Electronic Supplementary Information

Molecular simulation of diffusion mechanism of nanorods in cross-linked network

Bo-Ran Zhao[a], Bin Li*[a], Xinghua Shi*[b,c]

[a] School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai, 519082, China.

*E-mail: libin76@mail.sysu.edu.cn

[b] Laboratory of Theoretical and Computational Nanoscience, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing 100190, China.

*E-mail: shixh@nanoctr.cn

[c] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, China

Contents

Mucus cross-linked network construction

In a three-dimensional box, 140 polymer chains are distributed randomly, with 100 coarse-grained (CG) beads in each chain, to construct the cross-linked network with high density. The diameter of each CG bead is 1 σ, where σ is the length unit of the simulation system. We set every fifth bead as the active bead, a bond is created when the distance between the two active beads on different chains is smaller than 1.1 σ. Then the cross-linked network is generated, after the simulation runs for 1×10^8 steps with a timestep $\delta t = 0.005\tau$, here τ is the time unit of the system. For the network with low density, the system includes 66 polymer chains with chain length of 100 CG beads, and set every eighth bead as the active bead, then construct the sparse network by following same procedure as dense network. The pore size distributions of the constructed cross-linked networks with high density and low density is shown in Fig. S1.

The method of calculating the major axis vector of nanorod

The unit vector parallel with the major axis of nanorod ($\mathbf{e}_{\parallel}$), as well as the unit vectors perpendicular to the major axis of nanorod ($\mathbf{e}_{\perp 1}$ and $\mathbf{e}_{\perp 2}$), obtained *via* Jacobian transformation for radius of gyration tensors of nanorod,[1,2]

$$\mathrm{A}=\begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix} \rightarrow \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{bmatrix} \begin{bmatrix} S_1 & S_4 & S_7 \\ S_2 & S_5 & S_8 \\ S_3 & S_6 & S_9 \end{bmatrix} \quad (1)$$

with $S_{ab} = \frac{1}{n} \sum_{n=1}^{i} (a_i - a_{cm})(b_i - b_{cm})$, where a and b indicate x, y or z components of the CG bead coordinates, a_{cm} and b_{cm} are x, y or z components of center of mass of nanorods. λ_1, λ_2 and λ_3 are the three eigenvalues, and we sort them as $\lambda_1 > \lambda_2 \approx \lambda_3$, which represents the cylinder or rod shape. The matrix $[S_1 \quad S_2 \quad S_3]^T$ corresponding to the maximum eigenvalue λ_1 is the major axis vector $\mathbf{e}_{\parallel}$ of nanorod, and the other two are $\mathbf{e}_{\perp 1}$ and $\mathbf{e}_{\perp 2}$.

Description of video files

Fig.8_E-b.mp4: the trajectory movie corresponds to the 3D trajectory (b) in Fig. 8E;

Fig.8_F-b.mp4: the trajectory movie corresponds to the 3D trajectory (b) in Fig. 8F,;

Fig.8_G-a.mp4 and Fig.8_G-b.mp4: the trajectory movies correspond to the 3D trajectories (a) and (b) in Fig. 8G, respectively;

Fig.8_H-b.mp4: the trajectory movie corresponds to the 3D trajectory (b) in Fig. 8H;

Fig.9_D-b.mp4: the trajectory movie corresponds to the 3D trajectory (b) in Fig. 9D;

Fig.9_E-b.mp4: the trajectory movie corresponds to the 3D trajectory (b) in Fig. 9E;

Fig.9_F-a.mp4 and Fig.9_F-b.mp4: the trajectory movies correspond to the 3D trajectories (a) and (b) in Fig. 9F, respectively;

References

[1] B. Li, L. Zhao, H. J. Qian and Z. Y. Lu, *Soft Matter*, 2014, 10, 2245-2252.

[2] C.-M. Lin, Y.-Z. Chen, Y.-J. Sheng and H.-K. Tsao, *React. Funct. Polym.*, 2009, 69, 539-545.

