

Supporting Information

Dynamic heterogeneity flow promotes binding reactions in a dense system of hard annular sector particles

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This supplementary information includes some simulation details, supplementary tables S1, S2 and supplementary figures S1-S10.

The rotational dynamics of ASPs are handled by the same method as in the paper[1], which could also be used as simulation tools in LAMMPS and HOOMD. The total mass of a single ASP can be calculated by summation of all composed beads. Setting the mass of each Lennard-Jones bead as unit, the center of mass of ASP is

expressed by $\bar{r} = \left[\frac{1}{n} \sum_{i=1}^n x_i, \frac{1}{n} \sum_{i=1}^n y_i \right]$, where i runs from 1 to n , and n is the number of beads on each ASP. Then, the moment of inertia of each particle can be calculated as

$$I = \sum_{i=1}^n m_i |r_i - \bar{r}|^2, \text{ with the mass } m_i \equiv 1.$$

In a NVT ensemble, we treat the particle rotational motion as an additional degree of freedom. From the equipartition theorem, on average, each quadratic degree

of freedom has an energy of half of $k_B T$, so

$$mv_x^2 = mv_y^2 = I\omega^2 = k_B T$$

in which $\omega = \tau_c / I$, where τ_c is the torque exerted on an ASP, $\tau_c = \sum_{i=1}^n F_i \times (r_i - \bar{r})$, where F_i is the force on the i th bead of the ASP.

The structural relaxation time and the rate of translational to rotational diffusion coefficients are calculated (Figure S10). And the results show a decoupling of the rotational and translational diffusion. Similar decoupling phenomenon has also been reported in glass forming systems[2].

Table S1. Comparison of the reaction probabilities between different trajectory sequences.

sequence:	10 ⁵ step-length/10 ⁸ MD steps			10 ⁴ step-length/10 ⁸ MD steps			
	ϕ_A :	0.150	0.300	0.480	0.150	0.300	0.480
P_R -total		0.0413	0.1202	0.0095	0.0419	0.1207	0.0094
P_R -dimer ([M]+[M] \rightleftharpoons [D])		0.0412	0.1156	0.0021	0.0418	0.1159	0.0022
P_R -n-mer		0.0001	0.0046	0.0074	0.0001	0.0048	0.0072
R_{n-mer}		0.0035	0.0380	0.7789	0.0018	0.0395	0.7664

The first series are sampled with snapshots selected in a sequence of 1.0×10^8 MD steps with a 1.0×10^5 MD steps interval, and the second series is sampled with snapshots selected in another sequence of 1.0×10^8 MD steps with a 1.0×10^4 MD steps interval.

Table S2. Fitting the self-intermediate scattering function (F_s) in the stretched exponential form $\exp[-(t/\tau)^\beta]$.

ϕ_A	Fitting equation
0.400	$1.02 * \exp(-(t/60.8)^{0.62})$
0.430	$1.015 * \exp(-(t/95.8)^{0.60})$
0.450	$1.02 * \exp(-(t/131.8)^{0.585})$
0.460	$1.02 * \exp(-(t/170.8)^{0.58})$
0.470	$1.02 * \exp(-(t/205.8)^{0.57})$

