Electronic Supplementary Information:
Analysis of the Internal Motions of Thermoresponsive Polymers and Single Chain Nanoparticles

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Contents

1 Effect of Random Crosslinking on ψ_p and $C_p(t)$

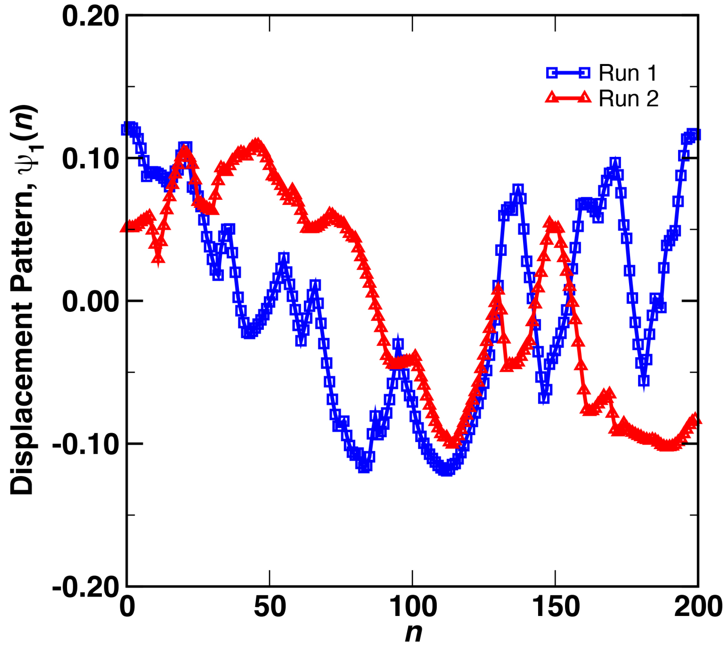

Figure S1: Comparison of the first mode $\psi_1(n)$ for SCNPs ($N = 200$ and $x_c = 15\%$) with different pairs of crosslinked monomers. The modes between two independent runs are distinct due to different crosslinking interactions.

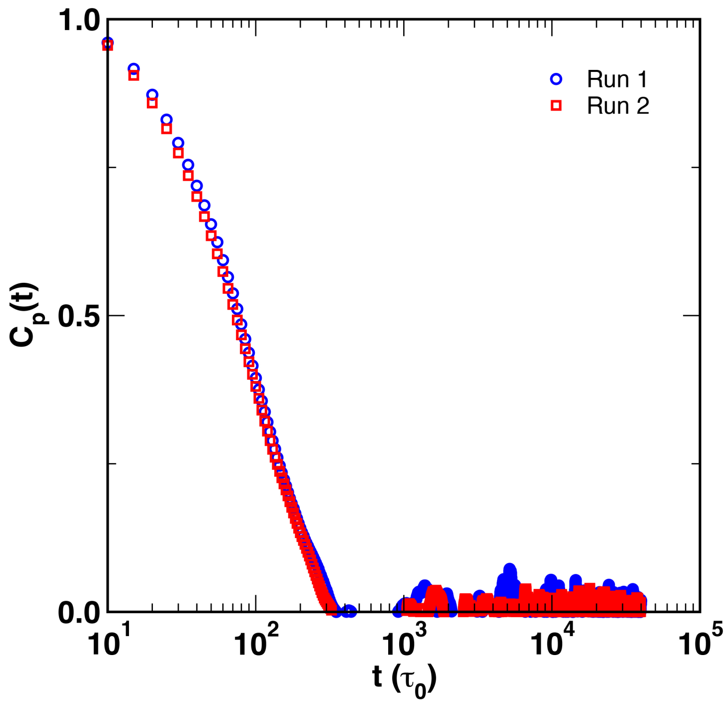

Figure S2: Comparison of the autocorrelation function $C_p(t)$ ($p = 1$) for SCNPs ($N = 200$ and $x_c = 15\%$) with different pairs of crosslinked monomers. $C_p(t)$ is virtually identical between independent runs, despite the modes being distinct from each other as shown in Fig. S1.