Additional tables and figures

Table S1. The root mean squared radii of gyration (R_g) of the LNRs with different rigidities.

k_{rod} (k_BT/rad^2)	250	25	2.5
R_g (σ)	5.91	5.74	4.45

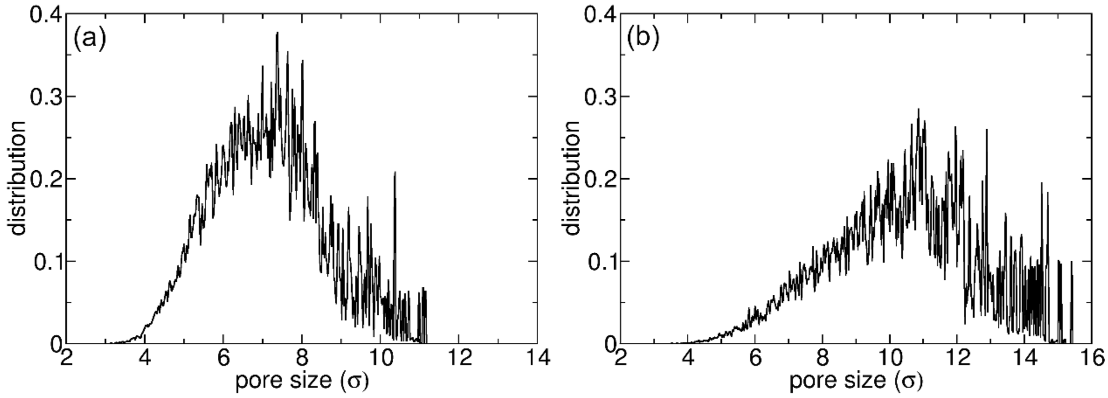

Fig. S1 The normalized pore size distributions of cross-linked networks with high density (a) and low density (b).

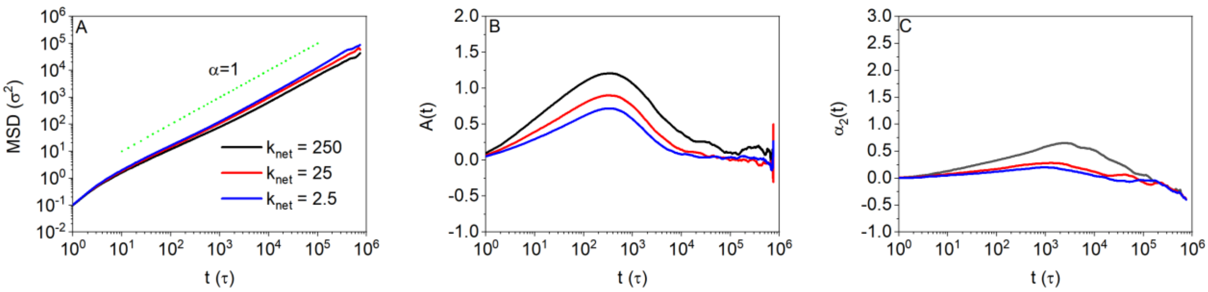

Fig. S2 MSDs (A), A(t) values (B) and non-Gaussian parameters (C) of LNRs with k_{rod} = $250\ k_BT/rad^2$ in low density network, respectively. The legends show different rigidities of network.

