# Molecular simulation of hybrid polymer nanocomposites with organic nanodimers and inorganic nanorods: from structure and dynamics to viscosity

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Polymer nanocomposites (PNCs) are cutting-edge materials that enhance polymer matrices with nanoparticles to achieve superior performance. The properties of these composites are significantly influenced by interactions at the nanoparticle-polymer interface. This study explores how inorganic nanorods (NRs) and various organic nanodimers (NDs)—differentiated by their interaction with the polymer and including Janus types—impact the structural, dynamical, and viscosity of PNCs. Through molecular simulations, we reveal how these nanoparticles interact within block copolymer and homopolymer matrices. Our findings show that NDmonomer interactions notably affect ND organization and improve barrier properties, while the structuring of NRs contributes to increased mechanical resistance. Furthermore, different PNCs provide a wide range of thickening behavior depending on the polymer matrix and the embedded nanoparticles. We observe increments of up to six times the melt's viscosity when both nanoparticles are introduced in copolymers. The viscosity of the systems is evaluated using a non-equilibrium method, the SLLOD algorithm, and the Green-Kubo relation to obtain both the shear-thinning curve and the zero-shear viscosity value. These results underscore the importance of nanoparticle interactions and configurations in determining PNC behavior, providing critical insights for advancing material design and functionality.

# I. INTRODUCTION

Polymer nanocomposites (PNCs) are advanced hybrid materials that integrate nano-sized particles with a polymer matrix. The introduction of nanofillers can significantly impact the local dynamics and morphology of polymer chains, as well as the intrinsic properties of the pristine polymer, leading to changes in its mechanical, thermal, and rheological behavior on a macroscopic scale. When carefully engineered, PNCs can greatly enhance a wide range of industrial applications, including coatings, paints, electronics, food packaging, and personal care products.<sup>1–9</sup> These enhancements include improved thermal and electrical conductivity,<sup>10–13</sup> altered viscosity,<sup>14,15</sup> glass transition temperature<sup>16</sup> and other key properties.<sup>17–19</sup> PNCs can also be engineered to respond to environmental changes, such as magnetic $^{20,21}$ or electric fields.<sup>22</sup> These adaptive materials are increasingly used to address advanced technological challenges. For example, various fillers like carbon nanotubes, carbon black, and graphene have been explored in the development of environmentally friendly high-voltage cables.<sup>12</sup> Among these, carbon nanotubes stand out for their exceptional performance, making them particularly valuable in both research and industrial applications.<sup>22</sup>

The exceptional properties of PNCs compared to pristine polymers are often attributed to the intricate balance of enthalpic and entropic forces at the nanoscale between host polymer and nanoparticles (NPs). The small size of NPs results in a high surface-to-volume ratio, which increases the interface between the NPs and the polymer matrix. This expanded interface allows more polymer chains to interact with the NPs. Furthermore, the relative size of the NPs to the polymer chains affects chain relaxation across various time scales and influences the polymer's response to external stimuli. Enthalpic interactions, typically dominant,<sup>23</sup> can be adjusted by modifying the NP surface, such as by using grafted polymeric ligands.<sup>24</sup> In contrast, entropic interactions are strongly influenced by the relative sizes and geometries of the NPs and polymer chains. However, the impact of these interactions can vary, as different studies have produced conflicting results regarding their effect on the mobility of polymer chains and NPs.<sup>25,26</sup> Notably, incorporating NPs instead of microfillers into the mesh leads to a more continuous distribution of particles, a key feature for improving mechanical properties. Variations in filler size and NP concentration significantly influence the properties of PNCs.<sup>27,28</sup> The reduced size of nano-sized fillers enables a lower weight for PNCs, with NP contributions typically around 5 wt.%. This reduction in weight not only decreases costs but also enhances interfacial features across a larger, more filler-populated volume.<sup>29</sup>

The foundation of a PNC lies in the polymer itself, which consists of long chains of identical monomers that can assemble in various configurations, such as rings,<sup>30–32</sup> branched structures,<sup>33</sup> or linear forms.<sup>34</sup> These polymer chains are not always composed of a single type

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of monomer; different monomers can combine to form Copolymers come in diverse configuracopolymers. tions, including alternating copolymers $^{35,36}$  and block copolymers.<sup>37</sup> Block copolymer (BCP) melts are intriguing materials because of their ability to spontaneously form highly ordered periodic nanostructures, including body-centered cubic spheres, hexagonally-packed cylinders and lamellar phases, which result from the inherent heterogeneity of the BCP chains, where chemically distinct monomers are organized into blocks.<sup>38,39</sup> This characteristic makes BCP melts particularly valuable for applications requiring precise nanoscale spatial control. BCPs incorporating NPs are particularly effective for modulating enthalpic and entropic contributions because they exhibit microphase-separated domains. This separation fosters favorable thermodynamic and geometric interactions between the two species, allowing precise control over the position and orientation of the NPs and thus proposing promising applications, for instance, in semiconductor lithography.<sup>36</sup>

Thanks to the proliferation of biosynthetic, chemical, and physical experimental methods for creating intriguing anisotropic shapes, research on these systems has extended from PNCs incorporating spherical NPs<sup>15,40,41</sup> to PNCs with rod-like,<sup>42–44</sup> disk-like<sup>45,46</sup> or other exotic<sup>42,47</sup> NPs. Interactions ranging from attractive to repulsive, and their effects on particle structure and dynamics have also been investigated.<sup>14,48</sup> Most research in this area remains at an early stage and generally focuses on spherical NPs with a single interaction site, primarily driven by theoretical and simulation studies.<sup> $\overline{49-52}$ </sup> Our study advances the field by developing PNCs incorporating a novel combination of varied NP geometries, nanorods (NRs) and nanodimers (NDs). The latter feature two distinct interaction sites, and the mixture of both NPs provide new insights into the properties of PNCs tested *in silico.* As an additional contribution to the field, we combine both equilibrium and non-equilibrium simulation techniques to capture the complete viscosity range of our PNCs, an approach that has rarely been used in the past and allows us to define the validity range for each method. Molecular simulations play a crucial role in advancing our understanding of PNCs by providing detailed insights into the microscopic interactions at the interface between polymers and NPs. In fact, these interfacial interactions have a profound impact on the rheological  $^{14,15}$ and dynamical<sup>53</sup> properties of the system. For instance, recent work by Li et al. investigated silane surface modifications to optimize these interactions between a silica substrate and cis-1,4-polyisoprene (PI) using atomistic molecular dynamics, with the aim of enhancing the development of future silica-PI nanocomposites.<sup>54</sup> Simulations can uncover other microscopic features that would otherwise be inaccessible, such as the precise orientation of PNC components,<sup>52,55</sup> or provide a detailed local image of strain around NPs.<sup>56</sup>

In this study, we employ coarse-grained Langevin Dynamics (CG-LD) simulations to investigate the transport properties of PNCs incorporating either single or multiple types of NPs. We examine how these properties are influenced by the structural and dynamic characteristics that unfold at the microscopic scale. Coarsegrained models are particularly well-suited for simulating large polymeric systems, as they are not constrained by specific chemical compositions, allowing for the generalization of many properties across different polymer species.<sup>30,57</sup> Polymer chains are modeled using the beadand-spring model developed by Kremer and Grest<sup>58,59</sup> for semiflexible chains,<sup>60,61</sup> a method recently demonstrated to accurately replicate certain real-world polymer properties.<sup>62,63</sup> We investigate a matrix of linear diblock copolymers, well above their entanglement length, and compare it with a homopolymer (HP) mesh. For NPs, we assess the effects of polymer-grafted inorganic NRs and organic NDs, which can be homogeneous or Janus, when incorporated into the polymer melts. The choice to use organic and inorganic particles in our study is driven by their distinct interactions with the polymer matrix and each other: organic polymers interact broadly with other organic materials, such as those composing the NDs. The Janus nature of these NDs aligns with the BCP chain distinction, allowing for targeted interaction with different polymer blocks. Also, much of the recent research has been focusing on silica and metallic NRs in different environments, which is a key reason for incorporating them in our PNCs.<sup>47,64,65</sup> The paper is structured as follows: Section II describes the PNC model; Section III details the simulation methodology and system parameters; Section IV presents the simulation findings; and Section V concludes the study. Additional details on the model are provided in Appendix A.