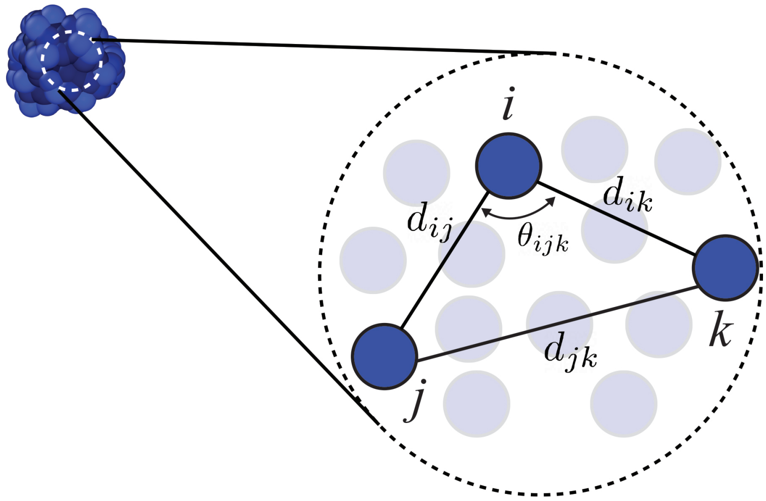

Figure S3: Schematic of the local structural quantities that were computed for each SCNP prior to UMAP. d_{ij}, d_{ik}, d_{jk} and θ_{ijk} were calculated for all sets of 3-monomers $\{i, j, k\}$ within the particle.

2 UMAP Procedure for Single Chain NPs

Uniform Manifold Approximation & Projection (UMAP) was performed on Gaussian kernel density estimators (KDEs) of local structural information using the `umap-learn` package in Python. This approach was motivated by recent work from Reinhart and coworkers that characterized the self-assembled morphologies of sequence-defined polymers using UMAP.[1,2] Following their approach, the structural quantities $\theta_{ijk} = \cos^{-1}(\mathbf{r}_{ij} \cdot \mathbf{r}_{ik})$, $d_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, $d_{ik} = |\mathbf{r}_k - \mathbf{r}_i|$, $d_{jk} = |\mathbf{r}_k - \mathbf{r}_j|$ and $l_{ijk} = d_{ij} + d_{ik}$ were computed for all possible sets of 3-monomers $\{i, j, k\}$, for all SCNP systems, at 500 000 time step intervals during the production phase of the simulations. These values were combined into a single dataset and used to generate histograms of their values (e.g., d_{jk} vs. θ_{ijk}). The structural quantities are illustrated in Fig. S3. Next, normalized KDEs (L^1-norm) were generated from the histograms, examples of which are shown in Fig. S4 for two unique SCNPs ($N = 50$, $x_c = 10\%$) (a) with residual correlations in $C_p(t)$ and (b) without. The full set of histograms and KDEs is provided in Section 3 of the ESI. Finally, the normalized KDEs for different pairs of structural quantities were used as inputs to the UMAP procedure (`n_neighbors = 5, min_dist=0.1`) to embed the SCNP systems into the local structure manifold $\mathbf{Z}$. We chose, arbitrarily, to label the axes of the embedding of (θ_{ijk}, d_{jk}) as (Z_0, Z_1), of (θ_{ijk}, l_{ijk}) as (Z_0, Z_2), and of (d_{jk}, l_{ijk}) as (Z_1, Z_2),