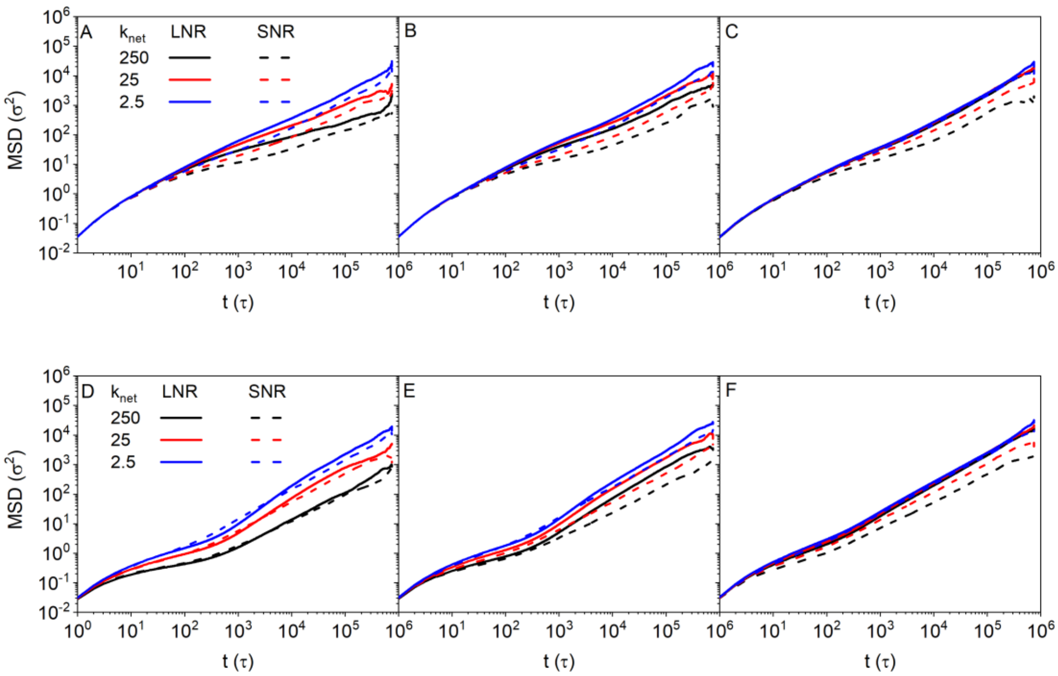

Fig. S3 (A-C) The MSDs parallel with axes of nanorods; (D-F) the MSDs perpendicular to axes of nanorods. The LNRs are represented by solid curves and SNRs are represented by dashed curves. The k_{rod} values are 250 (A,D), 25 (B,E) and 2.5 (C,F) $k_B T/rad^2$, respectively. The legends show different rigidities of network.

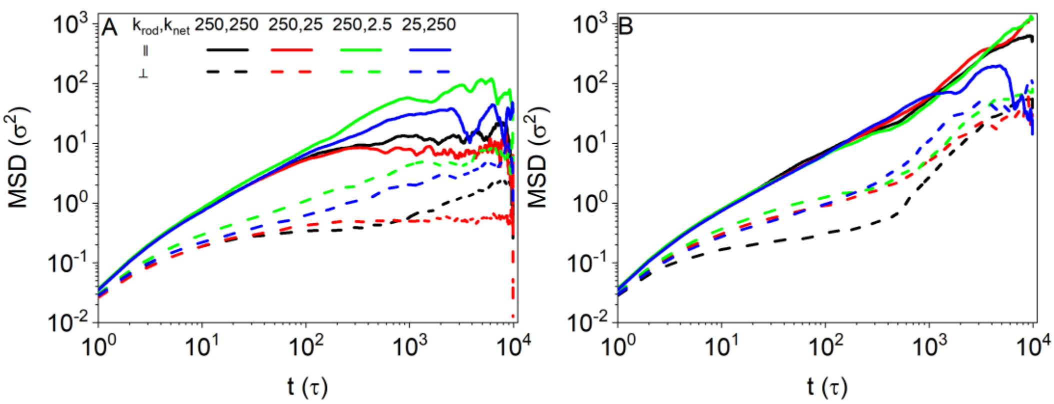

Fig. S4 The absolute MSDs parallel with and perpendicular to the axes of LNRs within the selected period. (A) corresponds to (a) trajectories and (B) corresponds to (b) trajectories in Fig. 8 E-H, respectively. The legends show the direction of MSDs and different rigidities of network and LNRs.