0.480

$1.015 \cdot \exp(-(t/298.8)^{0.55})$

0.490

$1.02 \cdot \exp(-(t/400.8)^{0.52})$

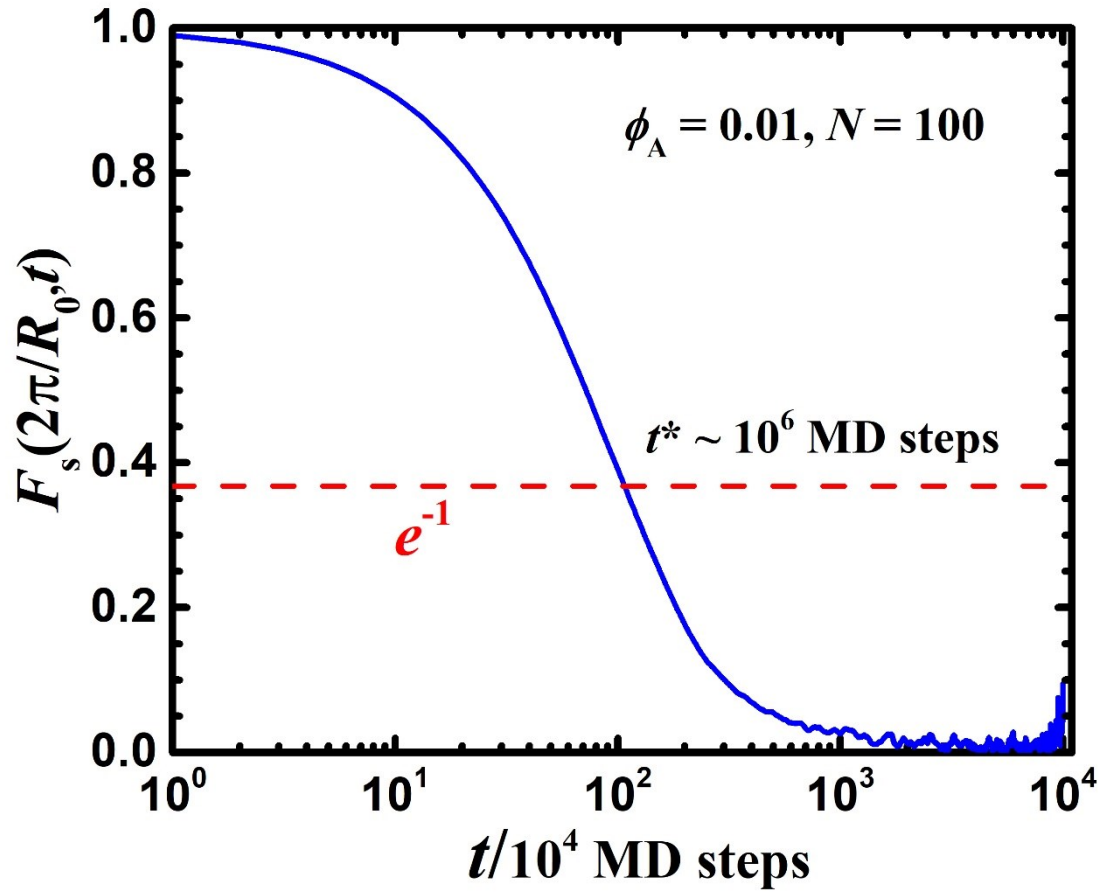


Figure S1. The self-part intermediate scattering function (self-ISF) of $\phi_A = 0.01$. The measured characteristic time (self-ISF decays to $1/e$) t^* is around 10^6 MD steps.

