

Electronic Supplementary Information for

**Size matters: asphaltenes with enlarged aromatic cores promote heat transfer
in organic phase-change materials**

Artem D. Glova,^a Victor M. Nazarychev,^b Sergey V. Larin,^b Andrey A. Gurtovenko^b and Sergey V. Lyulin^{*b}

^a*Department of Physics and Astronomy, The University of Western Ontario, 1151 Richmond Street, London, Ontario, N6A 3K7, Canada.*

^b*Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi Prospekt V.O. 31, St. Petersburg, 199004, Russia.*

E-mail: sergey.v.lyulin@gmail.com

Equilibration of paraffin-asphaltene samples

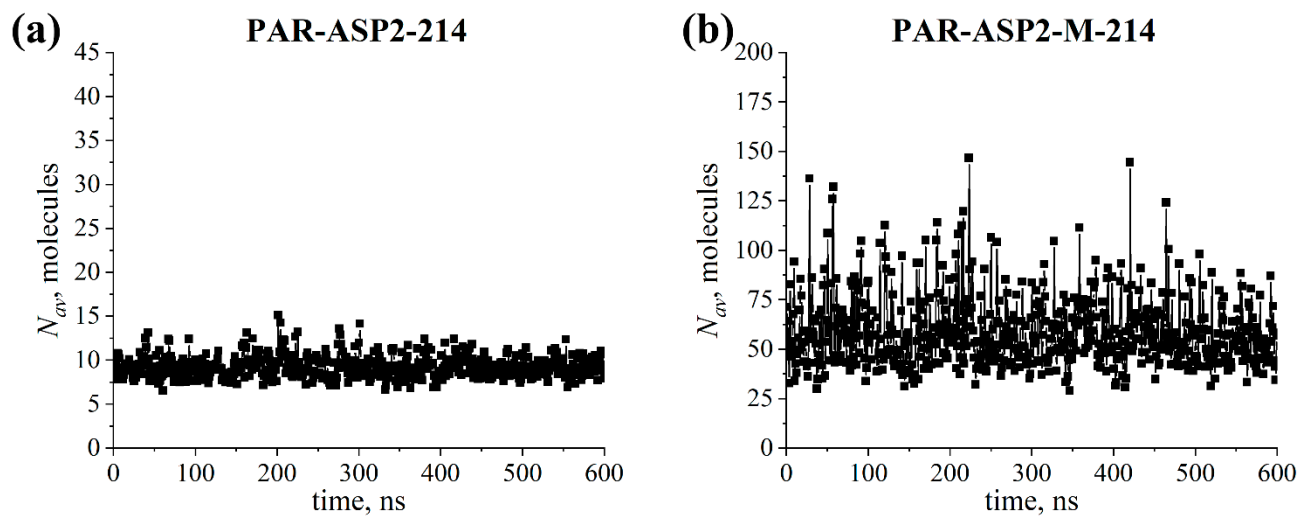


Fig. S1. Time dependence of average sizes N_{av} of asphaltene aggregates in the (a) PAR-ASP2-214 and (b) PAR-ASP2-M-214 systems.

