Structure and dynamics of a polymer-nanoparticle composite: Effect of nanoparticle size and volume fraction

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(Dated: April 20, 2018)

We use molecular dynamics simulations to study a semidilute, unentangled polymer solution containing well dispersed, weakly attractive nanoparticles (NP) of size $\sigma_N$ smaller than the polymer radius of gyration $R_g$. We find that if $\sigma_N$ is larger than the monomer size the polymers swell, while smaller NPs cause chain contraction. The diffusion coefficient of polymer chains ($D_p$) and NPs ($D_N$) decreases if the volume fraction $\phi_N$ is increased. The decrease of $D_p$ can be well described in terms of a confinement parameter, while $D_N$ shows a more complex dependence on $\sigma_N$, which results from an interplay between energetic and entropic effects. When $\phi_N$ exceeds a $\sigma_N$-dependent value, the NPs are no longer well dispersed and $D_N$ and $D_p$ increase if $\phi_N$ is increased.

I. INTRODUCTION

Understanding the motion of nanoparticles (NP) and macromolecules in complex fluids, such as polymer solutions and melts, is a problem of broad importance, with applications to many different fields. In material science, understanding how NPs move in a polymer matrix is fundamental for the production of nanocomposites with mechanical, thermal, optical or electrical properties superior to those of pure polymeric materials [1–3]. In biophysics, the dynamics of macromolecules in the cytoplasmic environment can have a strong influence on cellular functions, such as enzymatic reactions and self-assembly of cellular structures [4–6]. Also in medicine there is a growing interest in the topic, with the objective to develop new and more efficient forms of NP-mediated drug delivery [7, 8], a practice which is already in use for cancer treatment [9, 10].

In the past years, a lot of attention has been dedicated to the study of the motion of polymers and NPs in polymer solutions and melts, using theoretical [11–15] and experimental [16–25] approaches, as well as computer simulations [26–31]. Polymer-NP mixtures represent a tough challenge for theoretical physics mainly because of the large number of different length scales present: the NP diameter $\sigma_N$, the monomer diameter $\sigma$, the Kuhn length $L_K$, the radius of gyration $R_g$, and, in the case of concentrated solution and melts, the mesh size $\xi$ and the diameter of the Edwards tube $a$ [32, 33]. The behavior of these systems strongly depends on the length and time scale at which they are probed, and in certain conditions it is possible to observe interesting dynamical phenomena, like anomalous diffusion [11, 24, 25, 34, 35] or the breakdown of the Stokes-Einstein relation [11, 16–18, 27, 28, 36, 37]. Also the interaction between the different components, which depend on the microscopic details, can have a great impact on the system's structure and dynamics [13, 29, 38–41]. Understanding how all these factors affect the static and dynamic properties of the NPs in polymer solutions and melts is thus crucial for practical applications.

When studying polymer-NP mixtures, two main regimes can be identified depending on the NP diameter $\sigma_N$: the “colloid limit”, where the polymers are much smaller than the NPs ($2R_g/\sigma_N \ll 1$) and the “protein limit” or “nanoparticle limit” [42], where the size of the polymers is larger or comparable to that of the NPs ($2R_g/\sigma_N \gtrsim 1$). The colloid limit has been studied extensively and it is nowadays well understood in terms of effective depletion pair potentials [43, 44]. The protein limit, on the other hand, is much more problematic, since an accurate description in terms of effective pair potentials is not possible [45, 46]. In the present work, we will focus on the protein limit, using molecular dynamics simulations of a coarse-grained model.

With few exceptions [27, 31], most of the previous simulation studies of polymer-NP mixtures have focused on the dilute NP regime, in which the NPs can be assumed not to interact with each other and the properties of the polymer solution are expected to be unchanged by the presence of the NPs. Thus, the purpose of the present work is to study the diffusion of polymers and NPs in an unentangled, semidilute polymer solution in a wide range of NP volume fractions and NP diameters, up to values where the interaction between NPs cannot be neglected.

The paper is organized as follows: In Section II, the model and the simulation method and details are presented. In Section III we discuss the structural properties of the polymer-NP solution for different NP sizes.
and volume fractions, with a special focus on the structure of single polymer chains. In Section IV, we study the dynamical properties of the system in the presence of good NP dispersion, and in particular the diffusion coefficient of the centers of mass of the chains and of the NPs. Finally, in Section V we investigate the behavior of the system at high NP volume fraction, where the NP dispersion becomes progressively poorer until large polymer-free regions are formed. We conclude with a summary in Section VI.

II. MODEL AND SIMULATION METHOD

We performed NVT molecular dynamics simulations of a system of \( N_p = 500 \) polymer chains of length (degree of polymerization) \( N = 100 \) and a variable number \( N_N \) of nanoparticles of different diameters \( \sigma_N \). To simulate the polymer chains, we used the bead-spring model of Kremer and Grest [47]. All monomers interact via a Weeks-Chandler-Andersen (WCA) potential [48],

\[
U_{mm}(r) = \begin{cases} 
4 \epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} & r \leq 2^{1/6} \sigma \\
0 & \text{otherwise.}
\end{cases}
\]

In addition, bonded monomers interact via a finite extensible nonlinear elastic (FENE) potential,

\[
U_{\text{bond}}(r) = -\frac{1}{2} k_0 \sigma_0^2 \ln[1 - (r/r_0)^2],
\]

where \( k_0 = 30 \epsilon / \sigma^2 \) and \( r_0 = 1.5 \sigma \). With this choice of parameters the bond length at the minimum of the potential is \( r_0 = 0.961 \). The combined effect of the FENE and the WCA potentials prevents the chains from crossing each other at the thermodynamic conditions considered here [47].

In the following, all quantities are given in Lennard-Jones (LJ) reduced units. The units of energy, length and mass are respectively \( \epsilon, \sigma \) and \( m \), where \( \epsilon, \sigma \) and \( m \) are defined by Eq. (1) and \( m \) is the mass of a monomer. The units of temperature, pressure, volume fraction and time are respectively \( [T] = \epsilon/k_B, [P] = \sigma^3, [\phi] = \sigma^{-3} \) and \( [t] = \sqrt{m \sigma^2 / \epsilon} \).

For the interaction potentials involving the NPs, we use an “expanded Lennard-Jones” (expanded LJ) potential, which is a LJ potential shifted to the right by a quantity \( \Delta_{ij} \); as opposed to the standard LJ potential, in the expanded LJ potential the interaction range and the “softness” (slope) of the potential does not change when the NP size varies, as one can see in Fig. 1. Since experiments have shown that the thickness of the interfacial region surrounding a NP in a polymer matrix changes only weakly with the size of the NP [49], the expanded LJ is a better choice than the standard LJ potential when simulating polymer-NP mixtures [26, 27, 50].

![Monomer-NP potential](image)

**FIG. 1.** Monomer-NP potential \( U_{Nm}(r) \) (expanded LJ) compared to a standard LJ potential \( U_{LJ}(r) = 4[\sigma_{Nm}/r]^{12} - (\sigma_{Nm}/r)^6 \), where \( \sigma_{Nm} = (\sigma_N + \sigma_m)/2 \). The expanded LJ potential is cut and shifted at \( 2.5 \sigma \). The LJ potential is cut and shifted at \( 2.5 \sigma \).

The interaction between monomers and NPs and between two NPs has thus the following general form:

\[
U_{ij}(r) = \begin{cases} 
4 \epsilon \left( \frac{\sigma}{r_{ij}^c} \right)^{12} - \left( \frac{\sigma}{r_{ij}^c} \right)^{6} + \delta_{ij} & r \leq r_{ij}^c + \Delta_{ij} \\
0 & \text{otherwise,}
\end{cases}
\]

where \( \Delta_{ij} = (\sigma_N + \sigma_m)/2 - \sigma = (\sigma_N - \sigma)/2 \) and \( \Delta_{ij} \). The quantity \( \delta_{ij} \) is such that \( U_{ij}(r_{ij}^c + \Delta_{ij}) = 0 \). The cutoff distances are \( r_{ij}^c = 2.5 \) for the NP-monomer interaction and \( r_{ij}^e = 2^{1/6} \) for the NP-NP interaction. The interaction between monomers and NPs is therefore attractive, while the interaction between NPs is purely repulsive. A moderate attractive interaction between polymers and NPs is required in order to contrast aggregation (and eventually phase separation) of the NPs [39–41, 51].