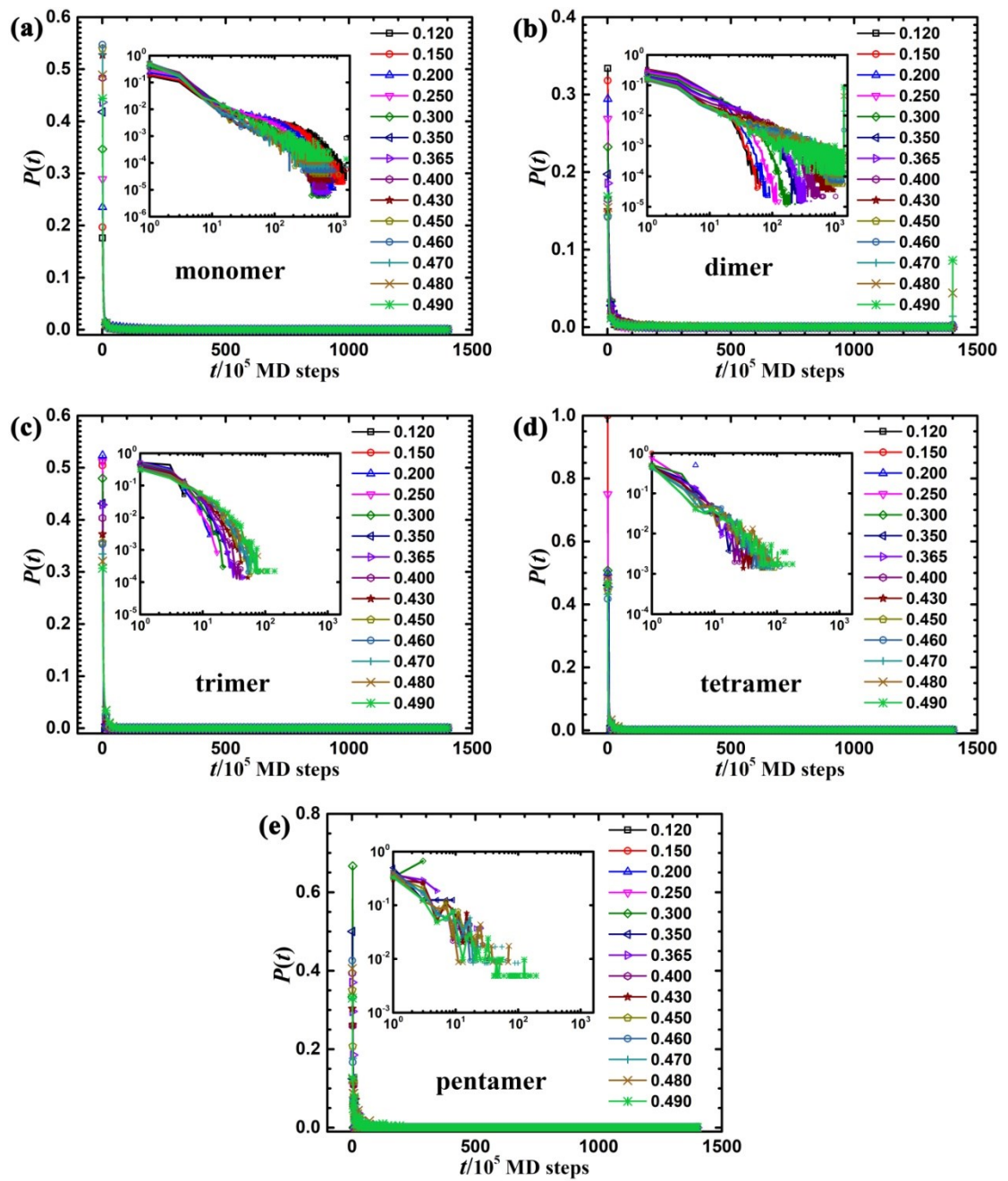


Figure S2 The distribution of lifetime for (a) monomer (b) dimer (c) trimer (d) tetramer and (e) pentamer of ASPs.

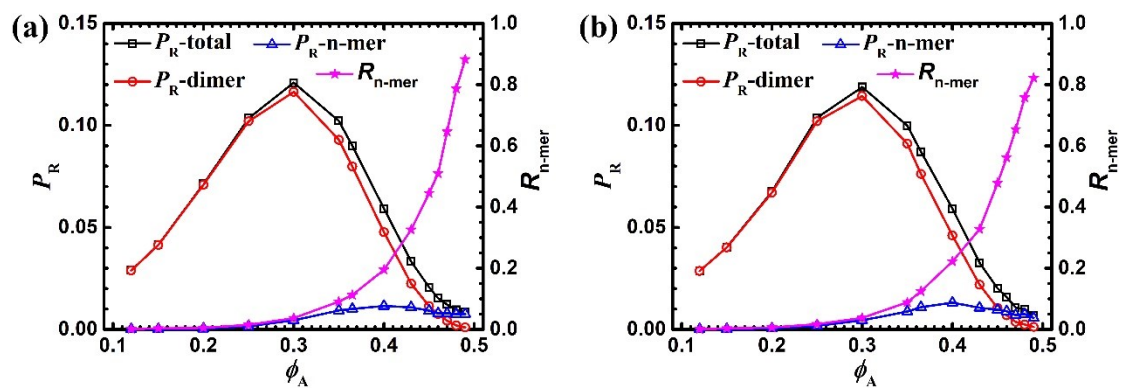


Figure S3. Reaction probabilities calculated through snapshots selected in a sequence of (a) 1.4×10^8 MD steps with a 1.0×10^5 MD steps interval and (b) 2.9×10^7 MD steps with a 1.0×10^4 MD steps interval.