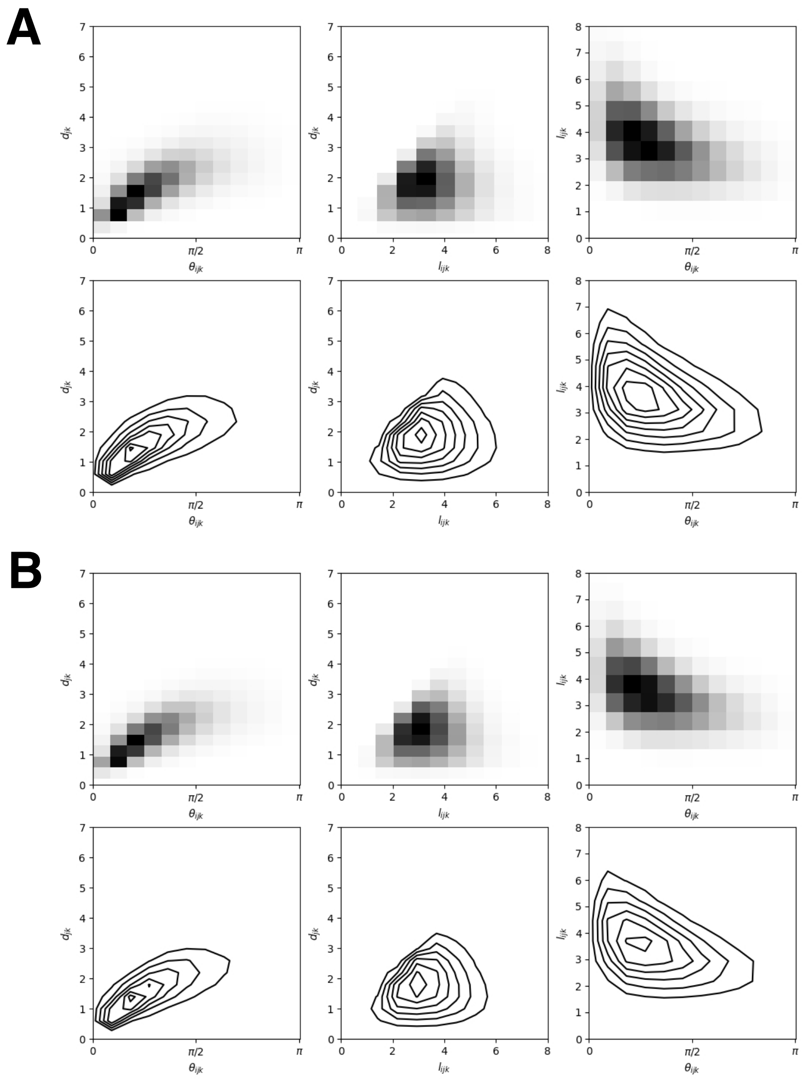

Figure S4: Structural histograms for SCNPs ($N = 50$, $x_c = 10\%$) for (a) a system exhibiting a residual correlation in $C_p(t)$ and (b) one without. In both (a) and (b), the top row is a histogram for (left to right) pairs of structural quantities (θ_{ijk},d_{jk}), (l_{ijk}, d_{jk}), and (θ_{ijk}, l_{ijk}). The bottom row contains normalized Gaussian kernel density estimations (KDEs) of the histograms.

3 Embedding of SCNPs into Z

The full results of the UMAP procedure are presented in Fig. S5 for different projections in **Z**. We found the projection along ($Z1$, Z_2) to most clearly show the similarities between the two classes of particles observed from the simulations.

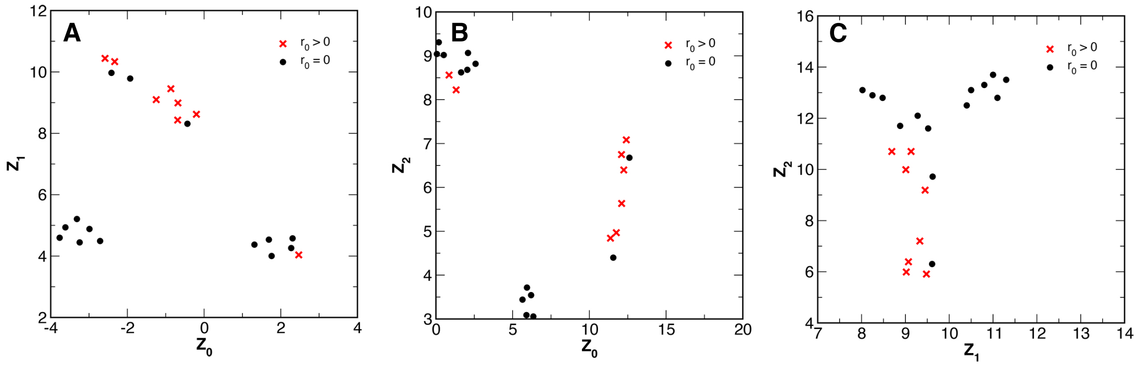

Figure S5: Manifold resulting from embedding (a) (θ_{ijk}, d_{jk}), (b) (θ_{ijk}, l_{ijk}), and (c) (d_{jk}, l_{ijk}) into **Z**. Red crosses correspond to SCNPs with residual correlations in $C_p(t)$ while black circles correspond to SCNPs that fully decayed exponentially.