![LAMMPS software](image)

In this study, we consider NP diameters \( \sigma_N = 1, 2, 3, 4, 5, \) and \( 7 \sigma \). We assume that the NPs have the same mass density as the monomers, \( \rho_{\text{mass}} = 6m/\pi \sigma^3 \), and therefore the mass of the NPs is \( m_N = m(\sigma_N/\sigma)^3 \).

We define the NP volume fraction as \( \phi_N = \pi \sigma_N^3 N_N / 6V \), where \( V \) is the total volume of the simulation box; the monomer volume fraction \( \phi_m \) is defined in an analogous way. In our simulations, \( \phi_m \) is larger than the overlap volume fraction [32], which can be estimated from the polymer’s radius of gyration at infinite dilution (see below) and for the pure polymer system has the value \( \phi_m^c = 2.98 \cdot 10^{-2} \). Moreover, since the entanglement length \( N_e \) [32] for this model is \( N_e \approx 85 \) at \( \rho_m = 0.85 \) [52] and since \( N_e \) scales approximately as \( \rho_m^{-2} \) [53–55], we are always in the unentangled regime [56].

All the simulations were carried out using the LAMMPS software [57]. The simulation box is cubic.
and periodic boundary conditions are applied in all directions. The initial configurations are prepared by randomly placing the polymers and the NPs in the box; initially, the NPs have diameter equal to that of the monomers ($\sigma_N = \sigma$) and overlaps between particles are allowed. The overlaps are then removed by using a soft potential whose strength is increased over a short amount of time (“fast push-off” method [58]). After the overlaps are removed, the diameter of the NPs is gradually increased until the desired value is reached, and finally the system is allowed to adjust its density until we reach pressure $P = 0.1$ at temperature $T = 1.0$. In the pure polymer systems, these parameters correspond to a monomer volume fraction $\phi_m = 0.147$ (monomer density $\rho_m = 0.280$). Finally, we switch to the $NVT$ ensemble and perform an equilibration run before starting the production run. During the $NVT$ simulations, the pressure fluctuations are always less than 14%.

The length of both the equilibration and the production runs is, $10^8\delta t = 3 \cdot 10^5$, where $\delta t = 3 \cdot 10^{-5}$ is the MD time step. In all cases, we verified that during the equilibration runs the NPs (polymers) diffused on average over a distance equal to several times their diameter (radius of gyration), and that their motion became diffusive (see below).

Both during the $NPT$ and the $NVT$ runs, the temperature is kept fixed by means of a Langevin thermostat, so that the force experienced by a particle $i$ (monomer or NP) is

$$m_i \ddot{r}_i = -\nabla_i U(\{r_i\}) - m_i \Gamma_i \dot{r}_i + 2m_i \Gamma_i k_B T \zeta(t), \quad (4)$$

where $\mathbf{r}_i$ is the position vector, $m_i$ the mass and $U(\{r_i\})$ is the total interaction potential acting on the particle. The second term of the right side of Eq. (4) represents viscous damping, with $\Gamma_i$ the friction coefficient, and the last term is a random, uncorrelated force representing the collisions with solvent particles. The Langevin thermostat acts therefore as an *implicit solvent*, in which every particle interacts independently with the solvent “molecules”, but hydrodynamic interactions between solute particles are not accounted for. We note that it has been recently pointed out that hydrodynamic interactions may affect the long-time dynamics of NPs in a polymer solution even at high monomer volume fractions [59], an observation which warrants further investigation.

The damping constant for the monomers is $\Gamma_m = 0.1$, while that of the NPs is chosen by imposing that the viscosity of the pure solvent calculated via the Stokes formula, $\eta_s = \Gamma_i m_i / 3 \pi \sigma_i$, is the same for both free monomers and NPs. Therefore we have $\Gamma_N = \Gamma_m \sigma_N / m_N$. For a more detailed discussion, see Sec. SI in the S.I.

Additional details about the simulations can be found in Tab. S2 in the S.I.

![Fig. 2](image.png)

**FIG. 2.** Snapshots of systems containing NPs of diameter $\sigma_N = 4$ at different volume fractions (yellow spheres: monomers, blue spheres: NPs). In systems (a) and (b), the dispersion of NPs is good, while in (c) and (d) it is poor. In system (d) the formation of large polymer-free regions is evident. The length of the simulation box edges are respectively 57.45 (a), 59.15 (b), 67.13 (c), and 93.57 (d).

### III. STRUCTURE

#### A. Nanoparticles

To give a feeling of what the simulated system looks like, we show in Fig. 2 some snapshots $\sigma_N = 4$ and different values of the NP volume fraction $\phi_N$. We can see how the NP dispersion, which is initially good (Figs. 2a-b), becomes progressively poorer as $\phi_N$ is increased (Fig. 2c), until eventually large polymer-free regions are formed (Fig. 2d). In order to characterize the structure of the systems when $\sigma_N$ and $\phi_N$ are varied, we start by analyzing some basic quantities, such as the radial distribution function $g(r)$ and the structure factor $S(q)$.

The radial distribution function $g(r)$ can be obtained from the pair correlation function $g(r)$ by performing a spherical average [60]. We recall that the pair correlation function of a system of $M$ particles with number density $\rho$ is defined as [61]

$$\rho g(r) = \frac{1}{M} \sum_{k=1}^{M} \langle \delta(\mathbf{r} + \mathbf{r}_k - \mathbf{r}_j) \rangle, \quad (5)$$

where $\langle \cdot \rangle$ denotes the thermodynamic average.
Figure 3 shows the NP-NP radial distribution function $g_{NN}(r)$ for $\sigma_N = 2$ and 4 and different values of the NP volume fraction $\phi_N$. For low values of $\phi_N$, $g_{NN}$ shows a peak at $r_s = \sigma_N + (2^{1/6} - 1) = \sigma_N + 1.245$, which corresponds to twice the distance at the minimum of the monomer-NP potential. This indicates that the NPs are well dispersed in the polymer solution and configurations in which two neighboring NPs are separated by a polymer strand are favored (this kind of configuration is schematically represented in Fig. 3a). We call this peak secondary peak.

When $\phi_N$ increases, another peak appears at $r_c = \sigma_N + (2^{1/6} - 1) = \sigma_N + 0.122$, which corresponds to the cutoff of the NP-NP potential and represents a configuration in which two NPs are touching; we therefore call it contact peak. Eventually, the contact peak becomes higher than the secondary peak, an evidence of the formation of large polymer-free regions (Fig. 2d).

The structure factor is defined as [61]

$$S(q) = \frac{1}{M} \sum_{k,j=1}^{M} \langle \exp[-i\mathbf{q} \cdot (\mathbf{r}_k - \mathbf{r}_j)] \rangle, \quad (6)$$

where $\mathbf{q}$ is the wavevector. Since our configurations are isotropic, also in this case we will consider the spherically averaged structure factor $S(q)$ [60].