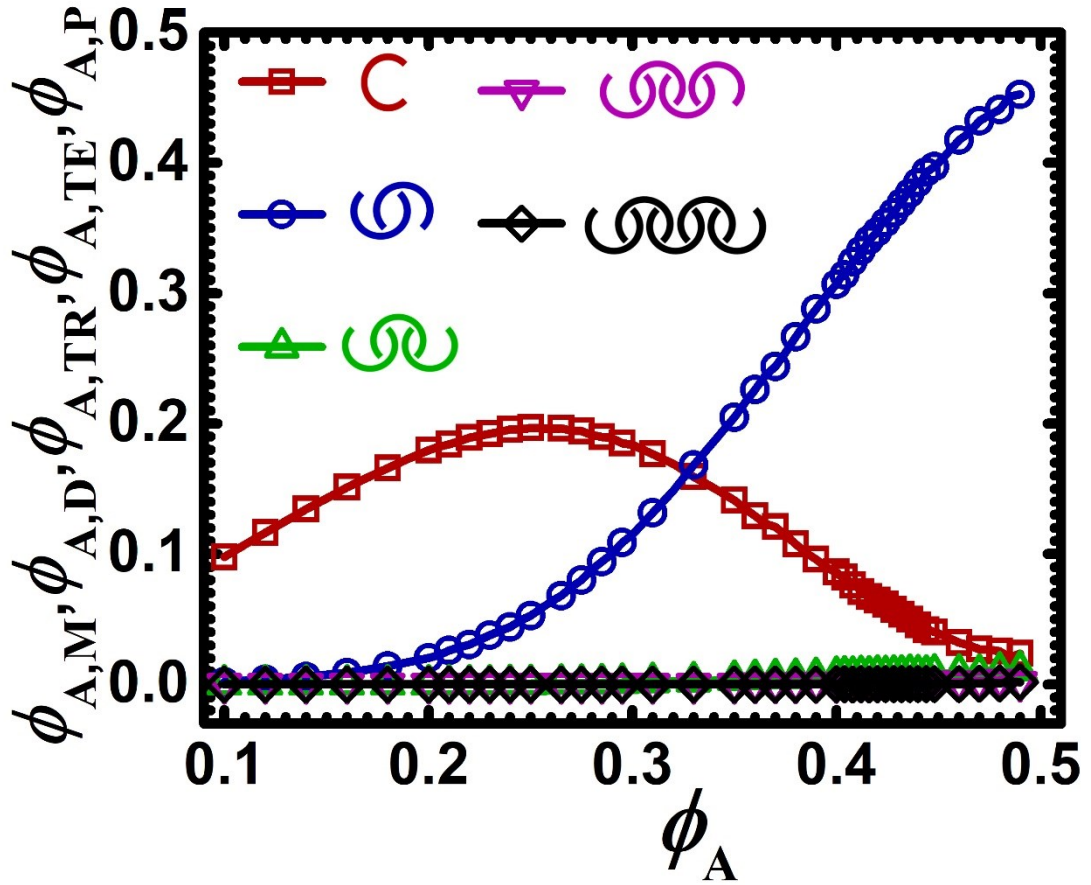


Figure S4. The area fraction of monomer ($\phi_{A,M}$, red square), dimer ($\phi_{A,D}$, navy cycle), trimer ($\phi_{A,TR}$, green up-triangle), tetramer ($\phi_{A,TE}$, magenta down-triangle) and pentamer ($\phi_{A,P}$, black diamond) as a function of ϕ_A . Both $\phi_{A,M}$ and $\phi_{A,D}$ show the same trend as that shown in experiments (Figure 2a)[3].