### II. MODEL

We investigate PNCs composed of melts containing 200 linear HP or BCP chains, referred to as HPNC and BCPNC, respectively. Each BCP chain is made up of two blocks of 100 beads each, labeled as  $M_1$  and  $M_2$ , both with diameter  $\sigma_0$ , the system unit length. By contrast, an HP chain consists of 200 identical monomers (or beads), labeled as M; we use M for the polymer beads when no distinction is required. Additionally, each system includes NDs, NRs or a mixture of both species. NDs consist of two beads that can either have identical interactions with the polymer, with either stronger  $(ND_1)$  or weaker  $(ND_2)$  repulsion parameters, or be heterogeneous, with two distinct lobes (ND<sub>J</sub>, for Janus). Finally, NRs of length 7.5 $\sigma_0$  are made up of 8 partially overlapping beads of diameter  $1.5\sigma_0$ , resulting into a length-to-diameter aspect ratio of q = 5. All species are schematically reported in Fig. 1 and the full list of systems studied is summarized in Table I.

We have developed our polymer model based on the CG Kremer & Grest (KG) model, which offers high computational efficiency while preserving the essential chem-



FIG. 1. Schematic representation of the species modeled in this work.

TABLE I. Summary of homopolymer nanocomposites (HP-NCs) and block-copolymer nanocomposites (BCPNCs) investigated in this study, incorporating nanodimers (NDs), nanorods (NRs), or a combination of both. Homogeneous NDs are composed of either identical beads with stronger (ND<sub>1</sub>) or weaker (ND<sub>2</sub>) repulsion parameters, while Janus (J) NDs consist of two distinct lobes.

PNC types	Description
ND <sub>1</sub> -HPNC	200 HP chains and 40 $ND_1$
ND <sub>2</sub> -HPNC	$200 \text{ HP chains and } 40 \text{ ND}_2$
ND <sub>J</sub> -HPNC	200 HP chains and 40 $ND_J$
ND <sub>1</sub> -BCPNC	200 BCP chains and 40 $ND_1$
ND <sub>2</sub> -BCPNC	200 BCP chains and 40 $ND_2$
ND <sub>J</sub> -BCPNC	200 BCP chains and 40 $ND_J$
NR-HPNC	200  HP chains and $66  NR$
NR-BCPNC	200  BCP chains and $66  NR$
ND <sub>1</sub> /NR-HPNC	200 HP chains, 40 NR and 40 $ND_1$
ND <sub>2</sub> /NR-HPNC	200 HP chains, 40 NR and 40 $ND_2$
ND <sub>J</sub> /NR-HPNC	200 HP chains, 40 NR and 40 $\rm ND_J$
ND <sub>1</sub> /NR-BCPNC	200 BCP chains, 40 NR and 40 $ND_1$
ND <sub>2</sub> /NR-BCPNC	200 BCP chains, 40 NR and 40 $ND_2$
ND <sub>J</sub> /NR-BCPNC	200 BCP chains, 40 NR and 40 $\rm ND_J$

ical details characterizing the behavior and properties of polymeric materials.<sup>58,59</sup> Following the approach of Everaers *et al.*,<sup>62</sup> we have further refined the KG model by incorporating a tunable degree of chain stiffness. In line with the KG model, all non-bonded interactions are represented by the purely repulsive Weeks-Chandler-Anderson (WCA) potential, with the exception of those between NRs and polymers. These interactions are attractive at moderate distances, as typical for polymergrafted metallic NPs, and are thus described by the Lennard-Jones (LJ) potential. This choice also avoids depletion-driven entropic clustering of NRs into crystals (see Section S2 of the Supplementary Materials for additional details). Consequently, the following potential describes all non-bonded interactions:

$$U_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left[ \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^6 + \frac{\psi}{4} \right] H(r_c - r),$$
(1)

where H(r) is the Heaviside step function,  $\varepsilon_{\alpha\beta}$  represents the interaction energy between two generic beads  $\alpha$ and  $\beta$ , r is the distance between their center of mass,  $\sigma_{\alpha\beta}$  is the geometric mean of their radii, and  $\psi$  is 1 for WCA interactions and 0 for LJ interactions. The cut-off distance is set to  $r_c=2^{1/6}\sigma_{\alpha\beta}$  for WCA and to  $r_c=6\sigma_{\alpha\beta}$  for LJ potentials. The interaction energy is measured in units of  $\varepsilon_0 = k_B T N_A = 2.475 \text{ kJ}$  $mol^{-1}$ , with  $k_B$  the Boltzmann constant, T the absolute temperature, and  $N_A$  the Avogadro number. The selfinteraction energy for each component of the PNCs is set to  $\varepsilon_{\alpha\alpha} = \varepsilon_0$ , except for NRs, where a higher repulsion is applied, fixed at  $\varepsilon_{\rm NR,NR} = 2.5\varepsilon_0$  to prevent clustering. Cross-component interactions are calculated using the Lorentz-Berthelot combination rule,  $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha}\varepsilon_{\beta}}$ , except for NP-M non-bonded interactions, which are adjusted according to their type: NR,  $ND_1$ ,  $ND_2$  or Janus ND. In order to mimic the typical BCP microphase separation, the repulsive interaction between  $M_1$  and  $M_2$ monomers is obtained by setting  $\varepsilon_{M_1,M_2} = 2.5\varepsilon_0$ . The complete list of interactions are listed in Table S1 of the Supplementary Materials. We notice that  $ND_2$  beads interact via a purely repulsive potential, but with substantially reduced repulsion strength compared to  $ND_1$ . This is due to the lower value of the cross interaction between monomers and ND<sub>2</sub> beads,  $\varepsilon_{2,M_k}/\varepsilon_0 = 0.1$  with  $k = \{1, 2\}$ , compared to the self-interaction between ND<sub>2</sub> beads,  $\varepsilon_{2,2}/\varepsilon_0 = 1$ . In the work of Everaers and coworkers, many polymer melts are coarse-grained and parametrized onto the KG model.<sup>62</sup> We use CG polyethylene as the basis of our model. According to their study, each bead of polyethylene is characterized by a value of  $\sigma_0 = 0.42$  nm and  $m_0 = 44.07$  g mol<sup>-1</sup>, which results in a time unit of  $\tau_0 \equiv \sigma_0 \sqrt{m_0/\varepsilon_0} = 3.55$  ps. The effective interaction diameter is also derived using the Lorentz-Berthelot rule, namely  $\sigma_{\alpha\beta} = \sqrt{\sigma_{\alpha}\sigma_{\beta}}$ , with  $\sigma_{\alpha} = \sigma_0$ , 1.5 $\sigma_0$  and 3 $\sigma_0$  for polymer, NR and ND beads, respectively. We aim to use NP sizes that are smaller than the individual microdomains found in BCPs. This ensures that the NPs are small enough to interact with the BCP structure at a scale that influences its properties, without disrupting the overall domain organization.<sup>23</sup> The NP sizes selected fit this purpose, aligning with those previously reported in experiments<sup>66</sup> and simulations.<sup>14,27,64</sup> The mass of the polymer beads is set to  $m_0$ , whereas NP beads are significantly heavier. In particular, we consider NDs to be organic, with the same density as the monomers,  $\rho_{\rm ND} \approx \rho_{\rm M} \text{ kg/m}^3$ , and for NRs we set  $\rho_{\rm NR} \approx 3.3 \rho_{\rm ND}$ . The former reproduces the typical density of an organic polymer, whereas the latter is close to the density of light metals and silica. With these values of densities, the resulting NP masses read  $m_{\rm ND} \approx 53 m_0$ and  $m_{\rm NB} \approx 32 m_0$ , which is in agreement with the typical range of masses in other studies on PNCs.<sup>32,52,67</sup> Finally,

the number of NDs and NRs is set to obtain a concentration between 5 and 8 wt%.