4 Structural Histograms and KDEs for SCNPs

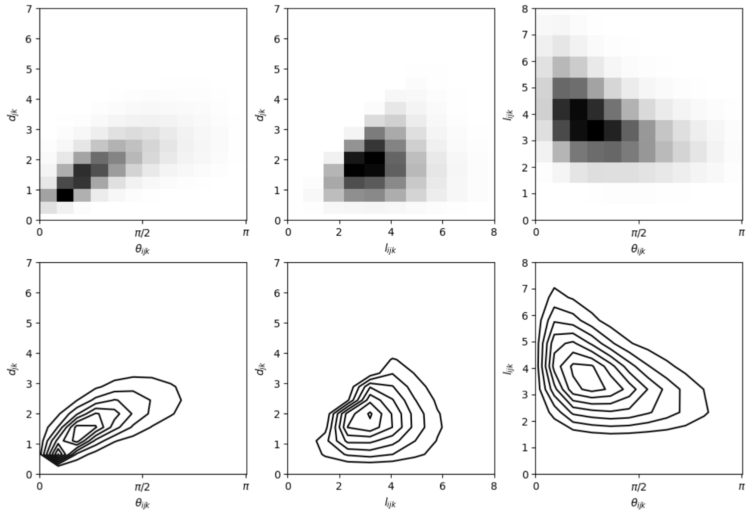

Figure S6: Local structure for SCNP with $N = 50$ and $x_c = 2.5\%$ exhibiting long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

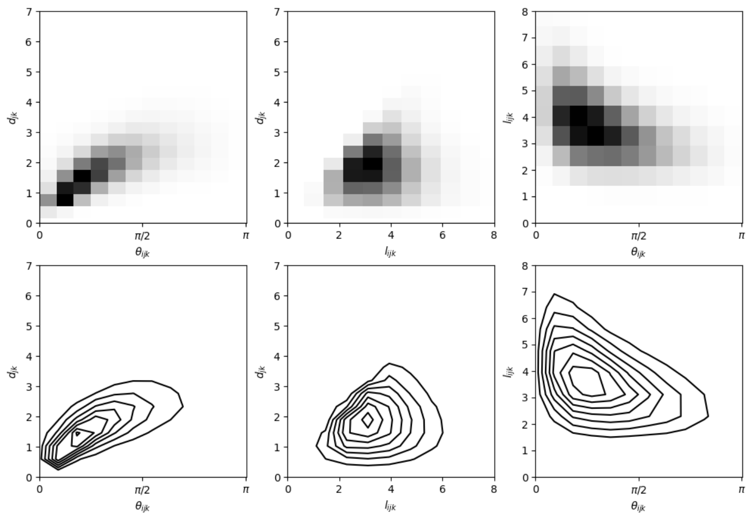

Figure S7: Local structure for SCNP with $N = 50$ and $x_c = 10\%$ exhibiting long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

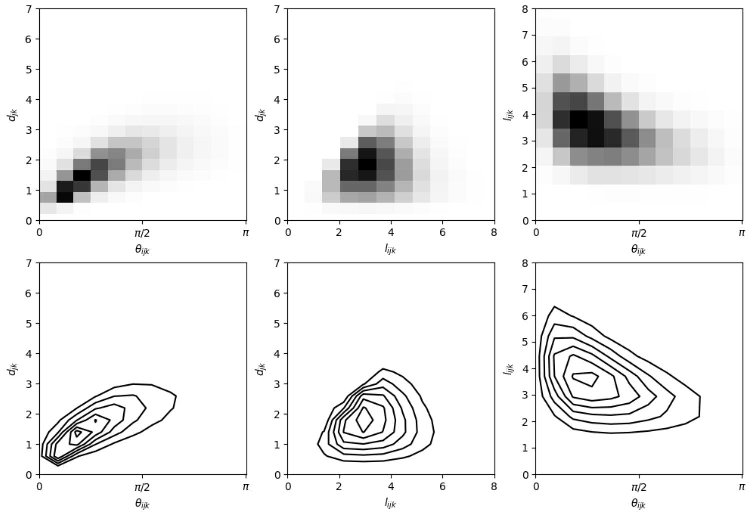

Figure S8: Local structure for SCNP with $N = 50$ and $x_c = 10\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