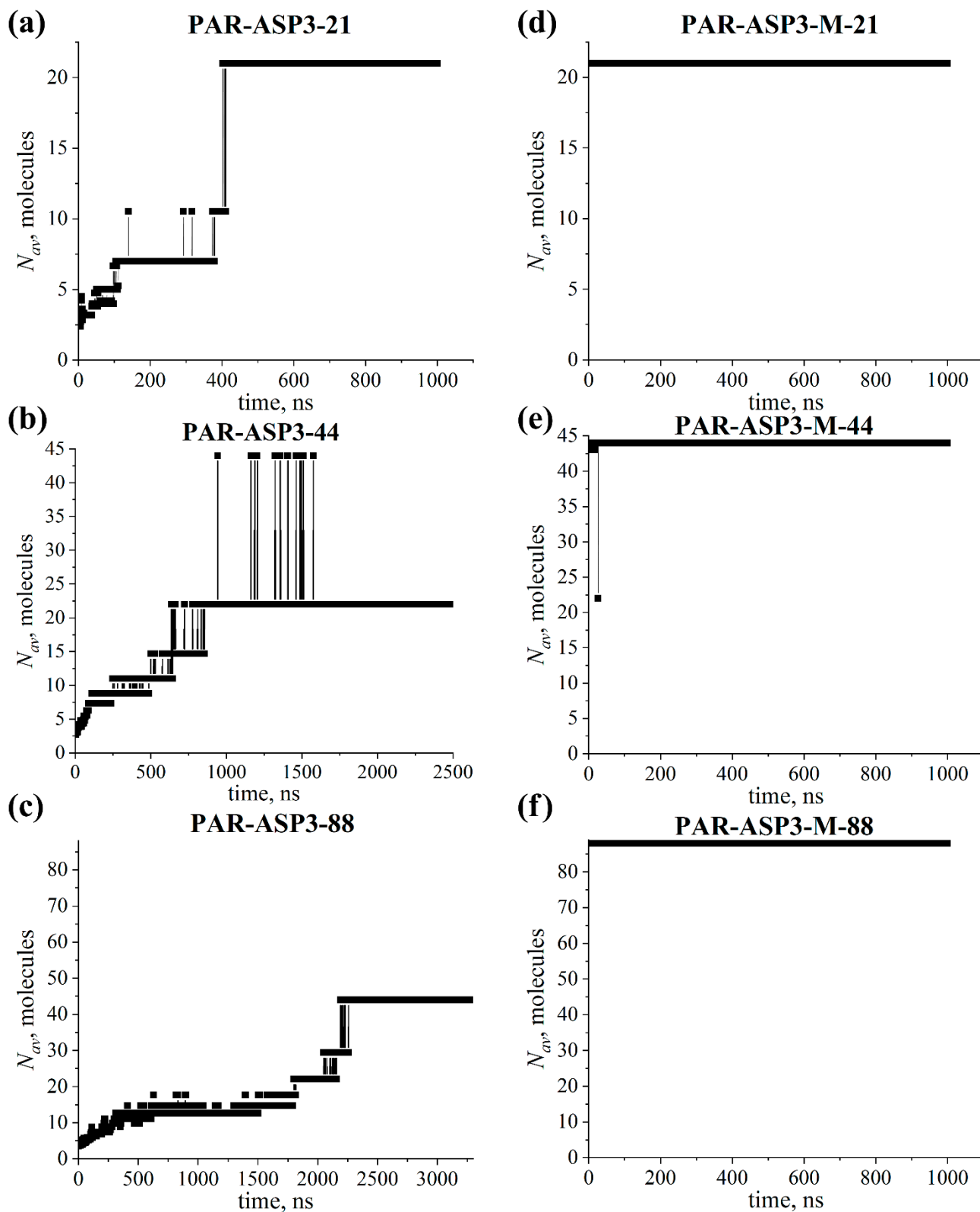


Fig. S2. Time dependence of average sizes N_{av} of asphaltene aggregates in the (a) PAR-ASP3-21, (b) PAR-ASP3-44, (c) PAR-ASP3-88, (d) PAR-ASP3-M-21, (e) PAR-ASP3-M-44, and (f) PAR-ASP3-M-88 systems.

Anisotropy of the thermal conductivity tensor

Table S1. Components of the thermal conductivity tensor of the systems studied.

