in three replicated MD simulations carried out at 10°C. Hydrogen atoms of nPD were omitted for clarity.

they differed in assigned initial velocities: the A and C series had the initial velocities randomly generated for, respectively, 26.85°C and −123.15°C, the B series had the initial velocities set for the final configuration in the pre-equilibration MD run, which corresponded to 8.49°C.

For each of 15 MD simulations, we determined the average density and the fraction of nPD molecules in the gel phase (Table S1). For simplicity, nPD molecule was considered to be in the gel phase if it adopted an extended conformation, i.e. a conformation, in which all consecutive non-terminal main-chain C–C–C–C torsions are in the trans conformation. In Figure S1, we show snapshots of the initial and final configurations obtained in three replicated MD simulations at 10°C. A zip file containing selected configurations of nPD in the PDB format is also available for download from `http://pubs.acs.org`.

Table S1: Results of three series of MD simulations (A, B, and C) of pentadecane (nPD) carried out at temperatures from 8°C to 16°C (**Temp.**). The reported average values of densities (in kg/m^3, **dens.**) and fractions of nPD molecules in an extended (gel-like) conformation (in percentages, **%ext**) were calculated from five consecutive and non-overlapping 10 ns MD trajectory blocks in 50–100 ns time range. Only significant digits are shown. The figures in bold denote MD simulations in which co-existence of gel and liquid phases is seen. The fraction of nPD in the gel phase for six indicated MD simulations is in the range from 48.3 to 82.9%.

Temp.	**A**		**B**		**C**	
	dens.	**%ext**	**dens.**	**%ext**	**dens.**	**%ext**
8°C	**816.9**	**50.2**	**861.4**	**81.9**	**816.7**	**50.3**
10°C	759.6	1.7	**867.0**	**82.9**	**811.7**	**48.8**
12°C	757.8	1.6	**809.7**	**48.3**	757.7	1.6
14°C	755.7	1.6	755.7	1.5	755.7	1.6
16°C	753.8	1.5	753.7	1.5	753.7	1.5

References

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(2) Caleman, C.; van Maaren, P. J.; Hong, M.; Hub, J. S.; Costa, L. T.; van der Spoel, D. *J. Chem. Theory Comput.* **2012**, *8*, 61–74.