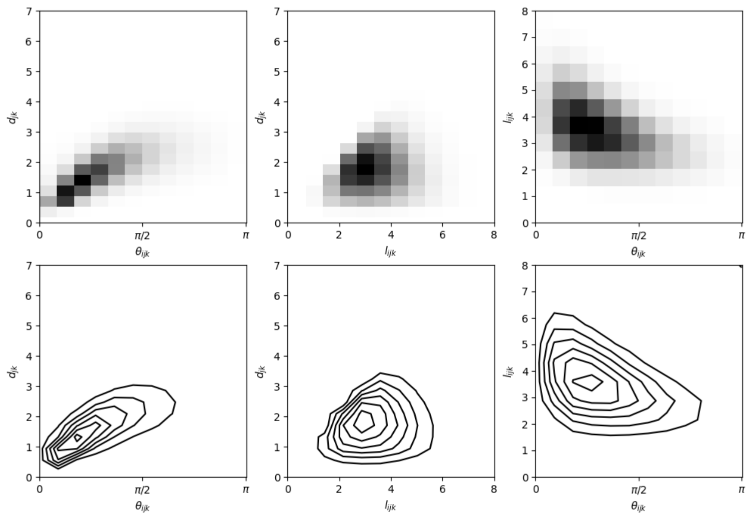

Figure S9: Local structure for SCNP with $N = 50$ and $x_c = 15\%$ exhibiting long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

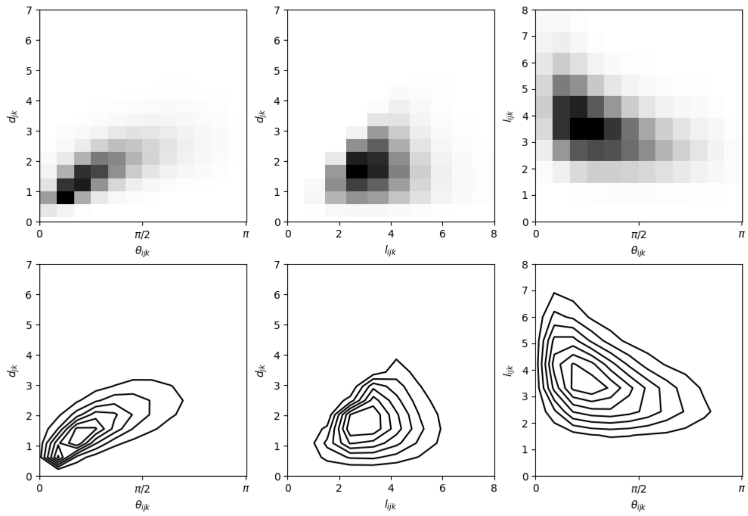

Figure S10: Local structure for SCNP with $N = 50$ and $x_c = 15\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

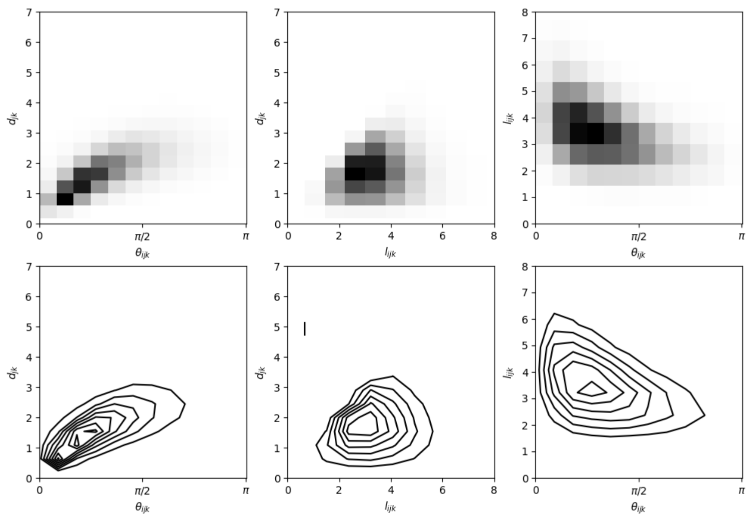

Figure S11: Local structure for SCNP with $N = 50$ and $x_c = 20\%$ exhibiting long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