System	Thermal conductivity coefficient, κ , W/(m·K)			
	κ_{xx}	κ_{yy}	κ_{zz}	$\langle \kappa \rangle$
PAR-ASP1-44	0.30 ± 0.02	0.33 ± 0.04	0.22 ± 0.03	0.28 ± 0.02
PAR-ASP1-99	0.23 ± 0.03	0.20 ± 0.01	0.20 ± 0.02	0.21 ± 0.01
PAR-ASP1-214	0.20 ± 0.01	0.19 ± 0.03	0.29 ± 0.03	0.23 ± 0.01
PAR-ASP2-214	0.20 ± 0.01	0.26 ± 0.02	0.18 ± 0.02	0.21 ± 0.01
PAR-ASP3-21	0.32 ± 0.01	0.31 ± 0.02	0.25 ± 0.02	0.29 ± 0.01
PAR-ASP3-44	0.29 ± 0.01	0.34 ± 0.01	0.51 ± 0.02	0.38 ± 0.01
PAR-ASP3-88	0.35 ± 0.01	0.32 ± 0.01	0.30 ± 0.01	0.32 ± 0.02
PAR-ASP1-M-44	0.28 ± 0.01	0.22 ± 0.02	0.22 ± 0.04	0.24 ± 0.02
PAR-ASP1-M-99	0.31 ± 0.05	0.28 ± 0.04	0.49 ± 0.02	0.36 ± 0.01
PAR-ASP1-M-214	0.91 ± 0.04	0.43 ± 0.04	0.78 ± 0.04	0.71 ± 0.02
PAR-ASP2-M-214	0.27 ± 0.01	0.22 ± 0.01	0.22 ± 0.02	0.24 ± 0.01
PAR-ASP3-M-21	0.33 ± 0.03	0.43 ± 0.02	0.32 ± 0.02	0.36 ± 0.01
PAR-ASP3-M-44	0.81 ± 0.02	0.55 ± 0.01	0.63 ± 0.02	0.66 ± 0.01
PAR-ASP3-M-88	1.44 ± 0.03	0.97 ± 0.02	0.56 ± 0.04	0.99 ± 0.02

Convergence of thermal conductivity calculations

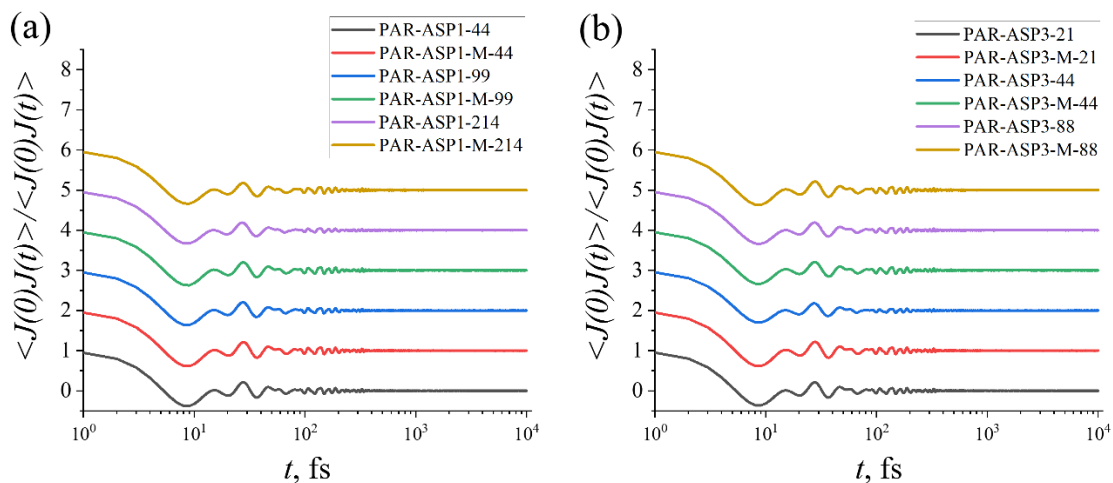


Fig. S3. Normalized autocorrelation functions of heat flux (HFACF) for selected paraffin-asphaltene systems as a function of time ($T=450$ K). Shown are the results for the last 10 ps interval of 1 ns-long NVE trajectories; the HFACF curves for other 10 ps intervals demonstrate similar behavior. Presented are the systems with ASP1/ASP1-M (a) and ASP3/ASP3-M (b) asphaltenes. For clarity, the curves for different systems are arbitrarily shifted relative to each other.