Because $S(q) - 1$ is the Fourier transform of $\rho g(r)$ [61], we can in principle find in the NP-NP structure factor $S_{NN}$ the same information that we find in $g_{NN}(r)$. If the position of the main peak of $g(r)$ is $r = r_0$, the main peak of $S(q)$ will usually be at $q_0 \approx 2\pi/r_0$, although the precise value of $q_0$ depends on temperature and density [62]. Hence, we expect to find the main peak of $S_{NN}(q)$ at $q \approx 2\pi/r_s$ at low NP volume fraction and at $q \approx 2\pi/r_c$ at high NP volume fraction, as we indeed observe in Figs. 4a-b. We also notice that, while in the $g(r)$ we can clearly distinguish two peaks at intermediate values of $\phi_N$ (Fig. 3), in the $S(q)$ their contributions interfere with each other and result in a single peak that is shifted towards higher wavevectors as $\phi_N$ is increased. Therefore, interpretation of $S_{NN}(q)$ might not always be straightforward.

In what follows, we will mainly consider those systems in which the NPs are well dispersed in the polymer so-
solution (Fig. 2a-b). As a qualitative criterion, we define a system with good NP dispersion as one where the secondary peak of $g_{NN}(r)$ is higher than or comparable to the contact peak. It should be noticed that the maximum volume fraction that we can reach while keeping a good NP dispersion depends on the NP diameter $σ_N$. To see this, we introduce a new quantity, the interparticle distance $h$, defined as $h = σ_N[(φ_N^N/φ_N)^{1/3} - 1]$ \cite{20}, where $φ_N^N$ is the maximum NP volume fraction; $h$ represents the average spacing between the surfaces of neighboring NPs \cite{20}. The definition is chosen in such a way that $h = 0$ for $φ_N = φ_N^N$. Making the assumption that the maximum NP volume fraction corresponds to a random close packing \cite{19–22}, we have $φ_N^N ≈ 0.637$ \cite{63} and consequently we define

$$h = σ_N[(0.637/φ_N)^{1/3} − 1].$$ (7)

In Fig. 5, we show the interparticle distance versus the NP volume fraction: filled (open) symbols represent systems with a good (bad) NP dispersion (according to the above defined criterion). As we can see, NP dispersion starts to become poor when $h ≈ 1$, i.e., when the average distance between the surface of neighboring NPs becomes comparable with the monomer size, in qualitative agreement with the snapshots shown in Fig. 2c-d.

**B. Polymers**

The radial distribution function of the monomers, $g_{mm}(r)$, is strongly dominated by the short-distance signals coming from the chain bonds (see Fig. S2 in S.I.), and therefore it is not easy to extract from it information about the medium and long range distribution of the monomers. Hence we focus our attention on the monomer–monomer structure factor, $S_{mm}(q)$, shown in Fig. 6.

Figure 6a, shows $S_{mm}(q)$ for $φ_N = 4$. At $φ_N = 0$ (pure polymer solution), there is a small peak at $q^* ≈ 1.4$ (inset of Fig. 6a), which in real space corresponds to a distance $r^* = 2π/q^* ≈ 4.5$. This peak reveals the presence of a typical length scale in the NP-free system, which can be interpreted as the average size of the holes in the polymer matrix \cite{64}. The main peak of $S_{mm}(q)$ is at $q_0 = 7.8 ≈ 2π/r_b$, where $r_b = 0.96$ is the average monomer–monomer bond length.

For $φ_N > 0$, the spatial arrangement of the NPs starts to be visible as a modulation in $S_{mm}(q)$, with a main peak appearing approximately at the same wavevector as the main peak of $S_{NN}(q)$, as we can see from Fig. 6b, where $S_{mm}(q)$ is compared to $S_{NN}(q)$. At even higher NP volume fraction, a signal starts to appear at $q = 0$, due to the fact that the polymers are getting far from each other (see Fig. 2d). If $φ_N$ was increased even more, eventually the monomer volume fraction would become smaller than the overlap volume fraction (dilute regime) and $S_{mm}(0)$ would saturate to $N$ \cite{32}.
Another important quantity to characterize the structure of the polymer mesh is the correlation length or mesh size $\xi$, which for the pure polymer solution ($\phi_N = 0$) can be estimated via scaling considerations [32, 33]:

$$\xi = \begin{cases} 
(R_g^* / \sqrt{3}) & \rho_m < \rho_m^* \\
(R_g^* / \sqrt{3}) (\rho_m / \rho_m^*)^{-\nu / (3\nu - 1)} & \rho_m > \rho_m^*. 
\end{cases} \quad (8)$$

where $R_g^*$ is the radius of gyration of an isolated chain, $\rho_m^*$ is the overlap monomer concentration and $\nu = 0.588$ is the Flory exponent [32] (the factor $1 / \sqrt{3}$ is justified by considering that when $\rho_m$ is not too high the mesh size can be extracted from the low-$q$ limit of the monomer-monomer structure factor, which is given by the Ornstein-Zernike relation $S_{mm}(q) = S_{mm}(0) / [1 + (\xi q)^2]$, and that at low monomer densities and low wavevectors $S_{mm}(q) \approx S_1(q) = N/[1 + (R_g^* q / \sqrt{3})^2]$, where $S_1(q)$ is the single chain monomer-monomer structure factor [32]. From the previous relations, it follows that for $\rho_m < \rho_m^*$ we have $\xi = R_g^* / \sqrt{3})$.

In this work, $R_g^* = 7.48$ and consequently, defining $\rho_m^* = N(4\pi R_g^3 / 3)^{-1}$ (other definitions are possible [33]), we get $\rho_m^* = 5.70 \cdot 10^{-2}$. Using these values we obtain from Eq. (8) $\xi = 1.27$ for the pure polymer solution ($\rho_m^* = 0.280$).

The structure of the individual polymer chains can be characterized by the function $p(r) = 4\pi r^2 g(r) / (N-1)$, where $g(r)$ is obtained by applying Eq. (5) to a single polymer chain (and, as usual, taking the spherical average). The quantity $p(r)dr$ represents the probability to find a monomer belonging to the same chain at distance between $r$ and $r + dr$ from a given monomer.

For a Gaussian chain, $p$ has the following expression [33]:

$$p_G(x) = \frac{8Nx}{\sqrt{\pi}(N-1)R_g} \left[ \frac{\sqrt{\pi}}{2} \left( 1 + 2x^2 \right) \text{erfc}(x) - xe^{-x^2} \right], \quad (9)$$

where $x = r / 2R_g$ and erfc$(x)$ is the complementary error function. This probability density peaks at $r \approx 0.74R_g$ [33].

In Fig. 7a, we show $p(r)$ for different values of $\sigma_N$ and $\phi_N$, along with $p_G$ for a Gaussian chain, Eq. (9), with $R_g = R_g(\phi_N = 0)$ (dashed line). We observe that, for small $\phi_N$, $p_G$ provides a good approximation of $p$ at intermediate and large $r$ (at small $r$, $p(r)$ is dominated by excluded volume interaction between nearest neighbors). For all values of $\phi_N$, $p(r)$ shows a very high peak at $r \approx r_b = 0.96$, corresponding to the first nearest neighbor, and a smaller peak at $r \approx 2r_b = 1.92$, corresponding to the second nearest neighbor. For values of $r$ larger than $2r_b$, this signal gets washed out, and ultimately $p(r)$ decays to zero. When $\phi_N$ increases, we observe two effects: The third nearest neighbor peak becomes more pronounced and the curve becomes broader.

This indicates that the presence of the NPs stretches the chains, causing them to become locally more ordered. We also note that $p(r)$ shows a modulation of wavelength $\approx \sigma_N + 1$, the first peak of which is clearly visible in Fig. 7a as a “bump” at $r \approx \sigma_N + 1$ (colored arrows). The presence of this modulation can be better appreciated by plotting the ratio $p(r)/p_0(r)$, where $p_0(r) = p(\phi_N = 0, r)$. In Fig. 7b, we report $p(r)/p_0(r)$ for $\sigma_N = 7$. As we can see, the effect of the NPs is to produce a “hole” in the range $0 \leq r \leq \sigma_N + 1$, but also to stretch the chain, increasing $p(r)$ significantly at larger distances. The modulation is clearly visible, with two bumps appearing at $r \approx \sigma_N + 1$ and $2(\sigma_N + 1)$ (small arrows).