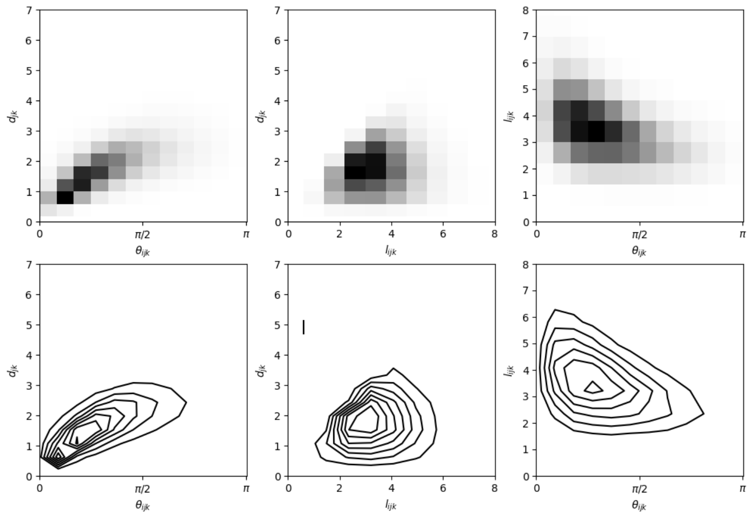

Figure S12: Local structure for SCNP with $N = 50$ and $x_c = 20\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

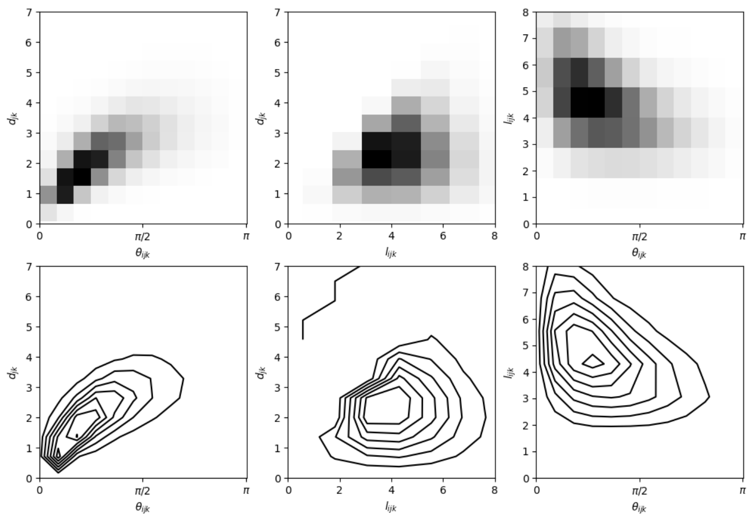

Figure S13: Local structure for SCNP with $N = 100$ and $x_c = 2.5\%$ exhibiting long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

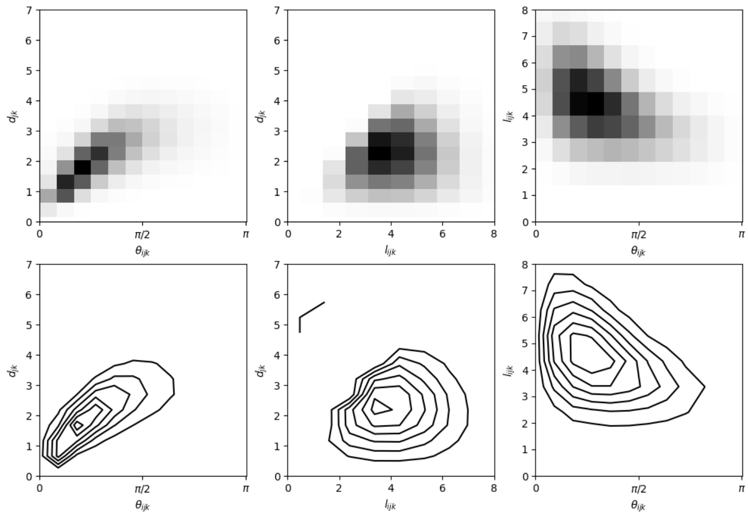

Figure S14: Local structure for SCNP with $N = 100$ and $x_c = 10\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