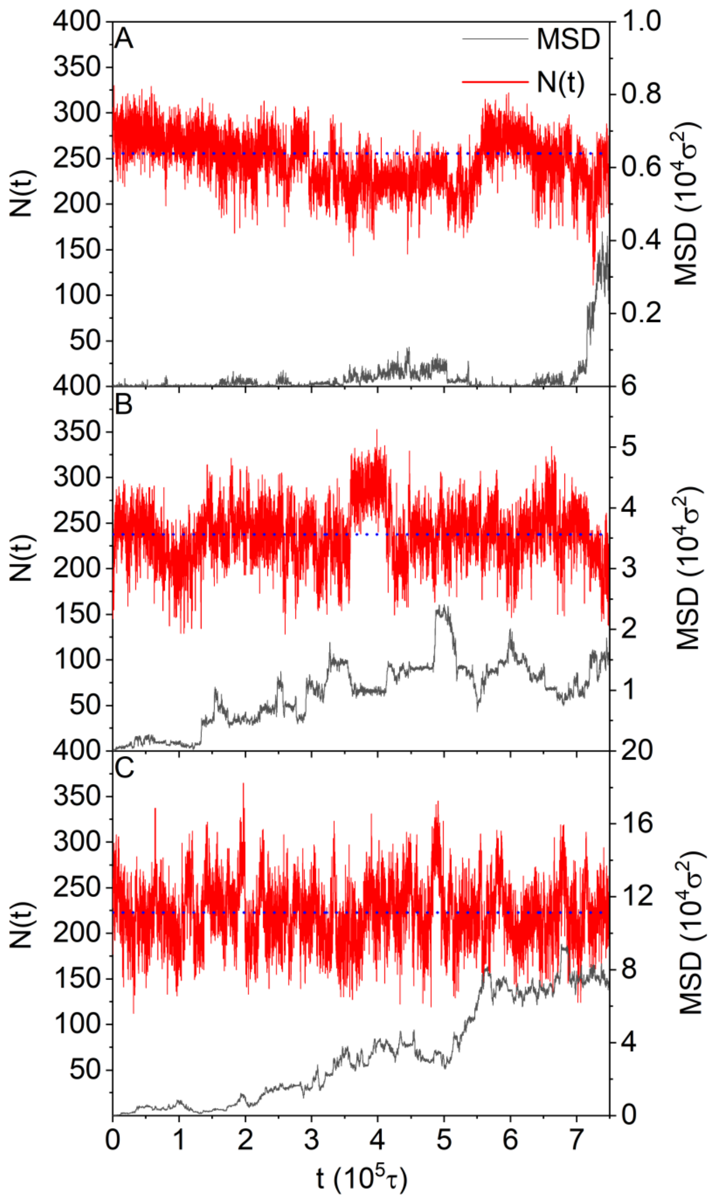

Fig. S5 The full time evolutions of *N*(*t*) values and MSDs of the selected LNRs. The rigidity of nanorod k_{rod} is fixed at 250 k_BT/rad^2, and the k_{net} parameters are 250 (A), 25 (B) and 2.5 (C) k_BT/rad^2, respectively.