Following the KG model, bonded interactions between contiguous polymer beads are described by combining the Finitely Extensible Nonlinear Elastic (FENE) potential with the LJ potential. Additionally, we incorporate a bending potential proposed by Faller and Müller-Plathe,<sup>60</sup> resulting in:

$$V_{\text{pol}}(r,\theta) = -\frac{1}{2}\lambda_0 R_0^2 \log\left[1 - \left(\frac{r}{R_0}\right)^2\right] + U_{\text{MM}}(r) + \kappa_\theta (1 - \cos\theta),$$
(2)

where  $R_0 = 1.5\sigma_0$  is the maximum bond extension,  $\lambda_0 = 30\varepsilon_0\sigma_0^{-2}$  determines the bond resistance to stretching,  $\theta$  is the angle between consecutive bonds, and  $\kappa_{\theta} = 2.156\varepsilon_0$  is the stiffness constant. The value of  $\kappa_{\theta}$  is the value that Everaers and coworkers assigned to polyethylene, which we also adopt here.<sup>62</sup> To ensure rigidity between the lobes of NDs, we employ the following harmonic potential:

$$V_{\rm ND}(r) = \frac{1}{2} \lambda_{\rm ND} (r - r_{\rm ND})^2 ,$$
 (3)

where  $\lambda_{\rm ND} \simeq 10^3 \varepsilon_0 \sigma_0^{-2}$  and  $r_{\rm ND} \simeq 2.5 \sigma_0$ . Because NRs are significantly longer, maintaining their rigidity with a simple harmonic potential is impractical, even with extremely large spring constants. To address this, we use virtual sites to keep the NR beads fixed in their positions during the simulation. This method ensures the desired stiffness without the need for excessive bonding energy, which can lead to computational difficulties. The mass is assigned to two massive but non-interacting sites that provide the essential mass distribution. These massive sites are kept at a constant distance  $\ell_{\rm mass}$  from the NR center of mass by introducing a distance constraint. Since NRs are one-dimensional structures, preserving the center of mass is achieved by assigning half the NR mass to each of the two massive sites. For rotational movement, the conservation of the inertia tensor requires the massive sites to be located at:

$$\ell_{\rm mass}^2/d_b^2 = \begin{cases} \frac{N_b^2 - 1}{3}, & \text{for } N_b \text{ even,} \\ \frac{1}{3}(N_b + 1)(N_b + 2), & \text{for } N_b \text{ odd.} \end{cases}$$
(4)

where  $N_b$  is the number of beads in a NR and  $d_b$  the distance between the centers of two consecutive beads. Setting  $N_b$  implies ensuring that the volume of our CG model of a rod-like particle,  $V_{\rm NR}$ , does not fall below that of an equally-long spherocylinder,  $V_{\rm SC}$ , by more than a given threshold value. To fulfill this condition, the number of beads in a NR is found to be

$$N_b(\xi, q) \ge 1 + \frac{(q-1)^{3/2}}{\sqrt{\xi(3q-1)}}$$
. (5)

where  $\xi \equiv 1 - V_{\rm NR}/V_{\rm SC}$  is referred to as coefficient of rugosity. For q = 5 and  $\xi = 0.1$ , we find  $N_b = 8$  (see Appendix A for details).

## **III. SIMULATION METHODOLOGY**

We perform CG-LD simulations in the canonical (NVT) ensemble using GROMACS 2019.4. The temperature is maintained at T = 298 K. The simulation box is a cube with a side length of  $L = 35.94\sigma_0$  and periodic boundary conditions. The simulations use a time step of  $\delta t = 2$  fs. Starting with an isotropic initial configuration of polymers generated using polyply,<sup>68</sup> we then randomly insert the NPs in the quantities specified in Table I. For all simulations, the volume is fixed at  $L^3$ , and the inclusion of NPs induces a slight increase in polymer density of less than 7%. As we will see, this minor density variation does not affect the structural and dynamical trends, as they remain consistent across all systems. To characterize our model PNCs, we analyze their structural, dynamical, and transport properties. For the structural properties, we calculate the radial distribution function of the NPs relative to the other beads, examine the relationship between the radius of gyration  $R_{gyr}$ and the end-to-end distance  $R_{ee}$  of the polymers (as a measure of ideality), and compute the mean squared internal distance. The dynamical properties we measure include the self-part of the van Hove correlation function, the non-Gaussian parameter, and the mean squared displacement. For the transport properties, we evaluate the translational diffusion coefficients and viscosity. Starting with the structural properties, we define a function  $\mathscr{I}$  to assess the evolution of ideality, inspired by the relationship between the radius of gyration and the end-to-end distance for ideal chains:

$$\langle R_{\rm gyr}^2 \rangle = \langle R_{\rm ee}^2 \rangle / 6 \,, \tag{6}$$

$$\mathscr{I}^2 \equiv 6 \langle R_{\rm gyr}^2 \rangle / \langle R_{\rm ee}^2 \rangle \,. \tag{7}$$

where  $\langle \cdot \rangle$  denotes ensemble average. According to this definition, ideal chains are expected to yield a value of  $\mathscr{I} \sim 1$ .

Mean squared internal distance. The mean squared internal distance (MSID) measures the average bonding distance between monomers in a polymer chain. It is used to ascertain that the systems are fully relaxed and free of local strains within the polymer chains:

$$\langle R^2(n) \rangle = \frac{1}{N_c} \left\langle \sum_{i=1}^{N_c} \left[ \frac{1}{N-n} \sum_{j=1}^{N-n} |\mathbf{r}_{i,j} - \mathbf{r}_{i,j+n}|^2 \right] \right\rangle$$
(8)

where  $N_c$  is the number of chains, N the number of beads in a polymer chain, and n the distance between the  $j^{\text{th}}$  be ad and the  $(j+n)^{\rm th}$  be ad along the chain. At equilibrium, the MSID is related to the end-to-end distance through the equation:

$$\langle R_{\rm ee} \rangle \simeq \sqrt{(N-1)\langle R^2(n) \rangle} \,.$$
 (9)

This arises from the fact that the equilibrated chain can be modeled as a random walk of N monomers, each separated by a distance  $R_n$ . Consequently, it shall approach  $\langle R_{\rm ee} \rangle \sim R_n \sqrt{N}$ .

Self van Hove Function. The presence of both slow and fast-moving polymer chains and NPs, which can give rise to heterogeneous dynamics, can be quantitatively assessed using the self-part of the van Hove correlation function (SVHF). This function provides a probabilistic distribution of the displacements that polymer chains or NPs undergo over time. The SVHF is defined as:

$$G_s(\mathbf{r},t) \equiv \frac{1}{N} \left\langle \sum_{i=1}^N \delta\left[\mathbf{r} - (\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0))\right] \right\rangle, \quad (10)$$

where  $\delta$  is the Dirac delta function, N is the number of particles, and  $\mathbf{r}_i(t)$  is the position of particle i at time t. The SVHF describes how particles move from their initial positions  $\mathbf{r}_i(t_0)$  at time  $t_0$  to new positions  $\mathbf{r}_i(t+t_0)$  after a time interval t. By analyzing  $G_s(\mathbf{r},t)$ , one can gain insights into the diffusion processes and dynamic heterogeneity within the system. This function helps identify the distribution and likelihood of different displacements, thus characterizing the movement patterns of slow and fast NPs in PNCs.

Non-Gaussian Parameter. The Non-Gaussian Parameter (NGP) is used to quantify deviations from Gaussian behavior in the displacement distribution of particles in a system. It is defined as

$$\alpha_2(t) \equiv \frac{d}{2+d} \frac{\left\langle \Delta \mathbf{r}(t)^4 \right\rangle}{\left\langle \Delta \mathbf{r}(t)^2 \right\rangle^2} - 1, \tag{11}$$

where  $\Delta \mathbf{r}(t)$  is the displacement of a particle during a time interval t,  $\langle \Delta \mathbf{r}(t)^2 \rangle$  and  $\langle \Delta \mathbf{r}(t)^4 \rangle$  are the mean squared and quartic displacements, respectively, and d is the dimensionality of the system (e.g., d = 3 for a threedimensional system). If the particle displacements follow a Gaussian distribution, the NGP will be zero, indicating that there are no non-Gaussian effects. Positive values of the NGP indicate that some particles experience shorter or longer displacements than the average, usually due to, for example, crowded environments, interactions, or aging effects.

*Diffusivity.* The translational diffusion coefficients are determined from the mean squared displacement (MSD) at equilibrium using the following equation:

$$D \equiv \lim_{t \to \infty} \frac{1}{2d} \frac{\mathrm{d} \left\langle \Delta \mathbf{r}(t)^2 \right\rangle}{\mathrm{d}t},\tag{12}$$

where D is the diffusion coefficient and  $\langle \Delta \mathbf{r}(t)^2 \rangle$  is the particles' MSD.