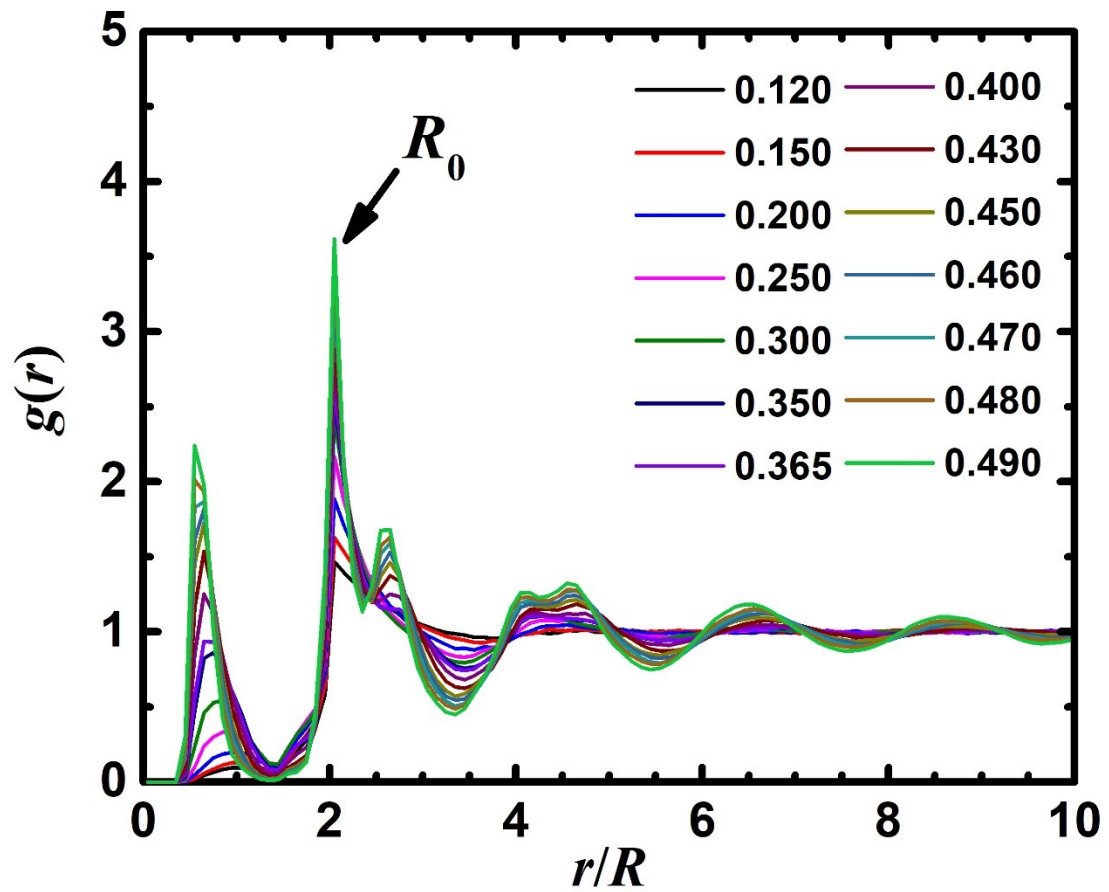


Figure S5. Radial distribution function of the ASPs system. The R_0 is the characteristic length used to set the wave vector in self-ISF.

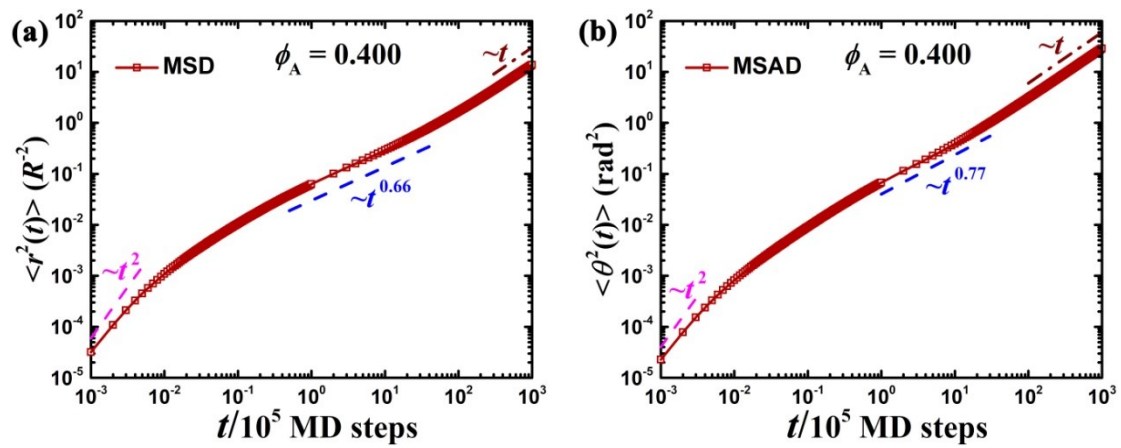


Figure S6. An example of (a) MSD and (b) MSAD curve showing three regimes in diffusion behavior at $\phi_A = 0.400$. The characteristic time period of ballistic motion is about 5×10^2 MD steps.