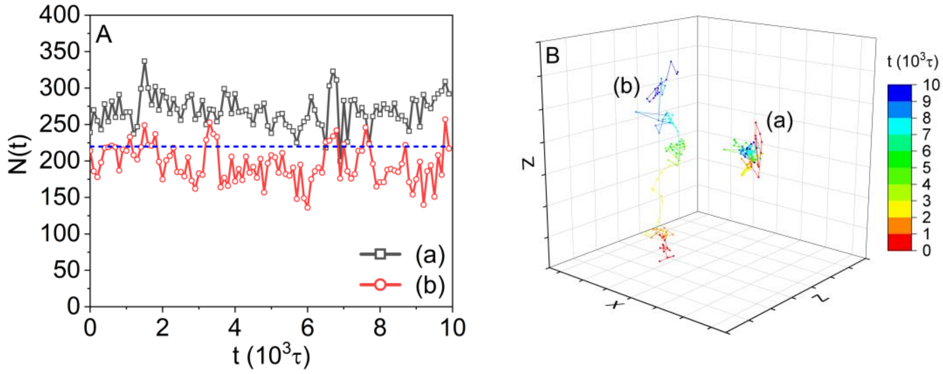

Fig. S6 (A) The time evolutions of surrounding dense network beads *N*(*t*) of LNR with $k_{rod} = 2.5\ k_BT/rad^2$, corresponding to the high *N(t)* values (a) and low *N(t)* values (b), in the dense cross-linked network with $k_{net} = 250\ k_BT/rad^2$; (B) the trajectories of center of mass of LNR when the *N*(*t*) values are high (a) and low (b), respectively.

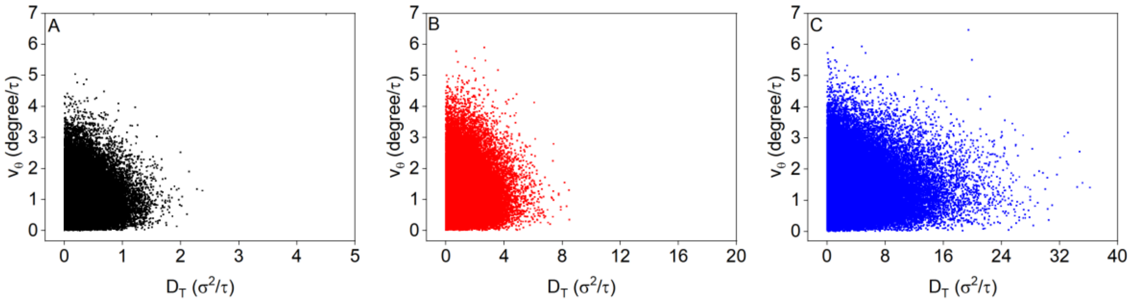

Fig. S7 The plotted data of instantaneous diffusion coefficients D_T and angular velocities v_θ of the SNRs with $k_{rod} = 250\ k_BT/rad^2$ in dense networks with different rigidities, the k_{net} parameters are 250 (A), 25 (B) and 2.5 (C) k_BT/rad^2, respectively.

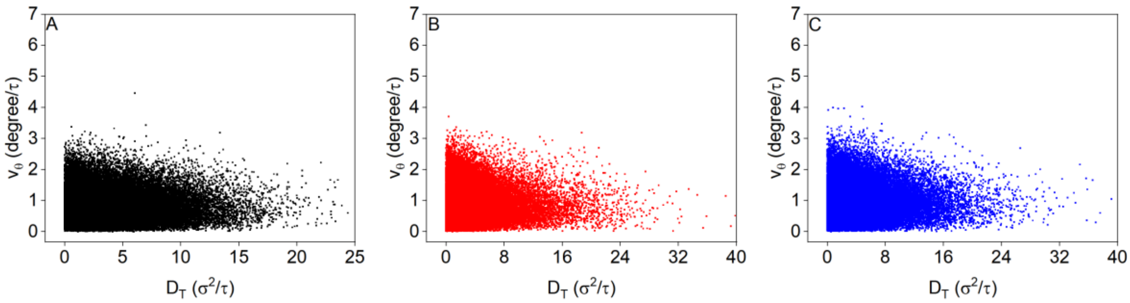

Fig. S8 The plotted data of instantaneous diffusion coefficients D_T and angular velocities v_θ of the LNRs with $k_{rod} = 250\ k_BT/rad^2$ in sparse networks with different rigidities, the k_{net} parameters are 250 (A), 25 (B) and 2.5 (C) k_BT/rad^2, respectively.