*Viscosity.* The viscosity of our model PNCs can be obtained using the off-diagonal components of the stress tensor through the Green-Kubo relation:

$$\eta_{ij} = \frac{V}{k_{\rm B}T} \int_0^\infty {\rm d}t \, \left\langle P_{ij}(t_0) P_{ij}(t+t_0) \right\rangle_{t_0} \quad (i \neq j) \,, \ (13)$$

where  $\eta_{ij}$  is the shear viscosity in the *ij*-plane, with  $\{i, j\} = \{x, y, z\}, V$  is the volume of the system and  $P_{ij}$  represents the off-diagonal component of the stress tensor. The integrand  $\langle \vec{P}_{ij}(t_0)P_{ij}(t+t_0)\rangle_{t_0}$  is the time autocorrelation function of the stress tensor, averaged over the time  $t_0$ . Using this method, the value of the zero-shear viscosity is averaged within a range that ensures its convergence across the three spatial directions, assuming an isotropic system. This method cannot however be applied to estimate the viscosity in the non-linear regime, where it changes with the shear rate. To this end, we employ a non-equilibrium method, the SLLOD method. $^{69,70}$  In particular, we impose a Couette flow in the equations of motion by introducing an initial velocity gradient, which is maintained through shear facilitated by the Lees-Edwards periodic boundary conditions. Assuming the imposed motion has a shear rate of  $\dot{\gamma}$  along the x-axis, denoted by  $\mathbf{e}_x$ , and acts on particles with random individual velocities  $\mathbf{v}_{\alpha}$ , a velocity gradient is created along the z-axis. Consequently, the equation of motion for a particle  $\alpha$  at position  $\mathbf{r}_{\alpha} = (x_{\alpha}, y_{\alpha}, z_{\alpha})$  with velocity  $\dot{\mathbf{r}}_{\alpha}$  given by:

$$\dot{\mathbf{r}}_{\alpha} = \mathbf{v}_{\alpha} + \dot{\gamma} z_{\alpha} \mathbf{e}_x \,. \tag{14}$$

The shear viscosity obtained is the ratio of the resulting off-diagonal stress to the applied shear rate:

$$\eta_{ij} = -\frac{\langle P_{ij} \rangle}{\dot{\gamma}} \quad (i \neq j) \,. \tag{15}$$

Here,  $\langle P_{ij} \rangle$  is the average off-diagonal component of the stress tensor. The SLLOD method facilitates the generation of a viscosity curve across various shear rates, ensuring that the viscosity value obtained through the Green-Kubo formula falls within the expected range—or at least, providing a lower bound for its value. However, the SLLOD method can become impractical if the shearing is too slow, necessitating the use of the Green-Kubo method in such scenarios. Therefore, combining both methods provides a complete and more comprehensive understanding of viscosity.



FIG. 2. Snapshots of various systems at approximately 7.5  $\mu$ s. Affine polymer and ND beads are shown in lime green and purple, while NRs in yellow. Top and bottom rows display, respectively, HPNCs and BCPNCs. Left, middle and right columns feature PNCs including, respectively, NDs, NRs and a mixture of both.

# IV. RESULTS

#### A. Structural properties

Fig. 2 presents illustrative snapshots of the systems studied, highlighting the distribution of NPs within the polymer matrix. Achieving a uniform NP distribution is essential for optimizing the nanocomposite's properties, as it prevents defects and aggregation that can compromise the mechanical, thermal, and electrical performance of the material. A uniform dispersion can, in principle, be achieved in HPNCs. However, when BCPs are employed, their tendency to undergo microphase separation leads to the formation of distinct domains, causing NPs to localize according to their chemical affinity with the copolymer blocks. A visual inspection of Fig. 2 reveals that BCP-NCs form an amorphous bicontinuous phase, primarily driven by the repulsive interactions between the  $M_1$  and M<sub>2</sub> blocks of the copolymer. This phase structure significantly influences the spatial distribution of NDs, causing them to preferentially accumulate at the  $M_1$ - $M_2$  interface. Additionally, the distribution of NPs within the polymer matrix is influenced by the degree of relaxation of the polymer chains. Complete relaxation eliminates residual local strains and dictates the overall conformation of the chains, which in turn affects the distribution of NPs throughout the matrix. To verify that our systems have achieved a good degree of relaxation, we analyzed the MSID, which quantifies the average squared distance between monomers along the polymer chain. Additionally, by comparing the MSID to expected theoretical values, predicted for an ideal or Gaussian chain, one can assess whether the polymer chains have reached an equilibrium state. Deviations from these expected values may indicate the presence of residual stresses or unrelaxed configurations, which could affect the overall behavior and properties of the system.

The MSID reveals a slight delay in relaxation for the BCPNCs, as depicted in the top frame of Fig. 3. This minor relaxation delay aligns with previous findings in long polymer chains, where entangled dynamics, particularly under conditions of spatial confinement, are known to slow the relaxation process.<sup>71-74</sup> In our simulations, this delay is likely due to the restricted volume within each region of the bicontinuous phase, which occupies roughly half the total volume of the simulation box. In contrast, the HPNCs, shown in the bottom frame of Fig. 3, exhibit complete relaxation, with the MSID reaching the expected plateau, indicating that the spatial confinement unique to BCPNCs is the primary factor behind this small effect. Despite these differences, all systems are largely equilibrated. Simulations were run for 5  $\mu$ s, with 4  $\mu$ s allocated to equilibration and 1  $\mu$ s to production. For viscosity calculations, simulations were extended to 22  $\mu$ s, using the final 5  $\mu$ s for production. MSID measurements confirmed that system stability was achieved within the initial 5  $\mu$ s and maintained throughout the extended duration. We observe only minimal deviations from full relaxation in the BCPNCs and the results are in very good agreement with theoretical predictions (dot-



FIG. 3. Mean squared internal distance (MSID) between polymer beads. The (a) and (b) panels correspond to BCP-NCs and HPNCs, respectively. For comparison, the MSID of pristine polymers is also included (represented by solid diamonds). The theoretical prediction is depicted with a black dot-dashed line. ND<sub>k</sub>-PNCs are shown with empty symbols, while ND<sub>k</sub>/NR-PNCs are represented by solid symbols. Solid and dashed lines are included as visual guides.

dashed lines in both frames). The theoretical estimate of the MSID for polymer melts composed of semiflexible chains, assuming no excluded volume effects, is described by the Freely Rotating Chain model:

$$\langle R^2(n)\rangle = n l_n^2 \left[ \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} - \frac{2 \langle \cos \theta \rangle (1 - \langle \cos \theta \rangle^n)}{n (1 - \langle \cos \theta \rangle)^2} \right],$$
(16)

with n the number of backbone bonds and  $l_n \approx 0.41$  nm the average distance between consecutive monomers. A combination of potentials, collectively denoted as  $W(\theta)$ , influences the beads and determines the average value of the bending angle:<sup>71</sup>

$$\left\langle \cos\theta\right\rangle = \frac{\int_0^{\pi} \mathrm{d}\theta\cos\theta\sin\theta e^{W(\theta)}}{\int_0^{\pi} \mathrm{d}\theta\sin\theta e^{W(\theta)}} \tag{17}$$

The simplest model with an analytical solution is  $W(\theta) = \kappa_{\theta}(1 - \cos \theta)$ . Substituting this into Eq. (17) gives  $\langle \cos \theta \rangle = \coth \left(\frac{\kappa_{\theta}}{k_B T}\right) - \frac{k_B T}{\kappa_{\theta}} = 0.563$ , or equivalently,  $\langle \theta \rangle = 55.71^{\circ}$ . This value closely approximates the behavior of HPNCs, as illustrated in Fig. 3b. However, long polymer chains, such as those in our system, are sensitive to this angular average due to cumu-

lative contributions along the chain, leading to an underestimation of MSID values for BCPNCs. The key difference between these cases is monomer heterogeneity. Specifically, M<sub>1</sub>-M<sub>2</sub> repulsion introduces an additional contribution to  $W(\theta)$ , accounting for the increased stiffness and, consequently, the larger MSID observed when the angular amplitude is constrained by a stronger WCA potential at the  $M_1$ - $M_2$  separation. By expressing this separation as a function of the bond angle,  $h_{\theta} \equiv |\mathbf{r}_{i+1} - \mathbf{r}_{i-1}| = l_n \sqrt{2 + 2\cos\theta}$ , the  $W(\theta)$  potential becomes  $W(\theta) = \kappa_{\theta}(1 - \cos \theta) + \frac{2U_{M_1M_2}(h_{\theta})}{200}$ . The factor  $\frac{2}{200}$  reflects that, once the microphase separation is complete, the M<sub>1</sub>-M<sub>2</sub> repulsion affects 2 out of every 200 monomers in each chain. This modified  $W(\theta)$  for BCP-NCs yields an average of  $\langle \cos \theta \rangle = 0.584$ , or  $\langle \theta \rangle = 54.25^{\circ}$ . a small but significant adjustment that more accurately approximates the measured MSID in BCPNCs, as shown in Fig. 3a.