Chain swelling in the presence of NPs has already been predicted theoretically [50] and observed in both simulations [51] and experiments [65–67]. In particular, Kara-
trantos et al. [51] have shown that polymer chains are unperturbed by the presence of repulsive NPs, while attractive NPs cause the polymer chains to be stretched and flattened when $2R_g > \sigma_N$ (which is always the case for the systems that we considered). Using the SC/PRISM theory, Frischknecht et al. [50] reached the same conclusions.

In order to quantify the expansion of the chains, we measure the radius of gyration $R_g$, defined as [32]

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\langle \mathbf{r}_i - \mathbf{R}_{CM} \rangle)^2,$$

(10)

where $\mathbf{R}_{CM}$ is the position of the center of mass of the polymer. In the pure polymer solution, we have $R_{g0} = R_g(\phi_N = 0) = 6.28 \pm 0.02$. In Fig. 8a we present the reduced radius of gyration $R_g/R_{g0}$ as a function of NP volume fraction for different values of $\sigma_N$. With the exception of $\sigma_N = 1$, there is a modest but clear increase of $R_g/R_{g0}$ with increasing NP volume fraction. We also notice that at fixed NP volume fraction the increase is stronger for smaller NPs, which suggests that chain expansion is mainly controlled by the NP excluded volume, which, at fixed $\phi_N$, is larger for smaller NPs [68].

Fig. 8a also shows that for $\sigma_N = 1$, $R_g$ decreases with increasing NP volume fraction. The reason is that NPs of this size have the largest surface-to-volume ratio, making the monomer-NP interaction (which scales approximately with the NP surface) very relevant. The consequence is that while in this range of $\phi_N$ the effect of the excluded volume is small, the effect of the interaction is large: Small NPs produce an effective attractive interaction between the monomers, which results in a decrease of $R_g$ and of the overall monomer volume fraction $\phi_m$ (we recall that all the simulations were performed at the same average pressure $P = 0.1$; see also Sec. V). We can therefore say that in this range of $\phi_N$, the NPs of size $\sigma_N = 1$ act like a poor solvent, promoting chain contraction.

In Fig. 8b we plot the reduced radius of gyration as a function of the interparticle distance $h$, Eq. (7). For $\sigma_N \geq 3$, the data fall on a master curve, confirming that in this range of NP size chain expansion is a geometrical effect, dominated by excluded volume: the NPs force the chains to less tortuous, therefore increasing their effective size. The fact that larger particles have a locally more “flat” surface that could enhance chain expansion does not seem to play a role in this size range, as we can conclude from the fact that data for different $\sigma_N$ fall on the same master curve. For $\sigma_N = 1$ and 2 the data do not fall on the master curve, for the reasons explained above (high surface-to-volume ratio promotes chain contraction). To provide a better resolution for small values of $h$, in the inset of Fig. 8b we plot $R_g/R_{g0}$ as a function of $1/h$ [50].

We can summarize our results by saying that NPs of size $\sigma_N \geq 2$ act like a good solvent, swelling the polymer chains, while NPs of size $\sigma_N = 1$ act like a poor solvent, causing them to contract. We note that this effect is expected to depend on the strength of the monomer-NP interaction: With stronger interactions, chain contraction could be observed also for $\sigma_N > 1$. Further study is needed in order to clarify this point.

**IV. DYNAMICS**

**A. Mean squared displacement**

To characterize the dynamics of the system, we study the mean squared displacement (MSD) of the NPs and of the centers of mass (CM) of the chains. We recall that the MSD of a system of $M$ particles is defined as [61]:

$$\langle r^2(t) \rangle = \frac{1}{M} \sum_i \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle.$$

(11)

In order to visualize more clearly the transition between the short-time ballistic regime, $\langle r^2(t) \rangle \propto t^2$, and the long time diffusive regime, $\langle r^2(t) \rangle \propto t$, we show in Fig. 9 the...
For an unentangled polymer mixture, they predicted that NPs of diameter $\sigma_N < \xi$, where $\xi$ is the mesh size, should always move diffusively, whereas the MSD of NPs of larger NPs, $\xi < \sigma_N < 2R_g$, should behave as follows:

$$
\langle r_N^2(t) \rangle \propto \begin{cases} 
  t & t < \tau_\xi \\
  t^{1/2} & \tau_\xi < t < \tau_{\sigma_N} \\
  t & \tau_{\sigma_N} < t,
\end{cases}
$$

(12)

where $\tau_\xi \propto \eta_0 \xi^3/k_B T$ and $\tau_{\sigma_N} \propto \tau_\xi (\sigma_N/\xi)^4$ are, respectively, the relaxation times of polymer segments of size $\xi$ and $\sigma_N$ (here $\eta_0$ is the viscosity of the pure solvent). For NPs larger than the polymers, $\sigma_N > 2R_g$, $\tau_{\sigma_N}$ must be replaced by $\tau_{R_g} \propto \tau_\xi (R_g/\xi)^4$. The crossover from subdiffusive to diffusive motion for NPs in polymer solutions has also been observed in experiments [24, 25].

Since at low NP volume fraction in our system $\xi \approx 1.3$, according to the scaling theory of Cai et al. one expects the MSD of the NPs of diameter $\sigma_N > 2$ to show subdiffusive behavior with exponent $\beta = 1/2$ at small $\phi_N$. However, no such behavior is observed for any value of $\sigma_N$. For small NPs, this may be due to the fact that the time window in which the subdiffusive behavior is expected to be present, i.e., $\tau_\xi < t < \tau_{\sigma_N}$, is too small, since $\tau_{\sigma_N} \propto \tau_\xi (\sigma_N/\xi)^4$. For larger NPs, this time window regime should be large enough to observe subdiffusion, and indeed for $\sigma_N = 7$ we observe a very weak subdiffusive transient, but the exponent $\beta$ close to 1. This is in agreement with previous simulations, which have also found that $\beta$ is not always equal to 1/2 in the subdiffusive regime appears, but rather gradually approaches this value as $\sigma_N$ is increased [69, 70].

In addition to the mean squared displacement, we have also studied the van Hove function [61] and the non-Gaussian parameter $\alpha_2(t)$ [71] of the NPs, finding that their dynamics is with a good approximation Gaussian, in agreement with experiments [24, 25] (see Sec. SIII in the S.I.). These results indicate that the relaxation dynamics of the NPs is not complex.

### B. Polymer diffusion

In order to make a more quantitative characterization of the dynamical properties of the polymers and the NPs, we now focus on the self diffusion coefficient $D$ (which for simplicity we will refer to as “diffusion coefficient”), which can be obtained from the MSD, Eq. (11), through Einstein’s relation [61]:

$$
D = \lim_{t \to \infty} \frac{\langle r^2(t) \rangle}{6t}.
$$

(13)

It is known that measurements of $D$ in systems with periodic boundary conditions suffer from finite-size effects because of long-ranged hydrodynamic interactions.
Although an analytical expression for the correction to \( D \) is available \([72, 73]\), it is not evident whether it can be applied to the motion of polymer chains and NPs in a concentrated polymer solution. For the NPs, such an expression is most likely not adequate when, as in our case, the NP size is smaller than the polymer size \([28]\). Therefore, for consistency we choose not to apply any finite size correction to the measured diffusion coefficients.

In the pure polymer system (\( \phi_N = 0 \)), the diffusion coefficient of the CM of the chains is \( D_{p0} = (1.14 \pm 0.02) \times 10^{-2} \). In Fig. 10a we plot the reduced diffusion coefficient of the polymer chains \( D_p/D_{p0} \) as a function of the NP volume fraction \( \phi_N \). We can observe that \( D_p/D_{p0} \) decreases with increasing NP volume fraction, with the decrease being stronger, at fixed \( \phi_N \), for smaller NPs. The data can be fitted to the empirical functional form \( D_p = D_{p0}[1 - (\phi_N/\phi_{N0})^{\alpha}] \), where \( \alpha \) increases with NP size (the values of \( \phi_{N0} \) and \( \alpha \) for the different NP diameters are reported in Tab. S1 in the S.I.) \([74]\). By using this relation, we can interpolate between the data points and plot \( D_p/D_{p0} \) as a function of the NP diameter \( \sigma_N \) for different volume fractions (Fig. 10b) and we observe that \( D_p/D_{p0} \) increases monotonically with \( \sigma_N \) at fixed \( \phi_N \).

