



# Length controlled kinetics of self-assembly of bidisperse nanotubes/nanorods in polymers



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## ABSTRACT

While there is a growing body of work that supports the self-assemblies of nanotubes and nanorods, little attention has been devoted to understand the relation between their length and the kinetics of self-assembly in polymer composites. Using dissipative particle dynamics (DPD) method, we simulated the temporal developments of equilibrium microstructures of nanotube dispersions with a bimodal length distribution in polymer matrix. The nanotube/polymer models were developed with different sets of interactions between the components. The equilibrium morphologies obtained for nanotubes are in good agreement with those proposed by previous experimental and theoretical studies. We found that long nanotubes could self-assemble into ordered honeycomb-like bundles as validated with the structure factor calculations. The self-assembly kinetics was quantitatively estimated at different stages and length scales using the variations in the pair-correlation functions. It was observed that the kinetics slowed down particularly in the initial stages of the self-assembly. This was mainly ascribed to the spatial interferences of bidisperse nanotubes as evidenced by laser scanning microscopy and simulated mean-squared-displacements (MSD). Furthermore, the developed microstructures were assessed in terms of the effective nanotube volume derived from Monte Carlo (MC) calculations and the frequency of nanotube-nanotube contacts. The simulations reported herein contribute to a microscopic interpretation of the literature results, and the findings of this paper contribute meaningfully to the design strategies aimed at achieving novel nanocomposites with optimal physical properties.

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## 1. Introduction

Nanofillers are attracting a great deal of attention due to their intrinsic characteristics and broad applicability in the areas such as optics [1], electronics [2] and catalysis [3]. Most of the nanofillers used are either spherical or isotropic particles mainly due to the ease of synthesis [4], consequently, leading to isotropic materials. One possible route to the development of the anisotropic structures

for mechanical, electrical and optical applications is to use anisotropic nanoparticles such as nanotubes and nanorods [5]. In many cases, a pre-requisite for effective application of nanotubes and nanorods is their stable and homogenous dispersion within the respective matrix due to the fact that agglomeration cancels out most of the benefits of its nano dimensions [6,7]. Therefore, for several other applications, a balance between a stable dispersion and control of the spatial distribution and orientation within the matrix is the key to exploit their outstanding properties on macroscopic scale [8]. The design and preparation of aligned or self-assembled nanotubes/nanorods have been actively researched recently [9] since the emergence of ordered structures can be used in several practical strategies for designing structural materials [10].

Self-assembly processes which are common in nature are mimicked or utilized as a reference to many dynamic [11] and multicomponent systems [12–14], from smart materials to self-

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healing structures [15,16] to sensors [17] and spontaneous development of patterned structures [18]. These assemblies are desired due to the modulation of their physical properties [4,19–23] which can be achieved either by equilibrating between aggregated and non-aggregated states of nanofiller [23,24], or adjusting their positions relative to one another in an aggregate [25]. Such spontaneous organization could be directly due to the specific interactions and/or indirectly through their environment. In this context, understanding the phenomena of the nanotube/nanorod self-assembly is essential for materials design; however, it poses many challenges considering the complex thermodynamic and kinetic behavior involved in the assembling process [26–28].

The increase in nanotubes (or nanorods) concentration in the matrix considerably enhances the probability of close tube (or rod) encounters and can eventually block each other's movements to an extent such that no further reorganization is possible [29,30]. Such phenomenon is referred to as rigidity percolation [30], or physical gelation, and is related to the kinetic arrest of the nanotubes/nanorods. For tubular nanoparticles such as carbon nanotubes (CNT), such a kinetic arrest has been experimentally determined to take place starting from the isotropic liquid state at extremely low nanotube volume fraction of  $\sim 0.003$  [31]. As for the rod-like nanoparticles, the corresponding gelation phenomenon of cellulose nanocrystals (CNCs) typically occurs at higher nanorod concentrations of  $\sim 0.08$  [30]. However, the length polydispersity and extreme aspect ratio of nanotubes and nanorods have important roles in triggering the transition before any liquid crystalline ordering. The monodisperse colloids of rod-shaped *fd* virus for instance are known to self-assemble in cholesteric/chiral and smatic phases [32–34] or even in columnar crystal phases [33], whereas high polydispersity (55%) of goethite nanorods can also form such ordered structures [35]. For nanotubes such as CNTs, only nematic phase has been reported thus far, mainly due to the large size distribution of nanotubes and difficulty in preventing particle aggregation [36–39]. This implies that, apparently, for the monodisperse systems it is easier to promote the prevalence of ordered phases [40,41] whereas for high polydispersity the large-scale rearrangements can be constrained by subsequent phase segregation [42]. Bacterial CNCs with an aspect ratio in the range of 50–100 [43,44] also show nematic ordering well below 1 wt% of CNC content [43]. For CNC nanorods which show high polydispersity depending on the source and method of extraction [30,45,46], the influence of the aspect ratio can be recognized as anisotropic phase for longer CNC nanorods [43] and isotropic fractionation of shorter nanorods [47].