TABLE II. Average end-to-end distance and radius of gyration of the PNCs studied.  $^{\rm a}$ 

		$\langle R_{\rm ee} \rangle \ (\rm nm)$		$\langle R_{\rm gyr} \rangle$ (nm)	
		BCP	HP	BCP	HP
Polymer melts		11.6	11.2	4.7	4.5
NR-PNCs		11.4	11.5	4.6	4.7
$ND_k$ -PNCs	$ND_1$	11.9	10.9	4.8	4.4
	$ND_2$	11.7	11.0	4.8	4.5
	$\mathrm{ND}_\mathrm{J}$	11.7	10.9	4.7	4.5
$\mathrm{ND}_k/\mathrm{NR} ext{-}\mathrm{PNCs}$	$ND_1$	11.7	11.5	4.8	4.6
	$ND_2$	11.8	11.5	4.8	4.6
	$\mathrm{ND}_\mathrm{J}$	11.8	11.5	4.8	4.5

 $^{\rm a}$  Errors for  $R_{\rm gyr}$  are all less than 0.2 nm, and for  $R_{\rm ee},$  they are below 0.1 nm.

In the equilibrium limit, the MSID should align with the end-to-end distance, which is closely related to the polymer chain's radius of gyration. As shown in Table II, these two quantities vary only slightly across the systems studied. In particular, the end-to-end distance is found to be close to the reference value calculated by Everaers et al.,<sup>62</sup> with a mass-normalized mean-square extension of  $\langle R_{ee}^{*2} \rangle / M_c = 1.400 \text{ Å}^2 \text{ mol g}^{-1}$ , where  $M_c = 200m_0$  is the mass of a polymer chain, yielding an approximate  $R_{ee}^* = 11.1$  nm. Furthermore, the ratio described in Eq. (6) remains consistently close to  $\mathscr{I} = 1$  across all systems, indicating that the polymer chains showcase a nearly ideal behavior and the deviations observed are minimal and within expected ranges. This is typical in concentrated linear melts, where interactions between chains are screened by neighboring chains.<sup>75</sup> The fact that the characterization of HP chains did not require a hindering correction, and that non-ideality only affects 2 out of 200 monomers in BCPs, supports this observation. This confirms that, although the BCP-NCs show slight delays in relaxation, the overall structural integrity and equilibration of the polymer chains are well-maintained across the systems. Theoretical predic-



FIG. 4. RDFs centered on NDs' centers of mass. Left and right columns (frames (a) and (b)) report, respectively, the RDFs for  $ND_k$ -PNCs and  $ND_k/NR$ -PNCs, while top and bottom rows (frames (c) and (d)) refer to BCPNCs and HPNCs, respectively. Empty and solid symbols refer, respectively, to  $ND_k$ -ND<sub>k</sub> and  $ND_k$ -M RDFs, with k indicated in the legend. The inset in frame (a) highlights the intercalation of a polymer chain between two NDs. Solid and dashed lines are guides for the eye.

tions from Eqs. (16) and (17) give end-to-end distances of  $\langle R_{\rm ee}^{\rm th}({\rm HPNCs}) \rangle = 10.9$  nm and  $\langle R_{\rm ee}^{\rm th}({\rm BCPNCs}) \rangle =$ 11.3 nm. Using CG-LD simulations, which confirmed the systems are ideal, we divided these values by  $\sqrt{6}$  to estimate the gyration radii:  $\langle R_{\rm gyr}^{\rm th}({\rm HPNCs}) \rangle = 4.4$  nm and  $\langle R_{\rm gyr}^{\rm th}({\rm BCPNCs}) \rangle = 4.6$  nm. These theoretical results align well with the measured polymer properties in Table II. In addition, the random walk approximation  $\langle R_{\rm ee} \rangle \sim R_n \sqrt{N}$  can be applied, where  $R_n$  represents the average distance between monomers, estimated to be between  $\sqrt{3.5\sigma_0^2}$  and  $\sqrt{4\sigma_0^2}$  and N = 200. The approximation grants values from  $\langle R_{\rm ee} \rangle = 11.1$  nm to 11.9 nm, which agrees well with the results given above.

To better quantify the distribution of NPs within the polymer matrix, we begin by examining the radial distribution functions (abbreviated as RDFs or g(r)). Fig. 4 presents the RDFs for ND<sub>k</sub>-ND<sub>k</sub> pairs across different PNCs, where  $k = \{1, 2, J\}$ , alongside the RDF of ND<sub>k</sub> relative to the polymer beads (indicated by three dashed curves that basically overlap) for comparison. Similar RDFs for NRs are shown in Figure 5. A first key observation is that the primary peak of the NP-M RDF, whether for NDs or NRs, consistently appears in the range of  $1.5 < r/\sigma_0 < 2$ , while the peak of the NP-NP RDFs is located approximately at  $3.5 < r/\sigma_0 < 4$  for NDs and  $2.5 < r/\sigma_0 < 3$  for NRs. Since the main peak represents the average distance between nearest neighbors, this distribution suggests that NDs and NRs are predominantly

surrounded by polymer chains that intercalate between them, highlighting a strong interaction between the NPs and the polymer matrix. We stress that, although both sets of NPs are similarly distributed, NDs and NRs exhibit distinct interactions with the polymer matrix. NDs interact via a purely repulsive WCA potential, while NRs through a LJ potential that simulates a soft grafting effect. The resulting distribution pattern confirms that our chosen interaction parameters effectively prevent clustering. The NPs do not aggregate or segregate from the polymer, but instead integrate seamlessly into the matrix, validating the formation of isotropic PNCs.

As discussed earlier, NPs embedded in BCPNCs are expected to localize at the interface between the two copolymer blocks. This is supported by the RDFs of  $ND_A$ ,  $ND_N$ , and  $ND_J$  relative to  $M_1$  and  $M_2$  (shown in Figs. S2 and S3 of the Supplementary Materials). The nearly identical RDFs for each ND family with respect to both copolymer blocks strongly suggest that these NPs are most likely situated at the M<sub>1</sub>-M<sub>2</sub> interface. The lower polymer density at this interface, compared to the bulk of each block domain, increases the configuration entropy of the NPs, resulting in a more thermodynamically favorable distribution.<sup>52</sup> For Janus NDs, this distribution is further enhanced by enthalpic contributions, as their dual-affinity—experiencing both attraction and repulsion with different monomers—intensifies their preference for the M<sub>1</sub>-M<sub>2</sub> boundary. A closer examination



FIG. 5. RDFs centered on NRs' centers of mass. Frames (a) and (b) refer to NR-PNCs and  $ND_k/NR$ -PNCs, respectively. Empty circles and squares refer to NR-NR RDFs obtained in HPNCs and BCPNCs, respectively. Solid circles and squares refer to NR-M RDFs obtained in HPNCs and BCPNCs, respectively. The inset in frame (b) highlights the intercalation of a polymer chain between two NRs. Solid and dashed lines are guides for the eye.

of Fig. 4 reveals two notable aspects of ND distribution. Firstly, in HPCNs, the distribution is largely structureless, with  $ND_k$ - $ND_k$  RDFs resembling those of a highly dilute fluid, except for a slight peak in the  $ND_N-ND_N$ RDF at  $r/\sigma_0 \simeq 4$  (empty circles). In contrast, the ND<sub>k</sub>- $ND_k$  RDFs in BCPNCs display more pronounced primary peaks, indicating the presence of short-range density correlations that extend over slightly longer distances. Essentially, NPs occupy all available space when dispersed in HPNCs, but in BCPNCs, they are confined to specific regions, resulting in closer proximity without leading to clustering. Secondly, the addition of NRs does not significantly affect the distribution of NDs within the polymer (right column of Fig. 4), at least within the concentrations explored in this study. To better understand this observation, we now turn our attention to the NRs<sup>3</sup> RDFs, presented in Fig. 5.

In the top frame of Fig. 5, we present the RDFs of NRs in NR-PNCs. Consistent with previous findings for ND<sub>k</sub>-PNCs, the peak of the NR-M RDF occurs at shorter distances than that of the NR-NR RDF, indicating that NRs are primarily surrounded by polymer chains, with no evidence of clustering. A similar pattern is observed in ND<sub>k</sub>/NR-PNCs (bottom frame of Fig. 5), mirroring the earlier results: the presence of NDs does not significantly alter the dispersion of NRs within the polymer. What

does affect the NRs' dispersion, however, is the polymer's architecture. As noted with NDs, BCPs tend to localize NRs within specific regions, while HPs promote their dispersion throughout the entire matrix. Finally, mixed ND<sub>k</sub>/NR-PNCs exhibit nearly complete homogeneity in the NR-ND<sub>k</sub> distribution, as shown in Fig. S4 of the Supplementary Materials. The nearly identical RDFs for the various types of NDs confirm the earlier observation from Fig. 5b: ND interactions do not significantly influence the structuring of NRs. This homogeneity is only slightly disrupted in BCPNCs due to their inherent space anisotropy, which, as previously noted, promotes the localization of NPs within specific regions of the polymer matrix.