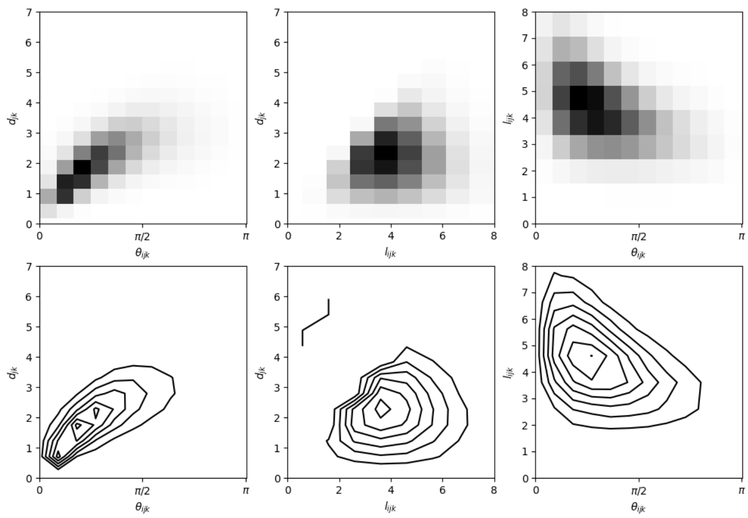

Figure S15: Local structure for SCNP with $N = 100$ and $x_c = 15\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

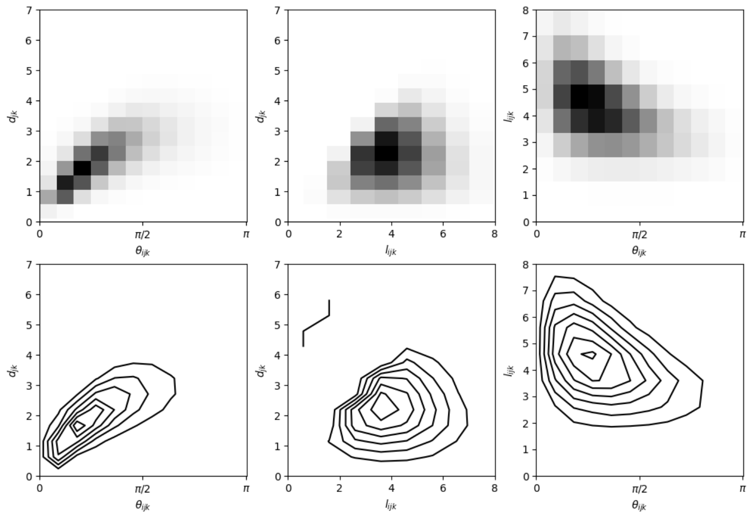

Figure S16: Local structure for SCNP with $N = 100$ and $x_c = 20\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

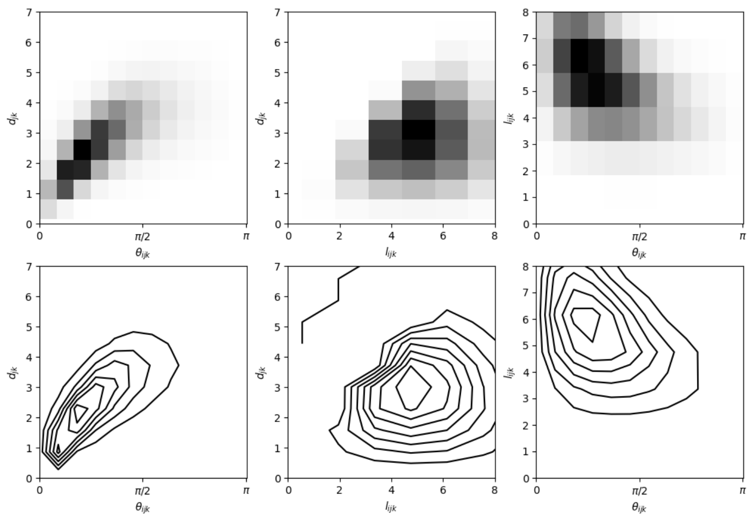

Figure S17: Local structure for SCNP with $N = 200$ and $x_c = 2.5\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