There are two possible causes (or a combination of the two) that can lead to the slowing down of the chains with increasing NP volume fraction: the increase of the number of obstacles to polymer motion and the increase of polymer-NP interfacial area, which, since the interaction between polymers and NPs is attractive, can result in a reduced chain mobility. A predominance of the first effect would imply that the slowing down of the polymers is a mostly entropic effect, while if the second effect is the most important the dynamics of the polymers is mainly controlled by enthalpy.

Composto and coworkers \([19–22]\) observed a similar slowing down of chain motion in a series of experimental studies on polymer nanocomposites containing large NPs (\( \sigma_N \gtrsim 2R_g \)). They found that the reduced diffusion coefficient of the polymers fall on a master curve if plotted versus a “confinement parameter”, defined as \( h/2R_g \), where \( h \) is the interparticle distance, given by Eq. (7). Since the collapse of the data was independent of the strength of the polymer-NP interaction \([21]\), the authors concluded that the slowing down of the polymers is entropic in origin, caused by the reduction of chain entropy as the chain passes through bottlenecks formed by neighboring NPs (entropic barrier model) \([19]\). Karatrantos et al. \([31]\), who have observed an analogous reduction in polymer mobility due to NPs in molecular dynamics simulations of NPs in unentangled and weakly entangled melts, have attributed this phenomenon to the increase in the polymer-NP interfacial area. Desai et al. \([38]\) have reported that the polymer diffusion coefficient in a simulated lightly entangled melt (\( N = 80, \rho_m = 0.85 \)) containing repulsive/weakly attractive NPs initially increases with \( \phi_N \), reaches a maximum around \( \phi_N = 5\% \) and decreases for higher values. An enhancement of chain diffusivity at low \( \phi_N \) has also been observed in simulations by Kalathi et al. \([28]\), possibly because attractive monomer-NP interactions were considered in their work.

Following Composto and coworkers \([19–22]\), we plot in Fig. 11 the reduced diffusion coefficient of the chains as a function of the confinement parameter \( h/2R_g \). With the exception of \( \sigma_N = 1 \), all the data fall on the same master curve, which is well approximated by the empirical expression \( D_p = D_{p0}[1 - \exp(-ah/2R_g)] \), with \( a = 4.88 \) (continuous line in Fig. 11).

Our finding that \( D_p/D_{p0} \) is only a function of the confinement parameter is rather surprising, since Composto and coworkers mainly considered NPs of size comparable to that of the polymers or larger, which could be considered as basically immobile \([19–22]\), while in our case \( \sigma_N < 2R_g \) and the NPs diffuse faster than the chains in almost all the systems considered (see Fig. S6 in S.I.). We notice, however, that while in our case the diffusion coefficient of the pure polymer solution (\( D_{p0} = 1 \)) is recovered at \( h/2R_g \approx 1 \), in Refs. 19–22 it is recovered only at much higher values of the confinement parame-
The diffusion coefficient of a hard-sphere probe particle of diameter $\sigma_N$ in a continuum solvent with shear viscosity $\eta$ is given by the Stokes-Einstein equation [61]:

$$D_{N0} = \frac{k_B T}{f \pi \eta \sigma_N},$$

(14)

where $f$ is a number between 2 and 3 which depends on the choice of the hydrodynamic boundary conditions: $f = 2$ for pure slip and $f = 3$ for pure stick boundary conditions [75]. If the particle is not a perfect hard sphere, for example because its shape is not perfectly spherical

C. Single nanoparticle diffusion

FIG. 12. Single NP diffusion coefficient multiplied by the effective hydrodynamic diameter of the NP $\sigma_h$ as a function of $\sigma_h/2R_g$ (blue circles), compared with the results from Ref. 27 (red diamonds). Filled symbols: $\sigma_h = \sigma_N$. Open symbols: $\sigma_h = \sigma_N + 1$. Continuous lines: slope of $-2$. The dashed vertical line marks the value $\xi/2R_g$ for our system.
or because there is adsorption of solvent molecules on its surface, \( \sigma_N \) must be replaced with an effective hydrodynamic diameter \( \sigma_h \) [76, 77]. It is well-known that Eq. (14) is inadequate to describe the motion of particles smaller than the polymer size in a polymer solution/melt [11, 16–18, 24, 25, 27, 28, 36, 37], because the continuum assumption breaks down when the size of the probe particle becomes comparable to the characteristic length scale of the solvent.

Cai et al. [11] have predicted three regimes for the diffusion of a NP of diameter \( \sigma_N \) in an unentangled polymer mixture: For \( \sigma_N < \xi \), where \( \xi \) is the mesh size, the NP diffusion coefficient should follow the Stokes-Einstein law: \( D_{N0} \propto k_B T/\eta_0 \sigma_N \), with \( \eta_0 \) the viscosity of the pure solvent (small size regime). If \( \sigma_N > \xi \), the motion of the NPs becomes coupled to the segmental relaxation of the polymer mesh, so that \( D_{N0} \propto k_B T/\eta_0 \sigma_N^3 \) (intermediate size regime). The relation \( D_{N0} \propto \sigma_N^{-3} \) for intermediate size NPs was originally proposed by Wyart and de Gennes using scaling arguments [36], and was also predicted by Yamamoto and Schweizer using mode-coupling theory [13] and subsequently a self-consistent generalized Langevin equation approach [14]. This prediction has also been confirmed by simulations [27, 70].

For even larger diameters, the Stokes-Einstein law (14) is eventually recovered, but with the viscosity of the pure solvent replaced by the bulk viscosity of the solution \( \eta \): \( D_{N0} \propto k_B T/\eta \sigma_N \) (large size regime). For this second crossover size, different versions of mode-coupling theory predict different values depending on the level of approximation and on polymer density, all of them of the order of the polymer diameter: \( \sigma_N = 2R_g \) (unentangled solutions and melts) [12], \( \sigma_N = 3R_g \) (unentangled melts and unentangled concentrated solutions) [13] and \( \sigma_N = 2R_g^2 \) (semidilute solutions) [15], where \( R_g \) is the radius of gyration of an isolated chain. The prediction that the crossover to Stokes-Einstein behavior should occur when the NP diameter is of the order of \( 2R_g \) has also been confirmed by experiments [17, 18, 24].

To test the validity of the Stokes-Einstein formula, Liu et al. [27] have used simulations to measure the single particle diffusion coefficient of NPs in simulations of a dense, unentangled melt \( (N = 60, \rho_m = 0.84) \). The results of their simulations are shown in Fig. 12 (red diamonds). The authors argued that the effective hydrodynamic radius of the particle, \( R_h = \sigma_N/2 \), should have the value \( R_h = (\sigma_N + 1)/2 \), which corresponds to the contact distance between a NP and a monomer (the same argument can be found in Ref. 78). By fitting their data in the size range \( \sigma_N < 2R_g \) with a power law \( D_{N0} \propto R_h^{-\gamma} \), they found \( \gamma \approx 3 \) (open red diamonds in Fig. 12), and for diameters \( \sigma_N > 2R_g \) recovered the Stokes-Einstein relation. The results of Ref. 27 are therefore in agreement with the prediction that \( D_{N0} \propto \sigma_N^{-3} \) [11, 13, 36] if one replaces the NP diameter \( \sigma_N \) with the effective hydrodynamic diameter \( \sigma_h = \sigma_N + 1 \). However, when plotting \( D_{N0} \) as a function of \( \sigma_N \) instead of \( R_h \) and fitting with a power law \( D_{N0} \propto \sigma_N^{-\gamma} \), one obtains instead \( \gamma \approx 2 \) (filled red diamonds in Fig. 12). Hence one must conclude that the value of the exponent \( \gamma \) depends on the exact definition of the effective NP diameter, which makes the comparison of simulation data with theoretical predictions a delicate matter, especially when the size of the NP is of the same order of magnitude as the monomer size (for large NPs, \( \sigma_N + 1 \approx \sigma_N \)).