#### B. Dynamical properties

To assess the mobility of NPs within the polymer matrix, we calculated the MSD for both NDs and NRs. The MSD analysis reveals three distinct dynamic regimes across all systems: an initial short-time ballistic regime of less than 10 ps in duration, a subsequent subdiffusive regime, and finally, a long-time diffusive regime. The short-time ballistic regime is characterized by the NPs moving freely within the polymer matrix, where their displacements are proportional to time. This is followed by a sub-diffusive regime, where the particles' movement becomes constrained by the surrounding chains temporarily trapping the NPs, restricting their movement and leading to a slower, sublinear increase in MSD with time. Finally, at longer timescales, the particles escape these restrictions, and their movement returns to a diffusive regime, where the MSD once again increases linearly with time. The MSD of NDs is significantly impacted by the specific type of ND used, whether it is a  $ND_1$ , a  $ND_2$ , or a Janus ND<sub>J</sub>. As illustrated in Fig. 6, the dynamics of HPNCs are not easily distinguishable when evaluating their MSD. However, these differences become more pronounced in BCPNCs, where ND<sub>2</sub> exhibits the highest diffusion rate,  $ND_J$  shows the slowest movement, and  $ND_1$  occupies an intermediate spot between the two. The enhanced mobility of  $ND_2$  in BCPNCs can be attributed to their indistinctive interactions with the two monomer species, either  $M_1$  or  $M_2$ , facilitating their movement across the bicontinuous phase. In contrast, the Janus ND<sub>J</sub>, experiences more complex interactions with the surrounding monomers due to its dual-affinity nature, specially under microphase separation. Its slower diffusion principally arises from the restricted movement caused by its interactions with the two monomer species, which bind the ND<sub>J</sub> more strongly to the microphase-separated region. In comparison, NRs exhibit a different behavior. The attractive interactions between NRs and monomers render them less sensitive to the specific type of ND or the polymer matrix. As shown in Fig. 7, the MSD of NRs across all NR-PNCs and  $ND_k/NR$ -PNCs systems are nearly identical, indicating that the NRs' diffusion

 $ND_k/NR$ -PNCs  $ND_k$ -PNCs  $\langle \Delta r^2 \rangle / \sigma_0^2$  in HPNCs  $\langle \Delta r^2 \rangle / \sigma_0^2$  in BCPNCs (b) (a) $10^{3}$  $10^{1}$ O ND<sub>1</sub>  $10^{-1}$  $\Box$  ND<sub>2</sub>  $\triangle$  ND<sub>J</sub>  $10^{-3}$ (d)(c) $10^{3}$  $10^{1}$  $10^{-1}$ -3 10  $10^{2}$  $10^{3}$  $10^{5}$  $10^{0}$  $10^{1}$  $10^{2}$  $10^{3}$  $10^{4}$  $10^{5}$  $10^{0}$  $10^{1}$  $10^{4}$  $10^6$ 10 $10^{-10}$  $t/\tau_0$  $t/\tau_0$ 

FIG. 6. Mean squared displacement of NDs in BCPNCs (top, frames (a) and (b)) and HPNCs (bottom, frames (c) and (d)) as indicated in the legend. Solid lines are guides for the eye. The diffusive regime is indicated with a dashed red line.



FIG. 7. Mean squared displacement of NRs in BCPNCs (top, frame (a)) and HPNCs (bottom, frame (b)) as indicated in the legend. The diffusive regime is indicated with a dashed red line.

is not significantly altered by the presence of different NDs or by the polymer environment, whether it be HP or BCP. This suggests that the diffusion dynamics of NRs are primarily governed by their interaction with the polymer monomers rather than by the composition of the nanocomposite or the type of NDs present. In order to quantify these small variations in NR diffusion and to discuss NDs movement in HPNCs, we rely on other methods of measuring the dynamics, like their diffusion coefficients and their SVDFs.

We derived the diffusion coefficients from the NPs' MSDs using the relation given in Eq. (12). The diffusion coefficients of the different families of NDs are summarized in Table III, while those for the NRs are detailed in Table IV. Our analysis reveals that NRs generally exhibit faster diffusion compared to NDs. This enhanced mobility is attributed to their lower mass—NRs are approximately 65% lighter than NDs. Additionally, NRs show less sensitivity to the type of ND or the specifics of the polymer matrix. As we said earlier, this is in part due to the LJ interactions that bind NRs to the polymer network, which tend to be less affected by variations in the ND type. Their diffusion coefficient reveals that NRs experience more restricted movement in BCP matrices than in HP matrices, particularly in the presence of  $ND_1$  particles. Despite this, the impact on the diffusion coefficient is less pronounced than for NDs. This suggests that the interaction between individual NPs and the polymer has a more significant effect on diffusion than the presence of different ND types. Among the NDs,  $ND_2$  in HP matrices are observed to be the fastest particles, while ND<sub>J</sub> in BCP matrices are the slowest. We remind the reader that ND<sub>2</sub> particles still interact repulsively with the polymer chains, but to a lesser degree than  $ND_1$  and other NPs. Additionally, we analyzed the polymer MSD and diffusion coefficients (see Section S4 of the Supplemen-



FIG. 8. Self-part of the van Hove functions of ND<sub>N</sub> (circles), ND<sub>A</sub> (squares), ND<sub>J</sub> (triangles) and NR (inverted triangles) in BCPNCs (top row, frames (a) and (b)) and HPNCs (bottom row, frames (c) and (d)) at  $t_1 = 10$  ns (left, frames (a) and (c)) and  $t_2 = 40$  ns (right, frames (b) and (d)). Dashed lines are Gaussian fits centered around the maximum.



FIG. 9. Self-part of the van Hove functions for monomers in BCPs (top panel, frame (a)) and HPs (bottom panel, frame (b)) at  $t_1 = 0.1 \ \mu$ s (diamonds) and  $t_2 = 1 \ \mu$ s (crosses). Dashed lines represent Gaussian fits centered on the peak.

tary Materials) and it revealed that the diffusive regimes of the polymers and nanoparticles operate on substantially different time scales, a temporal dissociation which strongly suggests that the polymer diffusion coefficient is unlikely to correlate significantly with the diffusion behavior of the various nanoparticle species. As discussed in the MSD section, the behavior of the Janus particles is strongly influenced by the segregation of monomers into distinct regions, with the key difference being that we can compare with HP systems now. In HP matrices, the dynamics of ND<sub>J</sub> are intermediate between those of homogeneous NDs, reflecting their hybrid nature and evidencing the tunability of their properties depending on the matrix used. In general, Table III reflects that slower diffusion of NDs is consistent across more complex systems, such as BCP matrices and ND/NR-PNCs.

TABLE III. Diffusion coefficients of NDs,  $D_{\rm ND}$  (nm<sup>2</sup>/ns), in different systems.<sup>a,b</sup>

	$ND_1$	$ND_2$	$\mathrm{ND}_\mathrm{J}$
$\mathrm{ND}_k ext{-HPNCs}\ \mathrm{ND}_k/\mathrm{NR} ext{-HPNCs}$	$\begin{array}{c} 0.085\\ 0.075\end{array}$	$0.131 \\ 0.127$	$0.112 \\ 0.097$
$\mathrm{ND}_k ext{-BCPNCs}\ \mathrm{ND}_k/\mathrm{NR} ext{-BCPNCs}$	$\begin{array}{c} 0.060\\ 0.046\end{array}$	$0.120 \\ 0.094$	$0.036 \\ 0.029$

<sup>a</sup> All errors are below  $0.003 \text{ nm}^2/\text{ns}$ .

<sup>b</sup> The different PNCs are listed in Table I.

The SVHF offers valuable insights into particle dynamics by quantifying the distribution of individual particle displacements. This function is instrumental in distinguishing between Gaussian and non-Gaussian behaviors in particle movements, enabling a comparison of the dy-

TABLE IV. Diffusion coefficients of NRs,  $D_{\rm NR}$  (nm<sup>2</sup>/ns), in different systems.<sup>a,b</sup>

	NR-PNCs	$ND_k/NR$ -PNCs			
		$ND_1$	$ND_2$	$ND_{J}$	
HP	0.173	0.145	0.184	0.183	
BCP	0.151	0.125	0.144	0.144	

<sup>a</sup> All errors are below  $0.002 \text{ nm}^2/\text{ns}$ .

