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Directed self-assembly of end-functionalized nanofibers: from percolated networks to liquid crystal-like phases

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Abstract

We explore the directed self-assembly (DSA) process of end-functionalized nanofibers (NFs) by performing coarse-grained molecular dynamics simulations. We find that by tuning their interactions, NFs aggregate and self-organize into networks with specific topologies ranging from percolated networks to liquid crystal-like long-chain phases. The underlying mechanism is explained through an analytical model from a minimum energy perspective. In addition to offering microscopic understandings of the DSA process, the findings reported here can also guide robust target-specific design of nanofibrous materials into organized network structures.

Keywords: directed self assembly, nanofiber networks, molecular dynamics simulations

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanostructured network materials usually feature hierarchical structures that could map properties of elementary building blocks towards macroscopic material performance. They appear widely in natural and synthetic materials. Exemplified systems include cytoskeletons (actin filaments, microtubules, intermediate filaments) that generate essential functions in the life cycle of a cell [1]. On the other hand, synthetic materials assembled from functional nanofibers (NFs) such as carbon nanotubes and nanowires promote high-performance structural, optoelectrical, and transport applications [2–6]. The key concepts in designing these networks for specific applications include the choice of material building blocks and to achieve a specific network topology through well-controlled, efficient processes. While the first point has been addressed in recent development of nanotechnology and has already witnessed notable progresses [7], the second one is yet to be achieved. Several theoretical and experimental explorations have been conducted in this direction, suggesting various controls of the process and products in forms of linear chains, side-to-side, or end-to-end networks [3, 4, 6, 8–11]. However, the insights into the material design diagram that lays the ground for optimized practical applications are still limited [3–5], which merits further fundamental analyses.

A number of candidate methods are available to fabricate nanostructured network materials. Bottom-up synthesis and top–down lithography could produce networks with specified geometry and topology. For example, reactive ion etching was used to fabricate phononic nanomesh structures [12]. Cyclodehydrogenation of linear polyphenylenes from molecular precursors leads to the formation of straight or zigzag graphene nanoribbons [13]. In stark contrast to these techniques, the directed self-assembly (DSA) process holds promise in a new dimension of material design, where nanostructured components spontaneously organize directly according to their specific interactions, and/or indirectly through environment cues [14, 15]. The process is widely utilized by nature in the production of biological materials such as proteins and nucleic acids through a broad spectrum of intermolecular interactions between biopolymers, such as electrostatic forces, van der Waals, hydrophobic interactions, and hydrogen...
bonding [1, 16, 17]. These nonbonded interactions enable controllable and even reversible network formation of nanostructures in the process, with the thermodynamic driving forces and environmental conditions modulated accordingly [3, 15, 18–22].

In this work, we explore the DSA process of NF networks by their specified body- and end-interactions. The ends of the NFs are functionalized to be adhesive that compensates repulsive interactions between the bodies of NFs, following the concepts established in recent experiments [6, 8, 23, 24]. Our simulation results show that by simply tuning the interfiber interaction, a wide spectrum of structures from percolated networks with distinct topologies and liquid crystal-like phases can be covered in a controllable way.

2. Models and methods

In this work, the DSA process of end-functional NFs is simulated following a coarse-grained molecular dynamics (CGMD) approach with implicit solvent implemented. A NF is represented by a linear chain consisting of \( N = 20 \) bonded beads (Figure 1). The distance \( r_0 \) between neighboring beads defines the coarse-grained length scale. The NF elasticity is described by linear and angular spring terms in the potential energy \( E \), i.e. \( E = E_0 + E_\alpha = k_r(r-r_0)^2 + k_\theta(1 + \cos \theta) \), where \( r_0 = 40 \text{ nm} \) is the equilibrium distance between neighboring beads in the same fiber and \( \theta = \pi \) is the equilibrium angle of the three neighboring beads. Without the loss of generality, we use material parameters for a multi-walled carbon nanotube (MWNT) for the model system explored in this study [25–27].

Figure 2. Possible configurations of two adjacent nanotubes with \( R_{\text{rep}} = 3r_0 \). The inset shows the evolution of interfiber angles with a minimum value at \( 60^\circ \) for \( R_{\text{coh}} = 2r_0 \).