In order to test these predictions, we have performed additional simulations at low NP volume fraction \( (\phi_N < 0.015) \) for \( \sigma_N = 10, 12, \) and 14. In Fig. 12 we show \( D_{N0}\sigma_h \) as a function of \( \sigma_h/2R_g \), with \( \sigma_h \) alternatively defined as \( \sigma_N \) and \( \sigma_N + 1 \) (blue circles). Also included are the data from Ref. 27 (red diamonds). We can see that \( D_{N0} \) decreases continuously for \( \sigma_h < 2R_g \), whereas at \( \sigma_h \approx 2R_g \) Stokes-Einstein behavior, \( D_{N0}\sigma_h = \text{const.} \), is recovered. Taking \( \sigma_h = \sigma_N + 1 \) we find in the range \( 0.6 \lesssim \sigma_h/2R_g \lesssim 1 \) a slope of approximately \( -2 \), which agrees with the theoretical predictions. However, the range in which we observe this slope is rather small and hence we cannot claim that our data confirm the theory. In particular, if we use the scaling estimate of Eq. (8) for the mesh size, \( \xi \approx 1.27 \), we can see that there is no sign of the transition from \( D_{N0}\sigma_h = \text{const.} \) to \( D_{N0}\sigma_h \propto \sigma_h^2 \) at \( \sigma_h \approx \xi \) (which corresponds to \( \sigma_h/2R_g \approx 0.10 \)) predicted in Ref. 11. However, a caveat is in order: We have verified that, as also reported in previous studies [27, 37, 38], the diffusion coefficient of small NPs decreases when the NP mass increases at fixed volume, i.e., when the mass density is increased. The effect becomes progressively weaker as \( \sigma_N \) is increased, and at \( \sigma_N = 7 \) no mass density dependence is observed. Nevertheless, this effect should be taken into account when comparing the results of simulations to those of experiments or to theoretical predictions. For a detailed discussion, see Sec. AI in the Appendix.

**D. Nanoparticle diffusion**

In the previous section, we have dealt with the motion of a single NP in the polymer solution, i.e., we have considered the dilute NP limit: We will now discuss the dynamics of NPs at higher NP volume fraction \( \phi_N \).

Only few simulation studies have considered high NP volume fractions. Liu et al. [27] have observed a reduction of the NP diffusion coefficient with increasing \( \phi_N \), and attributed the phenomenon to polymer-mediated interactions, i.e., to the formation of chain bridges between neighboring NPs that would hinder NP motion; it is not clear, however, what the typical lifetime of such bridges should be, and thus whether this explanation is correct. Karatzas et al. [31] have observed a similar reduction in NP mobility and argued that it is due “to both nanoparticle-polymer surface area and nanoparticle volume fraction” [31], implying that pure geometry and polymer-NP attraction both play a role. The importance of polymer-NP interaction in NP dynamics is beyond dispute: Patti [29] showed that the diffusion coefficient
of NPs in an unentangled melt decreases monotonically when the strength of the polymer-NP interaction is increased, with the decrease being stronger for smaller NPs. A monotonic decrease of NP diffusivity with the strength of the polymer-NP interaction was also observed by Liu et al. [27]. We mention, however, that this trend can be reversed (NP diffusivity increasing with increasing interaction strength) in strongly entangled systems, where the dynamics of the NPs is dominated by density fluctuations on length scales of the order of the tube diameter [13].

In Fig. 13a, we show the reduced diffusion coefficient of the NPs, $D_N/D_{N0}$, where $D_{N0}$ is the diffusion coefficient of a single NP in the polymer solution, as a function of the NP volume fraction $\phi_N$; also shown are data for $\sigma_N = 3$ and $T = 0.7$. Similarly to the diffusion coefficient of the chains, $D_N$ decreases with increasing NP volume fraction. The first thing that one can notice is that the decrease of $D_N/D_{N0}$ with the NP volume fraction is rather quick: Already at the modest volume fraction of $\phi_N = 0.1$, the diffusion coefficient is reduced by $\approx 40\%$ for NPs of diameter $\sigma_N = 2$ and $3$, and by $\approx 30\%$ for NPs of diameter $\sigma_N \geq 3$ (Fig. 13a). The most interesting characteristic of $D_N/D_{N0}$ is however the dependence on $\sigma_N$ at fixed $\phi_N$. To better visualize this, we have interpolated between the points in Fig. 13a in order to obtain approximately the reduced NP diffusion coefficient as a function of the NP diameter $\sigma_N$ at constant $\phi_N$ (Fig. 13b). The ratio $D_N(\sigma_N)/D_{N0}$ shows an initial increase with increasing $\sigma_N$, then an inflection point at $\sigma_N \approx 2.5$, and finally it reaches a plateau for $\sigma_N \geq 4$. Such a peculiar behavior can be interpreted in the following manner: At $\sigma_N \approx 1$, increasing the NP diameter at fixed volume fraction has the effect of reducing the polymer-NP interface, and therefore decreasing the total interaction energy between polymers and NPs, resulting in an enhanced NP diffusion. When the NP size becomes larger than the mesh size $\xi \approx 1.3$ (the exact value depends on $\phi_m$), the motion of NPs starts to be geometrically hindered by the polymer segments [11, 36], and as a result the dependence of $D_N/D_{N0}$ on the NP size weakens. Then, when the NPs become large enough, since the surface-to-volume ratio becomes smaller, the importance of the energetic contribution to the diffusion coefficient starts to decrease, resulting in another increase in the diffusion coefficient. Finally, for large NPs energy becomes irrelevant and $D_N/D_{N0}$ is completely controlled by geometry, and therefore is constant at constant NP volume fraction.

![FIG. 13. Reduced NP diffusion coefficient as a function of the NP volume fraction $\phi_N$ (a) and of NP diameter $\sigma_N$ (b).](image)

V. HIGHER NANOPARTICLE VOLUME FRACTIONS

If we keep increasing the number of NPs $N_N$ while keeping pressure and number of polymers constant, the volume of the simulation box will eventually start to increase proportionally to $N_N$. As a consequence, the NP volume fraction $\phi_N$ will reach a plateau, $\phi_N = \phi_N^{\text{max}}(\sigma_N)$, which corresponds to the value of $\phi_N$ for a pure NP system at temperature $T = 1.0$ and pressure $P = 0.1$. This situation corresponds approximately to the one depicted...
in Fig. 2d. If a standard LJ potential was used for the NP-NP interaction, $\phi_N^{\text{max}}$ would not depend on $\sigma_N$, since the interaction potential would only depend on the ratio $\sigma_N/r$ and all systems would be equivalent apart from a trivial distance rescaling. However, the expanded LJ potential, Eq. (3), does not simply depend on $\sigma_N/r$; therefore, pure NPs systems with the same $T, P$ and $\sigma_N$ are not equivalent.

In Fig. 14, we show the reduced volume of the simulation box $V/V_0$, where $V_0 = V(\phi_N = 0)$, as a function of $N_N$, for different values of $\sigma_N$. For $\sigma_N \geq 3$, the volume increases monotonically with the NP number. For $\sigma_N = 1$ and 2, on the other hand, there is a range of $N_N$ values in which we observe a decrease in volume (see Sec. III B). In the inset of Fig. 14 we show the NP volume fraction $\phi_N$ as a function of $N_N$. Initially, the volume is almost constant and therefore as a good approximation $\phi_N = \pi \sigma_N^3 N_N / 6 V_0$. Then, for larger values of $N_N$, the volume starts to increase proportionally to $N_N$ and $\phi_N$ reaches the plateau $\phi_N = \phi_N^{\text{max}}$.