<sup>b</sup> The different PNCs are listed in Table I.

namic properties across different species within the system. When analyzing the dynamics of NDs, we find that they cover distances comparable to those of NRs (Fig. 8), and both are significantly faster than the polymer beads (Fig. 9). Both the polymer beads and NPs SVHFs exhibit similar shifts and broadening, yet these changes occur over vastly different timescales. While monomers require approximately 1  $\mu$ s to achieve a certain displacement, NPs accomplish the same within just 30 ns, highlighting that NPs traverse the same distance as monomers but in only 3% of the time, or in other words, polymers are approximately 30 times slower. Additionally, the type of ND and the polymer environment play crucial roles in ND dynamics. Across all polymer types, the most mobile NDs are the ND<sub>2</sub>, whose dynamics remain largely consistent between BCPNCs and HPNCs. The other homogeneous ND,  $ND_1$ , exhibits similar behavior in both polymers, but the presence of  $ND_J$  introduces a significant difference. In HP systems, ND<sub>J</sub> dynamics are intermediate between those of  $ND_1$  and  $ND_2$ , as discussed when comparing their diffusion coefficients. By contrast, in BCP systems, the segregation of monomers into distinct regions considerably slows down ND<sub>J</sub>, making them the least mobile particles with the lowest displacement probability. Unlike NDs, NRs appear largely indifferent to the type of polymer, exhibiting similar SVHFs regardless of whether the environment is HP or BCP. As discussed earlier in this section, this insensitivity may stem from the non-selective LJ interactions that NRs have with M<sub>1</sub> and M<sub>2</sub>, which do not differentiate between the two polymers. When approximating the SVHFs with Gaussian fits (dashed lines in Figs. 8 and 9), the agreement with the simulation results is good around the peaks of the distributions, but significantly poorer at both tails, where the probability of slow and fast particles is respectively overestimated and underestimated. This results in a non-Gaussian dynamic behavior for the whole set of PNCs studied.

Deviations from Gaussianity are typically analyzed using the NGP, as defined in Eq. (11). The NGPs for our systems are displayed in Figs. S6 and S7 of the Supplementary Materials for NPs and monomers, respectively. The parameter statistics are highly sensitive to number density, leading to smoother curves for monomers, as they dominate the population within PNCs. These NGPs show a time-dependent behavior influenced by the various stages of exclusion at different timescales created by neighboring chain beads and NPs. Generally,  $\alpha_2$  remains close to zero at very short timescales, when the beads are still near their initial positions and have not yet been significantly affected by their nearest neighbors. As time progresses,  $\alpha_2$  increases, reaching a peak between  $t \simeq 10^2$  and  $10^5$  ns for NPs and up to two decades later for monomers. Deviations from Gaussianity are relatively small, especially for NDs in HPNCs, a result that is consistent with earlier observations for the HPNCs SVHFs in Figs. 8 and 9, where the Gaussian fits effectively capture the peaked region of the distributions, though they fall short in accurately representing their tails. The evident boost in non-Gaussianity for NDs in BCPs is a reflection of their structural features, which favor highly heterogeneous dynamical behavior, as NDs that stay close to the microphase separation move substantially slower than those moving across the matrix. At sufficiently long times, the dynamics of all species return to Gaussian behavior, leading the NGPs to decay to zero.

All these microscopic variations in diffusion behavior directly affect the macroscopic properties of the material, including its viscosity, as we will see in the next section.

### C. Viscosity

To better understand the connection between the behavior of individual NPs with the overall macroscopic rheological response of the polymer matrix, we combined equilibrium and non-equilibrium CG-LD and calculated the shear viscosity of HPNCs and BCPNCs incorporating  $ND_1$ , NRs or a mixture of both. Due to the demanding computational effort, we have not included PNCs with Janus or  $ND_2$ . Microscopically, viscosity measurements shed light on the complex interplay between the polymer with itself and with the NPs that may not be immediately apparent from structural or dynamical analysis alone. From an applications perspective, viscosity controls processability in manufacturing techniques and often correlates with mechanical performance. To this end, we used the Green-Kubo formalism for the equilibrium method, as stated in Eq. (13), and for the non-equilibrium method we used the SLLOD algorithm, which involves applying shear to the top plane of our system and displace it relative to the lower plane, as shown in Fig. 10 (Multimedia available online) and described in Eq. (14). This nonequilibrium procedure is essential for elucidating how NPs traverse the polymer and influence the material's flow and deformation characteristics.

Using the non-equilibrium method, the shear viscosity is obtained by calculating the ratio between the shear rate,  $\dot{\gamma}$ , and the off-diagonal component of the stress tensor in the plane where shear is applied, as shown in Eq. (15). In each PNC, we observe a stress threshold that must be exceeded before the viscosity reaches a plateau. This initial increase reflects the polymer's resistance to align with the direction of movement, which is especially significant for long and entangled polymer chains like



FIG. 10. Snapshots showing the shearing process of the PNCs studied to determine viscosity at the same shear rate,  $\dot{\gamma} = 6.67 \times 10^{-5} \text{ ps}^{-1}$  (Multimedia available online).



FIG. 11. Shear viscosity  $\eta$  as a function of shear rate  $\dot{\gamma}$  of homopolymeric systems (left, frame (a)) and copolymeric systems (right, frame (b)). Some error bars are smaller than the symbols used and might not be visible. The gray shaded regions, separated by a broken axis (logarithmic scale) and in the insets (linear scale), highlights the zero-shear viscosity obtained by equilibrium CG-LD simulations using the Green-Kubo relation (filled symbols). Outside this region, viscosity values are derived from non-equilibrium simulations using the SLLOD algorithm (empty symbols).

ours. After surpassing this threshold, we use the stable viscosity values to determine the shear viscosity, as illustrated in Fig. 11 (see also Section S6 of the Supplementary Materials for additional details). The shear-thinning behavior, with the viscosity decreasing with increasing shear rate, is evident in both the polymer melt and the PNCs. This non-Newtonian response of the system to

applied shear has been observed in experiments and simulations, capturing the shear-thinning behavior of polymeric materials.  $^{69,76,77}$ 

While the type of NPs and its interactions with the polymer may influence viscosity, these effects are subtle and not easily discernible at the scales and conditions studied with the non-equilibrium method. Differences are observed in BCPNCs, where NRs induce a slight plasticizing effect at shear rates of around  $10^{-4}$  ps<sup>-1</sup>. decreasing viscosity by approximately 1 cP. At  $\dot{\gamma} \lesssim 10^{-5}$  $ps^{-1}$ , the viscosity of NR-BCPNC and ND<sub>1</sub>/NR-BCPNC converges to that of the pristine polymer, while the viscosity of ND<sub>1</sub>-BCPNC decreases by approximately 5 cP. As a general tendency, the viscosity of different HPNCs does not change significantly at the shear rates investigated, which are not sufficiently slow to capture differences between the systems. At shear rates near the zero-shear limit, the polymer's response to deformation occurs on timescales just slightly shorter than the applied shear. This allows the polymer to partially recover from the shear, interfering with the deformation of the PNCs and resulting in lengthy, unfeasible simulations. In fact, for HP matrices, the yield shear rate<sup>78</sup> is eventually reached, with  $\eta \sim \dot{\gamma}^{-1}$ ; beyond this point, changes in shear no longer affect stress. At these timescales, the shear-induced changes outpace chain fluctuations, rendering shear effects imperceptible at the individual chain level. If computable, zero-shear viscosity values become decisive for characterizing and distinguishing our systems, as all the shear-thinning curves essentially coincide. To this end, we employed the Green-Kubo equilibrium method, which is specifically designed to determine zero-shear viscosity. This approach involves integrating the fluctuations in the stress tensor over large simulation times in an equilibrium simulation (see Eq. (13)). These dense polymeric systems involve highly complex interactions, and the stress autocorrelation function requires long simulation times to deplete. The interested reader can find additional details in Section S7 of the Supplementary Materials. Using the pristine polymer as a reference, we observe that the inclusion of NRs acts as a thickening agent when incorporated within BCP matrices, an effect similar to that produced by NDs in HPs. We notice that both sets of NPs tend to arrange homogeneously across the corresponding host polymers melts.

A reduction of chain free volume through particle inclusion is typically associated with increased viscosity, as predicted theoretically<sup>79</sup> and validated through simulations<sup>14,15,80</sup> and experiments<sup>65</sup>. In particular, NRs experience uniform attraction to all monomer types due to effective polymeric grafting modeled by the LJ potential, countering BCP microphase separation and introducing uniformity. Their distinct geometry provides a structural foundation for copolymer chains, enhancing the material's resistance to mechanical deformation. Their non-Gaussian dynamics, characterized by coexisting slow and fast particles as Fig. 8 indicates, further contribute to the viscosity of the two NR-PNCs by providing heterogeneous resistance to flow. While adding NRs significantly increases the viscosity in BCPs but has a very mild effect on HPs, a different scenario is observed with NDs. In this case, the effect on viscosity is significantly more relevant in HPs than in BCPs (see insets in frames (a) and (b) of Fig. 11). We believe that the uniform distribution of NDs in HPs, compared to their

preferential location at the interface between microphaseseparated domains in BCPs, increases the material's resistance to flow and thus their viscosity. Additionally, the non-Gaussian dynamics of NDs are almost negligible in HPs but more noticeable in BCPs. These results suggest that achieving a homogeneous behavior, whether structural or dynamical, is key to attaining higher viscosity.