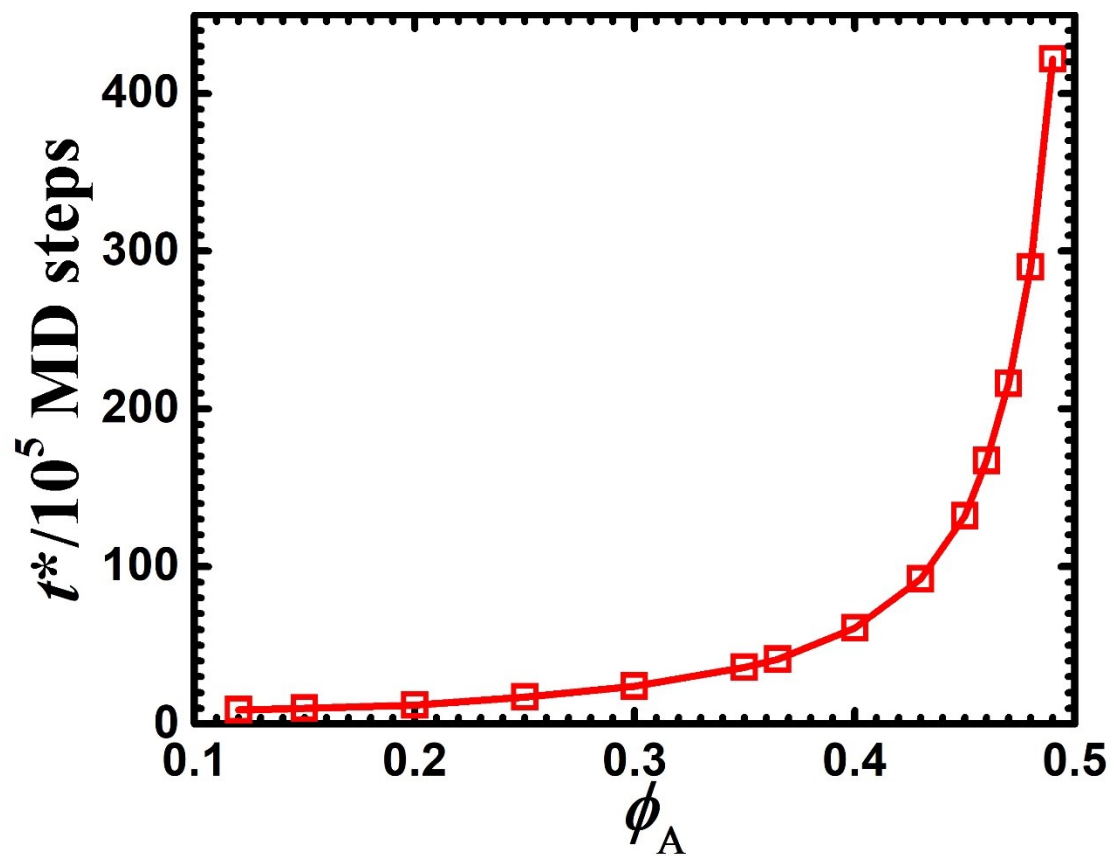


Figure S7. The measured characteristic time t^* obtained from self-ISFs at different ϕ_A .