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To simulate the engineered NFs, we classify inter-NF interactions into two different types (Figure 1). For beads at the two ends of a NF, we use a typical Lennard-Jones formula $E_{\text{LJ}} = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^6\right]$. We use the parameters $\varepsilon = 31 433 \text{ kcal mol}^{-1}$ that corresponds to the cohesive energy between the neighboring MWNTs, with an equilibrium distance of $R_{\text{coh}} = 2^{1/6}\sigma_{\text{coh}}$ $[25]$. The value of $R_{\text{coh}}$ can be tuned in experiments, for example, through the molecular weight of functional groups $[9]$. The interaction is truncated at a distance of $3\sigma_{\text{coh}}$, and the whole potential profile is shifted to set the interaction energy to zero at the cutoff distance. A Weeks–Chandler–Andersen soft-sphere potential function is used for the interaction between other beads in the bodies of NFs, which is a shifted, repulsive Lennard-Jones potential with the same value of $\varepsilon$, but a different cutoff distance at $R_{\text{rep}} = 2^{1/6}\sigma_{\text{rep}}$ $[28]$. It should be remarked here that when the cohesive energy between ends of NFs is significant compared to thermal fluctuation, i.e. $\varepsilon >> k_B T$, the absolute value of $\varepsilon$ has negligible effect on the DSA process.
The DSA process of NFs is simulated numerically by solving the Newtonian equations of motion for the beads, coupled to a Langevin thermostat with a damping factor $\gamma = 30 \text{ ns}$. This approach includes local hydrodynamics for the solvent effect \[29\]. The temperature of thermostat $T = 300 \text{ K}$ is much lower than the cohesive energy, i.e. $k_B T = 1.90 \times 10^{-3} e$, and thus the thermal fluctuation is relevant only for the thermal diffusion of NFs and their low-frequency vibrational modes. Periodic boundary conditions are applied to the simulation box with a fixed number of NFs dispersed as the simulation starts. The time step for numerical integration is $1 \text{ ps}$, which ensures energy conservation as the thermostat is turned off. All simulations are performed using the large-scale atomic/molecular massively parallel simulator \[30\].

3. Results and discussion

To understand the DSA process of an ensemble of end-functionalized NFs, we first explore the structural stabilities of final NF network structures analytically, from the perspective that they are typically associated with thermodynamic equilibrium and characterized by a minimum in the free energy landscape. Then we verify the theoretical insights into the DSA processes by performing CGMD simulations. We start from a model consisting of a pair of NFs, by considering the interaction between two NFs 1 and 2 with functionalized ends (figure 1(b)). The beads near the ends of two NFs are annotated as 1a, 1b, 2a, and 2b, respectively. The length of NFs with 20 beads is $l_{\text{avg}} = 0.8 \mu m$, and the distance between beads 1a, 1b, 2a, 2b near their ends are denoted as $r_{\text{fl}}$. With repulsive and cohesive interactions defined between the body and end parts of the NFs respectively, the total energy of the system can be decomposed into repulsive and cohesive contributions from them, i.e. $E_{\text{r}} = E_{\text{r}}(1a-2a) + E_{\text{coh}}(1b-2b)$. We neglect the entropic term in the free energy here by noticing that the thermal fluctuation $k_B T$ is much lower than the inter-NF interacting energy. Due to the repulsion between NFs at small distances, an preferable interaction applies, and the total energy of the system can be decomposed into repulsive and cohesive contributions from them, i.e. $E_{\text{fl}}(1a-2a) + E_{\text{coh}}(1b-2b)$. Then the DSA process can be minimized the total energy locally by reaching a metastable network structure. Figure 1(d) shows that with $r_{\text{fl}} = r_{\text{fl}} > r_{\text{fl}} > r_{\text{fl}} > r_{\text{fl}}$, two NFs align with a certain mis-orientation angle $\beta$. By further noticing that the term $E_{\text{fl}}(1b-2b)$ is positive, the value of $\beta$ is limited within a certain range, as will be discussed later. (iii) For $r_{\text{fl}} > r_{\text{fl}}$, there also exist several solutions for $r_{\text{fl}}$, and a parallel configuration with $\beta = 0$ is preferred energetically (see figure 1(e) for the illustration with $r_{\text{fl}} = 4r_{\text{fl}} > r_{\text{fl}} > r_{\text{fl}}$). From a practical point of view, the regime (ii) allows a rational design of network materials with controlled topology by tuning the inter-fiber interactions, e.g. the parameter $R_{\text{coh}}/r_{\text{fl}}$ or $R_{\text{coh}}/r_{\text{fl}}$. As a result, we will focus on the regime (ii) in our following discussions, where energetically stable network can be formed and tuned by the abovementioned parameters.