Since the number of polymer chains is constant, the increase of the volume at large $N_N$ results in a decrease of polymer volume fraction $\phi_m$, and therefore in a decrease of the polymer-NP interface per unit volume. This in turn causes a weakening of the polymer-mediated attractive interaction between NPs and consequently an increase of the free volume $V_{\text{free}} = V[1 - (\phi_N + \phi_m)]$. Both of these mechanisms result in an increase in the polymer and NP diffusivities. We can observe this effect in Fig. 15, where we show the normalized diffusion coefficient of both polymers and NPs for all the simulated systems, including those where good NP dispersion is not realized (open symbols): $D/D_0$ reaches a minimum corresponding to the value of $\phi_N$ at which the volume starts to increase, and it continues to grow as $\phi_N^{\text{max}}$ is approached. We note however that for $\sigma_N = 7$, $D/D_0$ shows a monotonic decrease. While in all the other cases we found that the pure NP system at $T = 1.0$ and $P = 0.1$ is a liquid, for $\sigma_N = 7$ it is a crystal, which means that as we approach $\phi_N^{\text{max}}$ the ratio $D/D_0$ will decrease and eventually reach a very small value.

VI. SUMMARY AND CONCLUSIONS

We have carried out molecular dynamics simulations of a mixture of polymers and spherical nanoparticles (NPs) in a wide range of NP volume fractions ($\phi_N$) and for different NP diameters ($\sigma_N = 1, 2, 3, 4, 5,$ and $7\sigma$, where $\sigma$ is the monomer size).

We have studied the structural properties of polymers and NPs, identifying the range of values of $\phi_N$ in which the NPs are well dispersed in the solution. In agreement with previous studies [50, 51, 65–67], we have found that the NPs of diameter $\sigma_N < 2R_g$ act like a good solvent, swelling the polymers. Surprisingly, however, we have also observed that NPs of the same size as that of the monomers, $\sigma_N = 1$, have the opposite effect, acting like a poor solvent. This is due to the high surface-to-volume ratio of small NPs, which causes the energetic contribution (which promotes chain contraction) to become stronger than the excluded volume contribution (which promotes chain expansion). Therefore, this effect is expected to depend on the strength of the monomer-NP interaction.

We have then analyzed the dynamical properties of the system, and in particular the diffusion coefficient of the NPs, $D_N$, and of the centers of mass of the polymer chains, $D_p$. We found that in the presence of good NP dispersion both $D_N$ and $D_p$ decrease monotonically with increasing NP volume fraction.

The reduction of $D_p$ in the presence of NPs can be well described, at fixed temperature, using the confinement parameter approach proposed by Composto and coworkers[19–22], which was originally developed for NPs of size larger or comparable to that of the polymers ($\sigma_N \gtrsim 2R_g$). The data for temperature $T = 1.0$ and $\sigma_N \gtrsim 2$ all fall on the same master curve when plotted as a function of a “confinement parameter”, which represents the average distance between the surfaces of neighboring NPs (interparticle distance $h$) divided by $2R_g$. Deviations from the master curve only appear at $\sigma_N = 1$. While the qualitative agreement between our data and those of Composto and coworkers is good, we observed quantitative differences, which can be explained by the fact that in our case, the NPs being smaller than the chains, it is not the whole chain, but rather segments of it that have to squeeze between the bottlenecks created by the NPs. Moreover, we note that data at a different temperature do not fall on the same master curve, indicating that interactions may play a relevant role, in contrast with the conclusions of Lin et al. [21].

The behavior of the reduced NP diffusion coefficient...
shows a complex dependence on $\sigma_N$, showing an initial increase followed by an inflection point around $\sigma_N = 2.5$ and finally a plateau for $\sigma_N \gtrsim 4$. We speculate that this behavior results from an interplay between energetic and entropic contributions, with the latter depending on the mesh size of the solution, $\xi$.

We have also studied the single NP diffusion coefficient, $D_{N0} = D_N(\phi_N \rightarrow 0)$, performing additional simulations with $\sigma_N = 10, 12, 14$ at low NP volume fraction. For $\sigma_N < 2R_g$ the diffusion is faster than what is predicted by the Stokes-Einstein formula, according to which $D_{N0} \propto \sigma_N^{-3}$. Stokes-Einstein behavior is recovered when $\sigma_N \approx 2R_g$, in agreement with previous studies [12, 17, 18, 24, 27]. Theoretical studies predicted that for $\sigma_N$ sufficiently smaller than $2R_g$ the NP diffusion coefficient should decrease as $D_{N0} \propto \sigma_N^{-3}$ [11, 13, 36]; Cai et al. [11], in particular, predicted that this behavior should be observed in the range $\xi < \sigma_N < 2R_g$. However, it is not clear whether our data confirm these predictions or not: The main obstacle to find a conclusive answer is that $D_N$ shows a dependence on the NPs’ mass density for $\sigma_N \lesssim 7$, a dependence which has been reported in previous studies [27, 37, 38]. This mass dependence becomes stronger with decreasing $\sigma_N$, making the interpretation of the data difficult. In light of this observation, we believe that care has to be taken when comparing the results of simulations to those of experiment and to theory, especially at low monomer volume fractions.

In conclusion, the behavior of a polymer-NP solution is very rich, and it is dictated by the value of many different parameters, most importantly the polymer-NP interaction and the NP size. In particular, since changing the polymer-NP interaction can lead to qualitatively very different behavior, we believe that systematic studies should be conducted in order to clarify the role of interactions. Comparison of simulation data with the available theories is complicated by many factors, such as subtleties in the definition of important quantities, e.g. the effective hydrodynamic radius and the mesh size, and the presence of broad cross-overs and inertial effects (mass dependence of the NP diffusivity). Other fundamental issues that remain to be fully clarified are the relevance of hydrodynamic interactions (recently investigated in Ref. 59) and finite-size effects. We can thus conclude that the investigation of polymer-NP composites will remain an important topic of research also in the future.

**APPENDIX**

**A1. MASS DEPENDENCE OF NP AND POLYMER DIFFUSIVITIES**

In previous studies of polymer nanocomposites [27, 38] and binary soft-sphere liquids [37] it has been shown that outside of the Stokes-Einstein regime not only the diameter, but also the mass density of a particle can affect its dynamics. In order to study this effect, we have run some simulations at low NP volume fraction and changed the NP mass while leaving the diameter fixed.

The results for the mean squared displacement (MSD) $\langle \mathbf{r}^2(t) \rangle$ of the particles are reported in Fig. 16 for the cases $\sigma_N = 2, \phi_N = 0.024$ and $\sigma_N = 7, \phi_N = 0.092$. At short times, the motion of the particle is ballistic and the mass dependence of the MSD is trivial:

$$\langle \mathbf{r}_N^2(t) \rangle = \langle v_N^2 \rangle t^2 = \frac{3k_BT}{m_N} t^2,$$

where $\langle v_N^2 \rangle$ is the mean squared speed of the NP. At longer times, when the motion becomes diffusive, i.e. $\langle \mathbf{r}^2(t) \rangle \propto t$, we can observe a much more interesting effect: While the motion of the larger NPs is unaffected by a change in the mass (Fig. 16b), the motion of smaller NPs presents a clear mass dependence (Fig. 16a).