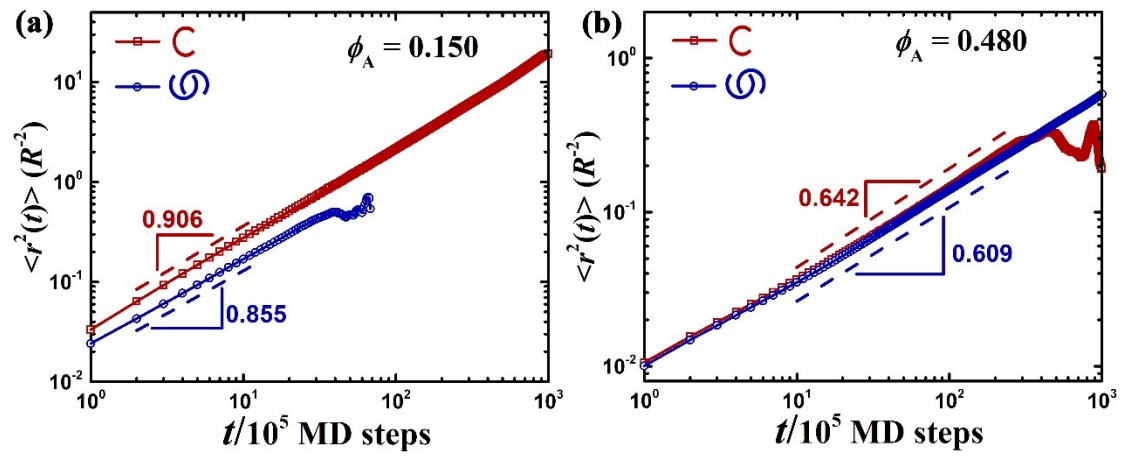


Figure S8. Examples to fit mean square displacement (MSD) before the characteristic time in power-law form $a \times t^d$. (a) $\phi_A = 0.150$ system. (b) $\phi_A = 0.480$ system.