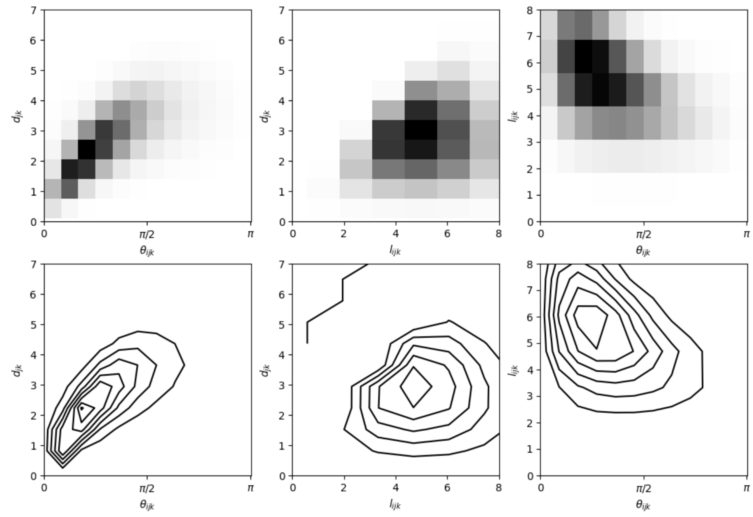

Figure S18: Local structure for SCNP with $N = 200$ and $x_c = 10\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

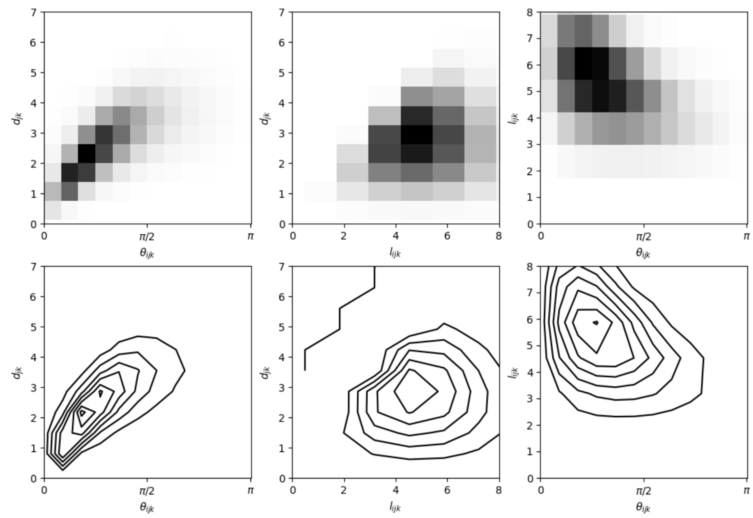

Figure S19: Local structure for SCNP with $N = 200$ and $x_c = 15\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

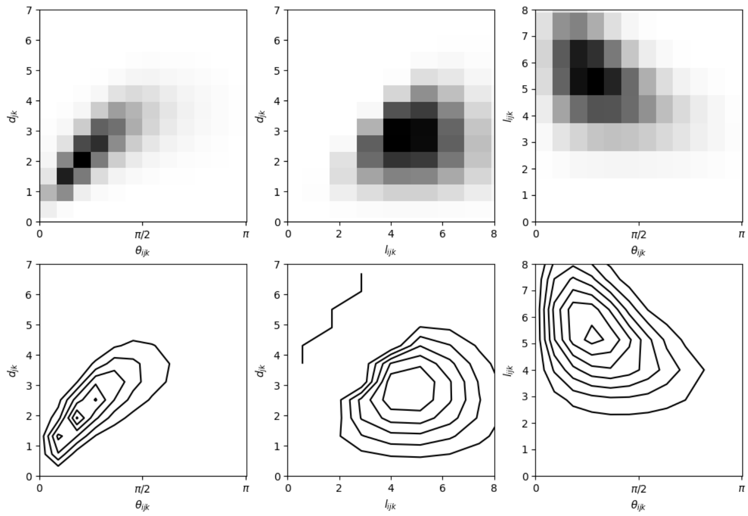

Figure S20: Local structure for SCNP with $N = 200$ and $x_c = 20\%$ that does not show long-time correlations in $C_p(t)$. The top row contains the histograms obtained from simulation snapshots, while the bottom row contains Gaussian kernel density estimations (KDEs) of the histograms.

References

[1] W. F. Reinhart, *Computational Materials Science*, 2021, **196**, 110511.

[2] A. Statt, D. C. Kleeblatt and W. F. Reinhart, *Soft matter*, 2021, **17**, 7697–7707.