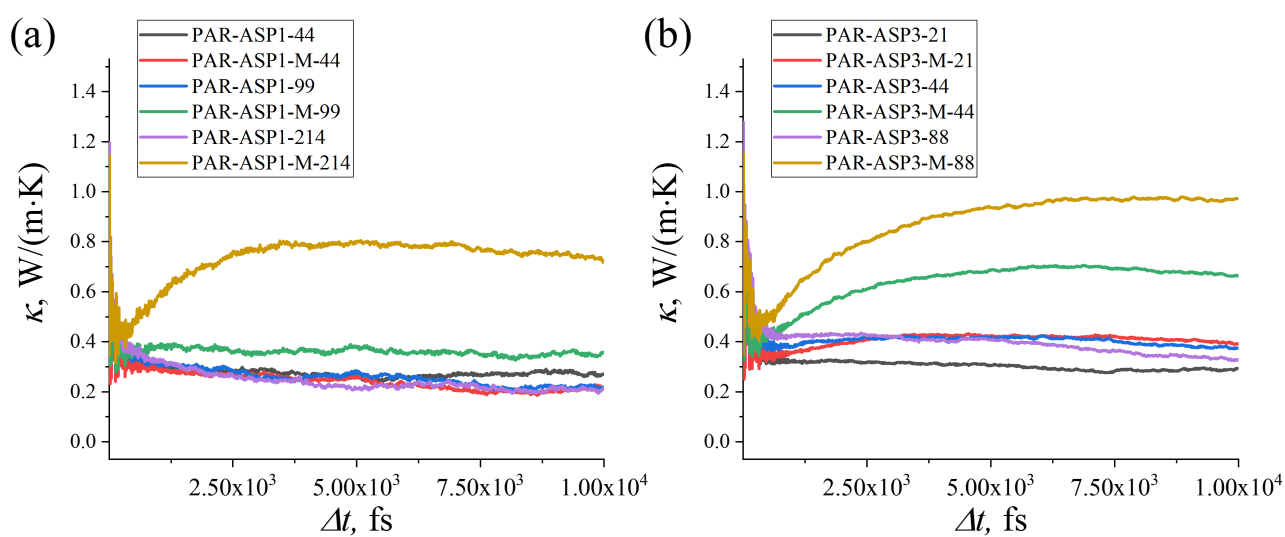


Fig. S4. The thermal conductivity coefficients calculated by the integration of the HFACFs presented in Fig. S3 as a function of time Δt used for the integration. Presented are the systems with ASP1/ASP1-M (a) and ASP3/ASP3-M (b) asphaltenes.