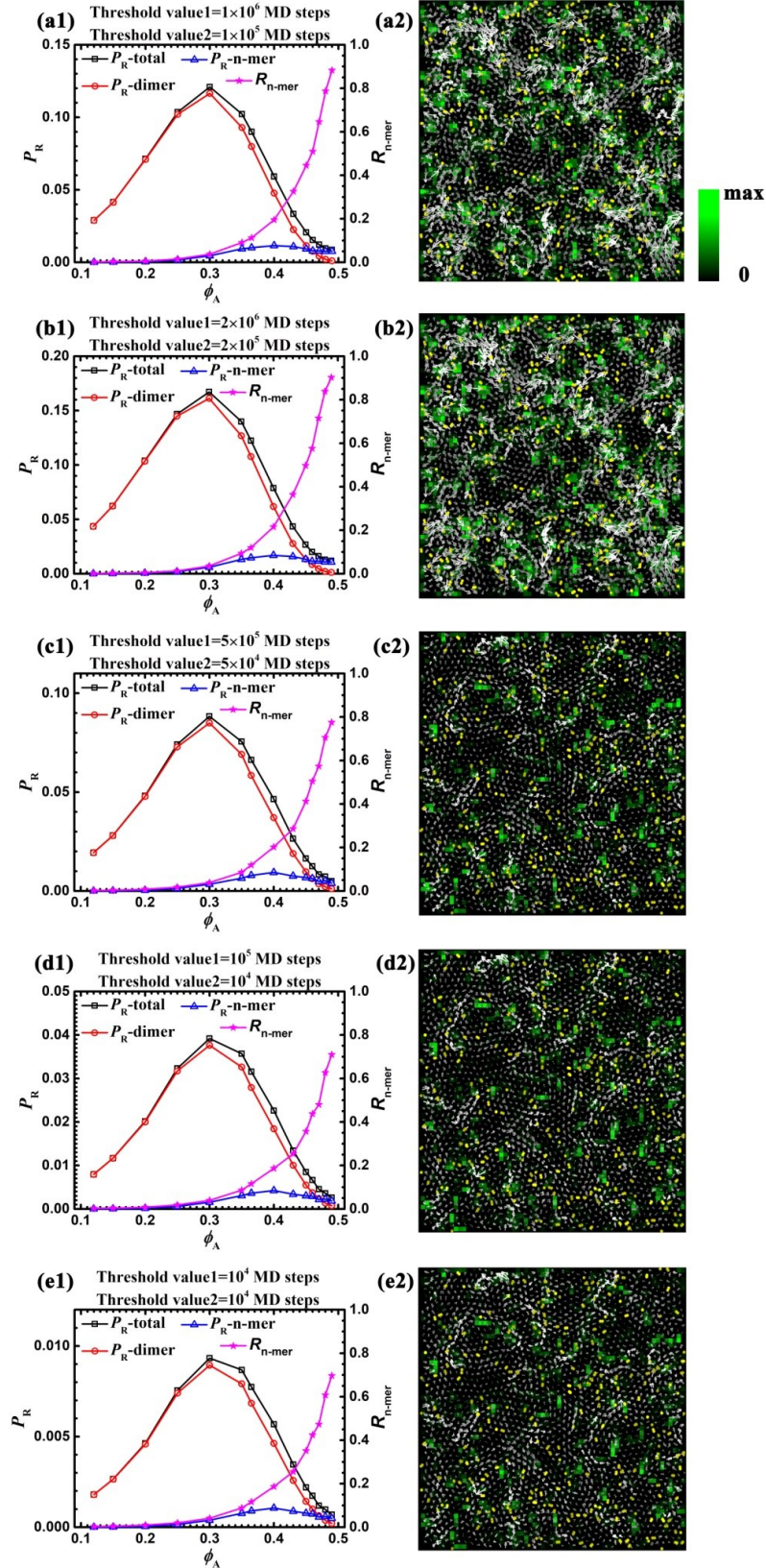


Figure S9. Left, Probability of dimerization ($P_{R-dimer}$, red cycle), n-merization ($P_{R-n-mer}$, $n \geq 2$, blue up-triangle) reactions, total reactions ($P_{R-total}$, black square) and the ratio of n-merization in total reactions (R_{n-mer} , magenta star) as a function of ϕ_A .

Right, the reaction capacity of all sub-regions in the system which is evaluated by the frequency that binding reaction events occur, are labeled with green color whose intensity is scaled with the reaction times on the displacement map. The 10% fastest rotation particles are labeled with yellow on mass center. (a) is calculate with the time thresholds in the manuscript. Others, calculate with the stable states defined as duration time longer than or equal to (threshold value1) (b) 2.0×10^6 MD steps (c) 5.0×10^5 MD steps (d) 10^5 MD steps (e) 10^4 MD steps, and the sub-stable states are define as the duration time between (threshold value1 and threshold value2) (b) 2.0×10^5 and 2.0×10^6 MD steps (c) 5.0×10^4 and 5.0×10^5 MD steps (d) 10^4 and 10^5 MD steps (e) 10^4 and 10^4 MD steps. In (a) and (b), results obtained in sequence of 1.4×10^8 MD steps with a 1.0×10^5 MD steps interval, and in (c-e), results obtained in sequence of 2.9×10^7 MD steps with a 1.0×10^4 MD steps interval. In (e), the threshold value1 is equal to threshold value2, we do not distinguish the stable state, sub-stable state and unstable state on particles, reaction events are counted once particle state changes between two continuous frames.

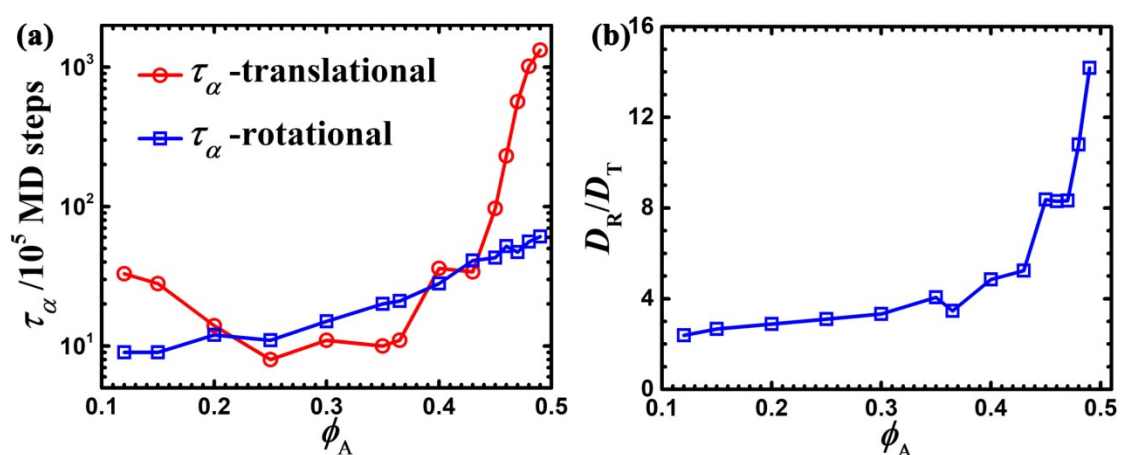


Figure S10. (a) The translational and rotational relaxation time and (b) the rate of translational to rotational diffusion coefficients as a function of ϕ_A .

References:

- [1] T. D. Nguyen, C. L. Phillips, J. A. Anderson, and S. C. Glotzer, *Comput Phys Commun* **182**, 2307 (2011).
- [2] K. V. Edmond, M. T. Elsesser, G. L. Hunter, D. J. Pine, and E. R. Weeks, *P Natl Acad Sci USA* **109**, 17891 (2012).
- [3] P. Y. Wang and T. G. Mason, *J Am Chem Soc* **137**, 15308 (2015).