We perform CGMD simulations to explore these concepts, where the NFs are considered as elastic rods through our coarse-grained bead-spring representation. Two representative models are constructed with different parameterization of $r_{\text{fl}}(1a-2a)$ and $R_{\text{coh}}(1b-2b)$. Both models are within the regime (ii) but the topology of DSA network is expected to be different as the range of allowed values for $\beta$ changes with the parameterization. By tuning $r_{\text{fl}}(1a-2a)$, i.e. the inter-end distance or size of ends, while keeping other parameters the same, we summarize the final network structures for models A and B in figures 2 and 3 respectively. In model A, we have $r_{\text{fl}} = 3r_{\text{fl}}$, and $0 \leq R_{\text{coh}} \leq r_{\text{fl}}$. The allowable values for angle $\beta$ between neighboring NFs can thus be mapped and plotted in figure 2(a). The results suggest that the allowable range becomes wider at larger values of $R_{\text{coh}}$. Even for $R_{\text{coh}}/r_{\text{fl}} = 0$, $\beta$ could vary between $60^\circ$ and $180^\circ$. In model B, we have $r_{\text{fl}} = 3r_{\text{fl}}$, and $0 \leq R_{\text{coh}} \leq 3r_{\text{fl}}$. Compared to model A, the region of allowed $\beta$ values in model B is much reduced (figure 3(a)), which shrinks into a single value of $180^\circ$ the limiting case with $R_{\text{coh}}/r_{\text{fl}} = 1$.

From the CGMD simulation results, the possible configurations of neighboring NFs after the DSA processes can be summarized as follows. For the 2D model A with $R_{\text{coh}}/r_{\text{fl}} = 0$, and $R_{\text{coh}}/r_{\text{fl}} = 1.0, 0.8, 0.6, 0.4$ and 0.2, the simulation snapshots of the final network structures are illustrated in figures 2(b)–(f). In our CGMD simulations, NFs are firstly dispersed randomly in the solvent. They then start to diffuse
Figure 2. (a) The range for allowable $\beta$ values predicted for model A, where $R_{\text{rep}} = r_0$, $0 \leq R_{\text{coh}} \leq r_0$. (b)–(f) Nanostructured networks self-assembled with parameters $R_{\text{coh}}/r_0 = 1.0, 0.8, 0.6, 0.4, 0.2$. NFs and their end beads are illustrated as solid lines and dots. Rings fully closed by NFs are shown in colors. The results show a broad distribution of ring types, corresponding to the wide allowable range of $\beta$, especially at large values of $R_{\text{coh}}$. Even for $R_{\text{coh}}/r_0 = 0$, $\beta$ could vary between $60^\circ$ and $180^\circ$. It should be remarked that the number of NFs is the same for all these simulations, and in panel (b) NFs could form bundles that cannot be distinguished from the illustration.