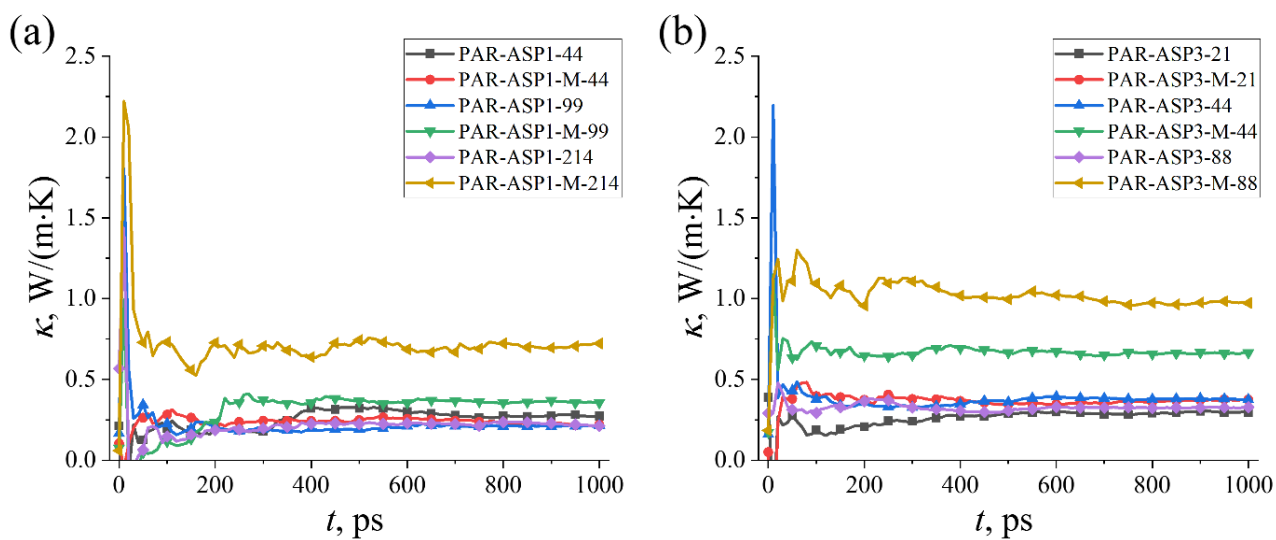


Fig. S5. The coefficient of thermal conductivity as a function of time ($T=450$ K). The thermal conductivity was calculated over a 1 ns-long trajectory with a time step of 10 ps. Shown are the systems with ASP1/ASP1-M (a) and ASP3/ASP3-M (b) asphaltenes. Only last 500 ps of the presented curves were used for calculating the average values of the thermal conductivity coefficients.

Definition of the vector normal to the asphaltene cores and the order parameter

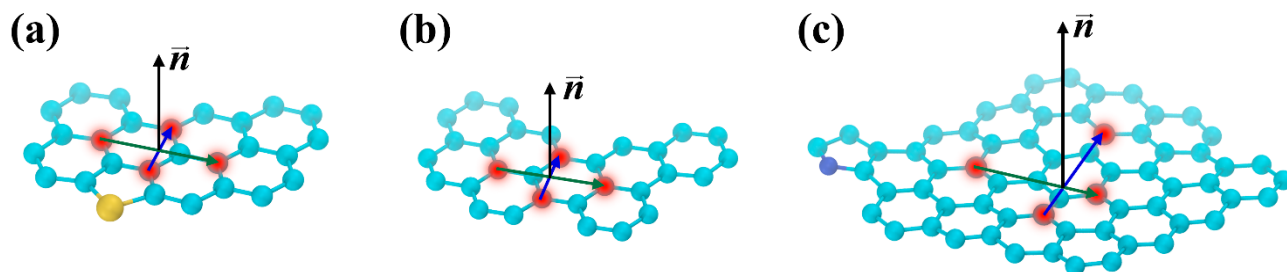


Fig. S6. Definition of vectors \vec{n} normal to the asphaltene cores in the case of (a) ASP1 and ASP1-M, (b) ASP2 and ASP2-M, and (c) ASP3 and ASP3-M molecules. The vectors \vec{n} were obtained as the cross products of blue and green in-plane vectors. Atoms that were used to form the in-plane vectors are marked in red. The order parameter was obtained as the largest eigenvalue of the ordering matrix with components $Q_{\alpha\beta} = \left\langle (2N_{asp})^{-1} \sum_{i=1}^{N_{asp}} (3 \cdot n_{\alpha}^i n_{\beta}^i - \delta_{\alpha\beta}) \right\rangle$, where N_{asp} is the number of asphaltene molecules in the system, n_{α}^i and n_{β}^i denote the projections of unit vectors \vec{n} normal to the i th asphaltene core on the box axes α and β ($\alpha, \beta = x, y,$ and z), $\delta_{\alpha\beta}$ is the Kronecker delta, and $\langle \dots \rangle$ denotes the average over time.