With the increasing difficulties in the way of realizing the underlying mechanisms in dispersions of such anisotropic nanoparticles, modelling and simulation techniques have raised tremendous attention [48]. Among various methods, mesoscopic approaches, which define a coarse-grained model of the material, have been extensively used to study the microstructure developments under equilibrium due to their feasibility to access longer time scales [49–55]. Detailed atomistic simulations, on the other hand, have been also applied to characterize the fundamental thermodynamic properties of such dispersions [52,56,57]. While there is a growing body of work that supports the self-assemblies of nanotubes and nanorods, little attention has been devoted to understand their length-controlled assemblies in polymer composites. In order to investigate the length effects, He et al. [58] report the impact of bidisperse nanorod mixtures on their self-assembled morphologies in block copolymers in terms of enthalpy (originated from nanorod-polymer interactions) and entropy (governed by the inherent anisotropy as well as translational entropy of shorter nanorods). However, there is no indication of how the length polydispersity might influence the evolutions of self-assembled

structures with time. This is a relevant question since dissipative particle dynamics (DPD) simulations of Hore and Laradji [59] showed in particular how important it is to consider the length effects of nanorods on the kinetics of phase separation phenomena in immiscible polymer blends.

Here, we present a systematic study of the self-assembly of generalized nanotubes and nanorods with two different aspect ratios, exploring the length effect and the influence of the bimodal length distribution of nanofillers. To do this, we employ the well-credited DPD method to simulate the developments of equilibrium microstructures of such dispersions. We observe that under certain conditions, these nanotubes self-assemble into ordered honeycomb-like bundles. More importantly, the kinetics of this self-assembly was quantitatively described in terms of the variations in the pair-correlation profiles. The results show a reduced self-assembly kinetics particularly in early stages for bidisperse mixtures. Possible correlation of such behavior is also studied with the help of cellulose nanorods where the length induced aggregation/dispersion and its influence on mechanical properties is observed. The detailed understanding of length controlled kinetics of self-assembly for a mixed system with varying aspect ratio of nanotubes, to the best of our knowledge, is the first of its kind. Taken together, the findings of this paper provide a valuable tool that opens innovative ways to implement new routes to design and produce novel composite materials with optimal physical properties.

## 2. Simulation details

### 2.1. Dissipative particle dynamics

DPD is a coarse-grained numerical method in which the degrees of freedom of the system are reduced by lumping a number of atoms into the so-called beads [60,61]. These beads interact with each other through three pairwise forces: (i) the conservative force  $F_{ij}^C$ , (ii) the dissipative force  $F_{ij}^D$ , and (iii) the random force  $F_{ij}^R$ . For any pair of  $i$  and  $j$  beads within the force cutoff radius  $r_c$ , these forces are given by

$$F_{ij}^C = a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \hat{r}_{ij}, \quad (1)$$

$$F_{ij}^D = -\xi_{ij} \omega^D(r_{ij}) r_{ij} [(v_i - v_j) \cdot \hat{r}_{ij}] \hat{r}_{ij}, \quad (2)$$

$$F_{ij}^R = \sigma_{ij} \omega^R(r_{ij}) r_{ij} \zeta_{ij} \hat{r}_{ij}. \quad (3)$$

In these equations,  $r_{ij}$  is the distance between the beads with the corresponding unit vector of  $\hat{r}_{ij}$  which points from bead  $j$  to bead  $i$ .  $v_i$  and  $v_j$  are the velocity vectors of beads  $i$  and  $j$ , respectively. The model parameters used in DPD include the maximum repulsion coefficient  $a_{ij}$ , the friction coefficient  $\xi_{ij}$ , the noise amplitude  $\sigma_{ij}$ , and a Gaussian random number  $\zeta_{ij}$ . In DPD formulation,  $\omega^D(r_{ij})$  and  $\omega^R(r_{ij})$  are the dissipative and random weight functions, respectively, which are often defined as

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2 = \left( 1 - \frac{r_{ij}}{r_c} \right)^2. \quad (4)$$

DPD is an efficient mesoscopic method to study the phenomena on longer time scales than the classical molecular dynamics [62]. This is mainly due to its coarse-grained representation of the system as well as the soft potential functions that it incorporates. For these reasons, DPD has been widely used to investigate multi-component systems such as polymer/layered silicates [60,63] and

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