Figure 3. (a) The range for allowable $\beta$ values predicted for model B, where $R_{\text{rep}} = 3r_0$, $0 \leq R_{\text{coh}} \leq 3r_0$. (b)–(f) Nanostructured networks self-assembled with parameters $R_{\text{coh}}/r_0 = 3.0, 2.0, 1.5, 1.1, 0.3$, respectively. These results show distinct features in comparison with those from model A. The distribution of ring types is much narrower, and the number of ring edges decreases smoothly with $R_{\text{coh}}/r_0$. 
around and interact with their neighbours. The dynamics continues to proceed with synergetic effects from both thermal agitation and viscous damping in the solvent environment. The evolution of network dynamics depends on the density of NFs. At low density, the diffusing process is rate limiting compared to the binding between NFs, so the growth in the early stage follows a step-growth mechanism where NFs aggregates step by step after nucleation of the network [3, 31]. However, as the density of NFs increases, the crowded environment restricts the mobility of NFs and leads to a spontaneous network formation where local topological imperfections may occur and be trapped. As the simulated NFs of MWNTs are relatively stiff, the motion of NFs consists of mostly translational and rotational diffusion, and weakly excited low-frequency modes such as wiggling. The energy $\sim k_B T$ partitioned into these modes defines the mobility of NFs, the efficiency of the DSA process, and thermal stabilities of final structures. Under the condition that $k_B T < \varepsilon$, cohesion between NF ends can hardly be perturbed and the entropic effect on the self-assembly process is negligible. When neighboring NFs diffuse into the interacting range between functionalized ends, they move towards each other and rotate. A final network configuration with the value of $\beta$ corresponding to the local energy minimum is eventually reached as the simulated DSA process converges. As more and more NFs approach together and the size of percolated network increases, the many-NF interaction perturbs the network structure and the value of $\beta$ could deviate from the optimal value. It should also be noted that flexibility of the fibers could modify the value of $\beta$ by accommodating significant bending deformation of the fibers. The spatially ordered network structures thus formed with relatively low entropy correspond to local minima in the complex global free energy landscape, trapped in a crowded environment.

As $R_{coh}/r_0$ varies, we find a wide variety of network structures, including isolated clusters, percolated networks that are reminiscent of certain classes of 2D Bravais lattices (with fiber ends as lattice sites), and liquid-crystal-like long NF phases. In model A, the allowable range for $\beta$ depends on $R_{coh}/r_0$, starting from $60^\circ$ at $R_{coh}=0$, and reaches $0^\circ$ at $R_{coh}=r_0$ (figure 2(a)). There exist a significant number of triangles and rhombuses formed in the final network.

![Figure 4](image-url)

**Figure 4.** The distributions of (a) interfiber angles, (b) rings and (c) the radial distribution function for the self-assembled 2D networks in the coarse-grained molecular dynamics simulations for model B. (d) Characteristic nanofiber configurations that correspond to the peaks in distributions of angles and rings, and the radial distribution function. $d$ is the interfiber distance.
(figures 2(b)–(f)), corresponding to the favor of $\beta \approx 60^\circ$. From identical NFs dispersed in 2D, only the five Bravais lattices (oblique, rectangular, rhombic, hexagonal, and square) and a linear array could form into an extended network structure with translation symmetry, and the triangular one has the highest packing density. The density of NFs immersed in the solvent could further alter the overall network structure. As the density decreases local percolated clusters could form. While as it increases, the network will become denser and the diffusivity of NFs will be reduced, which could retard the DSA process. In comparison with the simulation results, the simplified two-NF model in figure 1 provides a reliable prediction, although underestimation of the cohesion between NF ends should be expected, as the many-NF interactions is neglected in the analytical model.

In model B, as shown in figure 3(a), the allowable range of $\beta$ is much narrower. Only linear configuration with $\beta = 180^\circ$ is allowed at $R_{rep} = 3r_0$ and $R_{coh} = r_0$. The value of $R_{coh}/r_0$ is chosen from 3.0, 2.0, 1.5, 1.1 to 0.3 in the CGMD simulations. Topological analysis of the network structures shows a different trend compared to that in model A (figure 4(a)). The most probable distribution of $\beta$ increases as $R_{coh}/r_0$ decreases. To analyze the topology of DSA networks, we perform the ring statistics (figure 4(b)) [32] by considering the NFs as edges of rings. Close loops formed by the NFs can then be identified, in the sense that NFs with ends binding together are connected. The results distinctly show the transition in lattice structures from linked polygons to linear structures (figures 3(b)–(f)). It should be remarked here that rings not closed by NFs by this definition, although rich in our simulation results, are not counted in this analysis. To quantitatively measuring the structure, we further calculate the radial distribution function (RDF) of the NFs by considering them as individual point-like rigid objects. Their positions are defined as that of their centers of masses (figure 4(d)). The results show that distance between NFs increases as $R_{coh}/r_0$ decreases. Specifically, peaks in the RDFs (figure 4(c)) at 160, 480, 640, 720, 800 nm correspond to $\beta$ at 0°, 60°, 90°, 120°, and 180°. Representative lattice structures are schematically plotted in figure 4(d).