The mixed systems containing both  $ND_1$  and NRs exhibit notably higher viscosity values, up to 1600 cP in HPNCs and 4000 cP in BCPNCs. This increase in viscosity can be partially attributed to the higher NP concentration in these systems, which contain 7.8 wt% of NPs compared to 5 wt% in the other systems. However, the significant rise in viscosity is not solely due to the higher concentration but also due to a synergistic interaction between the different types of nanoparticles and the specific polymer matrices. In HPNCs, the increase in viscosity is almost entirely due to the action of NDs. Both  $ND_1$ -HPNC and  $ND_1/NR$ -HPNC exhibit similar viscosity ranges, indicating that adding NRs does not significantly change the viscosity of the melt. This suggests that NDs are the primary contributors to the viscosity increase in these systems. The uniform distribution of NDs in the homopolymer matrix enhances the material's resistance to flow, leading to higher viscosity. In contrast, the behavior in BCPNCs is different. In these systems, a substantial increase in viscosity is achieved only when both NDs and NRs are present. When NDs or NRs are added individually to BCPs, they have a very mild effect on viscosity. However, when both types of NPs are combined, their interaction within the block copolymer matrix significantly increases viscosity. This synergistic effect likely arises from the distinct interactions between the nanoparticles and the microphase-separated domains of the block copolymer. NRs provide a structural foundation for the copolymer chains, while the NDs disrupt the interface between microphase-separated domains, creating a more homogeneous distribution and enhancing the material's resistance to flow. Additionally, the non-Gaussian dynamics of NDs and NRs play a crucial role in this behavior. In BCPNCs, the combination of NDs and NRs results in a heterogeneous resistance to flow, characterized by coexisting slow and fast particles. This heterogeneity contributes to the significant increase in viscosity. In summary, the substantial increase in viscosity in mixed  $ND_1/NR$ -HPNCs and  $ND_1/NR$ -BCPNCs is due to the combined effects of higher nanoparticle concentration, the specific interactions between nanoparticles and polymer matrices, and the heterogeneous dynamics introduced by the presence of both NDs and NRs.

# V. CONCLUSIONS

In summary, we investigated the effects of incorporating NDs and/or NRs into PNCs with block BCP or HP matrices using CG-LD simulations. We focused on two types of homogeneous NDs with distinct interaction strengths with the polymer: stronger repulsion  $(ND_1)$ and weaker repulsion  $(ND_2)$ , as well as Janus NDs that exhibit both interaction types. Our findings reveal that the inclusion of NPs significantly impacts the PNCs' behavior, with variations driven by the nature of interactions at the polymer-NP interface (weak repulsion, strong repulsion or Janus) and the geometry of the nanoparticles (dimers or rods). Structural analysis demonstrated that  $ND_{k}$ -M interactions notably affect the organization of NPs within the polymer matrix. Specifically, Janus NDs  $(ND_J)$  in BCPs preferentially assemble at the interface between segregated polymer chain regions due to entropic and enthalpic forces. This can result in thermally stable and impermeable materials, with minimal impact on specific polymer properties such as the radius of gyration. Dynamical property analysis and diffusion coefficients indicated that ND<sub>2</sub> exhibits enhanced mobility, whereas ND<sub>J</sub> shows unique dynamics due to its dual nature. The self-part of the van Hove distributions revealed non-Gaussian dynamics and heterogeneity in particle movement, with some NPs moving significantly faster or slower than average. Our simulations also demonstrated that PNCs exhibit notable resistance to shearing, especially during the initial stages when the polymer chains are still organized in a disordered mesh. As shear is applied over a longer duration at a constant rate, the polymer chains gradually align with the shear direction, leading to the surpassing of a viscosity threshold. This stage became practically impossible to reach using the SLLOD algorithm, as no significant deviations from the melt were observed, emphasizing the importance of the Green-Kubo method for identifying differences in viscosity. In the zero-shear regime, the structural and geometrical peculiarities of NRs, as well as their higher heterogeneous dynamics, contribute to an increase in viscosity, especially in BCPs. Meanwhile, NDs alone can increase viscosity more noticeably in HPs, where they distribute uniformly as well. The significance of NDs' active functionality in BCPs becomes evident when combined with NRs, as the two NPs together cause a sixfold increase in viscosity compared to the melt alone. These insights underscore the importance of NP interactions, geometries and interplay in determining the performance of PNCs. Future research could explore the impact of NPs on other transport properties, such as thermal and electrical conductivity, to further understand the versatility and limitations of these materials.

#### SUPPLEMENTARY MATERIAL

The supplementary material includes detailed information on the PNC model, a discussion on the conditions leading to the formation of nanocrystals of NRs, additional radial distribution functions, the polymer's mean squared displacement and diffusion coefficients, the non-Gaussian parameter of nanoparticles and monomers, and further details on the calculation of the zero-shear viscosity. Additionally, we include a video of PNCs incoporating ND, NRs and a mixture of both species under shear.

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## AUTHORS DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

#### DATA AVAILABILITY STATEMENT

The software for generating the initial configurations of this study and for the analysis of the non-Gaussian parameter using GROMACS xtc files are openly available in Zenodo under an open-source Creative Commons Attribution license at https://doi.org/10.5281/zenodo. 14975093. Further data that support the findings of this study are available from the corresponding author upon reasonable request.

#### Appendix A: Rod rugosity

In our CG model, NRs are represented by aligning multiple beads in a straight line. Due to the overlapping nature of these beads, the resulting NR is not a perfect spherocylinder but has associated rugosity. To quantify this, we define the volume of the NR formed by the overlapping beads as  $V_{\rm NR}$  and the volume of an ideal spherocylinder as  $V_{\rm SC}$ . The rugosity is then given by:

$$\Delta V \equiv V_{\rm SC} - V_{\rm NR} \,. \tag{A1}$$

To calculate  $V_{\rm NR}$ , we consider that the intersections between two consecutive beads consist of two identical spherical caps sharing the same base. Let  $d_b$  be the distance between the centers of two adjacent beads, and  $N_b$ the total number of beads (with  $N_b - 1$  intersections). The volume occupied by these beads is:

$$V_{\rm NR}(r, d_b) = \frac{4\pi r^3}{3} + \left(\pi r^2 d_b - \frac{\pi d_b^3}{12}\right) (N_b - 1). \quad (A2)$$

Relating this to the volume of a spherocylinder with length L and two hemispheres at each end, we set  $L = d_b(N_b - 1)$ , leading to:

$$V_{\rm SC}(r, d_b) = \frac{4\pi r^3}{3} + \pi r^2 (N_b - 1) d_b \,. \tag{A3}$$

Combining these results, we find that the rugosity  $\Delta V$  is independent of the sphere radius r, but depends on L and  $N_b$ :

$$\Delta V(L, N_b) = \frac{\pi L^3}{12(N_b - 1)^2} \,. \tag{A4}$$

Since  $\Delta V$  does not have a minimum value, an optimal configuration based on radius, number of beads, or distance between centers cannot be determined. As expected,  $\Delta V$  approaches zero as  $N_b \rightarrow \infty$ . We can simplify the analysis by introducing the aspect ratio q:

$$q \equiv \frac{L+2r}{2r} = 1 + \frac{(N_b+1)d_b}{2r} \,. \tag{A5}$$

With this aspect ratio, the volume of the spherocylinder can be expressed as:

$$V_{\rm SC}(L,q) = \frac{4\pi}{3} \left(\frac{L/2}{q-1}\right)^3 + \pi L \left(\frac{L/2}{q-1}\right)^2.$$
 (A6)

To ensure that the excluded volume due to rugosity is a given percentage of the rod volume, we use:

$$N_b(\xi, q) \ge 1 + \frac{(q-1)^{3/2}}{\sqrt{\xi(3q-1)}},$$
 (A7)

where  $\xi$  is the desired percentage of rugosity relative to the rod volume. This relationship allows us to determine the minimum number of beads  $N_b$  based solely on the aspect ratio q and the rugosity parameter  $\xi$ .

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