As the DSA process explored here is driven by thermodynamic forces, a global energy minima of well-defined NFs network structures can hardly be reached during the finite simulation time, application of periodic boundary conditions, and relatively low thermal fluctuation from their environment. The characteristic network structures identified in model A and B, trapped by local energy barriers as well as lattice symmetries, show the robust relationship between assembled

\[ R_{coh}/r_0 = 3.0, 2.0, 1.5, 1.1 \text{ to } 0.3 \]

Distribution (arb. unit)

\[ R_{coh}/r_0 = 3.0, 2.0, 1.5, 1.1 \text{ to } 0.3 \]

\[ 0 \leq R_{coh} \leq 3r_0 \]

\[ 0^\circ, 60^\circ, 90^\circ, 120^\circ, \text{ and } 180^\circ \]

\[ 160, 480, 640, 720, 800 \text{ nm} \]

\[ 0^\circ, 60^\circ, 90^\circ, 120^\circ, \text{ and } 180^\circ \]

Figure 5. (a)–(c) 3D nanostructured networks formed from end-functionalized nanofibers with parameters $R_{coh}/r_0 = 3.0, 1.5, 0.3$, respectively. The simulation parameters are the same as the 2D simulations, where $R_{rep} = 3r_0, 0 \leq R_{coh} \leq 3r_0$. The results clearly show the transition from 3D connected networks to an assembly of linear chains by reducing $R_{coh}/r_0$. (d)–(e) The distributions of interfiber angles and the radial distribution function for the self-assembled 3D networks in the coarse-grained molecular dynamics simulations for model B.
topologies and inter-NF interactions at the functionalized ends, through parameters $R_{\text{coh}}/r_0$ and $R_{\text{cad}}/r_0$ respectively in this work. By raising the environment temperature, more regular network structures may be formed by allowing barrier-crossing events in the complex free energy landscape similarly as the situation in the protein-folding problem. However, strong thermal fluctuation could also perturb the as-formed network structures that are stabilized by the interaction between neighboring NFs. The density of NFs in the solvent could also be critical to the DSA process, and seeding or templating processes could enhance the yield and perfection of desired network structures. Ordered structures such as triangular, rhombus, square and hexagonal lattices and liquid crystal like NF phases could thus be rationally designed and fabricated without going to advance and intricate techniques. Although not investigated here, it is worth noting that the use of stimuli-response functionalization, e.g. thermal, electrical, optical active, or pH responsive, could further tune the interactions by external cues [33–35].

Although the aforementioned results are limited to 2D, the preceding analysis and CGMD simulations can be readily applied to DSA processes in 3D as well. Our representative results and structural characterization shown in figure 5 clearly confirm the design principle, showing that 3D lattice and linear structures can be formed by tuning parameters $R_{\text{cad}}/r_0$ in the range between 3.0 and 0.3, while keeping $R_{\text{coh}}/r_0=3.0$. As a result, the DSA processes produce percolated networks with different topologies or an ensemble of linear long fibers. The angle distribution and RDF statistics show the same trends with those identified in 2D. The findings are consistent with our model analysis and indicate a robust control of the network structures both at interfaces and in bulk solvents.

4. Conclusion

Here we investigated the DSA process of NFs in solvent. By simply tuning the interfiber interactions following an end-functionalization approach, we demonstrated robust controls of the network topology from triangular, rhombus, and hexagonal lattices to a linear, liquid-crystal-like phase by simply tuning the interfiber interaction, corresponding to the competition between the attractive interaction between NF ends and repulsion between the body of NFs. The two key parameters—the critical repulsive and cohesive distances—can be tuned, for instance, through the chemistry, charge, hydrophobicity, geometry of the NFs and functional groups. The 2D and 3D assembly processes could be realized at interfaces, e.g. air/water, oil/water, and in bulk solvents, which has been demonstrated in recent experimental studies [3, 4, 6, 10]. These findings offer promising opportunities for the design of nanostructured networks with organized and hierarchical topologies from simple, template-free, and spontaneous self-organizing processes, and thus hold promises in the development of functional materials by utilizing the unique structure-properties relationship of nanostructured materials.

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