This result can be better appreciated in Fig. 17a, where we show the NP diffusion coefficient $D_N$ as a function of the NP mass for different values of $\sigma_N$ and $\phi_N$ (here also the case $\sigma_N = 4, \phi = 0.054$ is shown). One recognizes that the mass dependence of the diffusion coefficient becomes weaker when the NP diameter is increased, and for $\sigma_N = 7$ it has disappeared almost completely. The result that the mass dependence of the long time diffusion co-

**FIG. 16.** (color online) Mean squared displacement of the NPs when varying the NP mass $m_N$ at fixed diameter $\sigma_N$, in the case $\sigma_N = 2, \phi_N = 0.024$ (a) and $\sigma_N = 7, \phi = 0.092$ (b).
The values of the NP volume fraction \( \phi \) when varying the NP mass \( m_N \).

FIG. 17. Diffusion coefficient of the NPs (a) and of the polymers (b) when varying the NP mass \( m_N \) at fixed diameter \( \sigma_N \). The values of the NP volume fraction \( \phi_N \) are 0.024, 0.054 and 0.092 respectively for \( \sigma_N = 2, 4 \) and 7. Open symbols: simulation without rescaling of the viscous friction coefficient \( \Gamma_N \). Dashed lines: slopes −0.25 (a) and −0.03 (b) for reference.

The diffusion coefficient of the polymer chains \( D_p \) is almost unaffected by changes in the NP mass density, as we can observe from Fig. 17b, although it is possible to see a very weak decrease of \( D_p \) for \( \sigma_N = 2 \). It is possible that the slowing down of the NPs has an effect on the dynamics of the polymers, but this effect is very weak at low NP concentrations. Further study should be dedicated to clarifying this point.

Finally, we have made some tests to determine whether the observed mass dependence is an artifact resulting from the scaling of the friction coefficient of the Langevin thermostat (see Sec. SI in the S.I.). To this aim, we ran some simulations where the friction coefficient of the NPs, \( \Gamma_N \), was kept constant and equal to that of the monomers: \( \Gamma_N = \Gamma_m = 0.1 \). The result is included in Fig. 17 (open blue circles). One sees that the effect of mass density is still present, but using \( \Gamma_N = 0.1 \) (fixed) has the effect of reducing the diffusion coefficient of the NPs, as one expects since this means that more massive NPs experience a higher solvent viscosity (we recall that \( \eta_s \propto \Gamma_N m_N / \sigma_N \)).

In conclusion, we have shown that the effect of mass density on the dynamical properties should be taken into careful consideration when performing molecular dynamics simulations of multi-component systems, such as polymer mixtures, binary fluids and solutions with explicit solvents. We think that the dependence of this effect on polymer and NP density and on polymer-NP interaction should be more thoroughly investigated in order to gain a better understanding of polymer-NP mixtures from the point of view of molecular dynamics simulations.

ACKNOWLEDGMENTS

We thank J. Oberdisse, L. Cipelletti, and K. Schweizer for fruitful discussions. This work has been supported by LabEx NUMEV (ANR-10-LABX-20) funded by the Investissements d’Avenir French Government program, managed by the French National Research Agency (ANR). Part of the simulations were performed at the Center of High Performance Computing MESO@LR in Montpellier. The snapshots in Fig. 2 have been realized with VMD [79].
SUPPLEMENTARY INFORMATION

SI. SCALING OF THE FRICTION COEFFICIENT OF THE THERMOSTAT

As discussed in the main text, we have used for our simulations a Langevin thermostat, so that the force experienced by particle \( i \) is

\[
m_\alpha \ddot{r}_{\alpha,i} = -\nabla_i U(\{r_{\alpha,i}\}) - m_\alpha \Gamma_\alpha \dot{r}_{\alpha,i} + \sqrt{2m_\alpha \Gamma_\alpha k_B T} \zeta(t),
\]

where \( \alpha \) denotes the particle type (\( m = \) monomer, \( N = \) NP). The mass and diameter of the monomers are respectively \( m_m = m \) and \( \sigma_m = \sigma \). The term \( \sqrt{2m_\alpha \Gamma_\alpha k_B T} \zeta(t) \) is a random force which represents collisions with solvent molecules, while \( \Gamma_\alpha \) is a viscous friction coefficient, which is related to the viscosity of the implicit solvent \( \eta_s \) by

\[
\Gamma_\alpha = \frac{C \eta_s \sigma_\alpha}{m_\alpha},
\]

where \( \sigma_\alpha \) is the diameter of the particle and \( C \) a coefficient which depends on the hydrodynamic boundary conditions.

In our simulations we made the assumption that every particle (monomer or NP) interacts with the implicit solvent as if it was a continuum with fixed \( \eta_s \). Therefore, from Eq. (S2) we get

\[
\eta_s = \frac{\Gamma_m m}{C \sigma} = \frac{\Gamma_N m_N}{C \sigma_N} = \text{const.} \Rightarrow \Gamma_N = \Gamma_m \cdot \frac{(\sigma_N m)}{(m_N \sigma)}.
\]

With this choice of the friction coefficient, the long-time diffusion coefficient of a particle in the pure (implicit) solvent \( D_{s,\alpha} \) follows the Stokes-Einstein law with viscosity \( \eta_s \):

\[
D_{s,\alpha} = \frac{k_B T}{\Gamma_\alpha m_\alpha} = \frac{k_B T}{C \eta_s \sigma_\alpha}.
\]

This way, \( D_{s,\alpha} \) depends only on the diameter of the particle, and not on its mass, as we can see from Fig. S1, where the mean-squared displacement (divided by time) of particles of various masses and diameters in the pure solvent is shown. We note that since \( \Gamma_m = 0.1 \) and \( m, \sigma = 1 \), the numerical value of the solvent viscosity is \( \eta_s = 0.1/3\pi = 1.06 \cdot 10^{-2} \).

SIII. MONOMER-MONOMER RADIAL DISTRIBUTION FUNCTION

In Figs. S2a-b, we report the monomer-monomer radial distribution function \( g_{mm}(r) \) for \( \sigma_N = 2 \) and 4. One sees that at low NP volume fraction the most prominent features of \( g_{mm}(r) \) are a sharp peak at \( r \approx r_b = 0.96 \) (first nearest neighbor distance in a chain) and a smaller one at \( r \approx 2r_b = 1.92 \) (second nearest neighbor). When the NP volume fraction is increased, the height of these two peaks increases. The reason is that, while the structure of the chain at the length scale \( r \lesssim 2r_b \) remains almost un_changed when \( \phi_N \) increases, the monomer density \( \rho_m \) decreases, because the volume increases and the number of monomers is fixed. Since \( g_{mm}(r) \) contains a factor \( \rho_m^{-1} \) (see Eq. (5) in the main text), this results in an increase of this function for \( r \lesssim 2r_b \). Incidentally, this is why the radial distribution function of a single polymer, used to derive the function \( p(r) \) (Eq. (9) in the main text) is a more sensible quantity when studying chain conformation.

Since \( g_{mm}(r) \) is dominated by the two peaks at \( r_b \) and \( 2r_b \) and shows only very small fluctuations around \( g_{mm}(r) = 1 \) at larger \( r \), we plot in Figs. S2c-d the function \( |g_{mm}(r) - 1| \), hence allowing to detect more easily the structure at large \( r \). For \( \sigma_N = 4 \), Fig. S2d, \( |g_{mm}(r) - 1| \) shows very clearly at intermediate and high \( \phi_N \) a long-range modulation with typical wavelength \( \sigma_N \), due to the presence of the NPs. Notice that, since we have taken the absolute value, the wavelength must be calculated as the distance between the \( n \)th peak and the \( (n + 2) \)th. For \( \sigma_N = 2 \), the presence of this modulation is less clear, because the size of the NPs is close to the monomer size and as a consequence the signal coming from the NPs cannot be distinguished well from the one coming from the monomers themselves.
FIG. S2 (color online) Monomer-monomer radial distribution function for $\sigma_N = 2$ (a) and $\sigma_N = 4$ (b) and different values of the NP volume fraction $\phi_N$.

SIII. VAN HOVE FUNCTION

The van Hove function $G(r,t)$ [61] can be written as the sum of a self and a distinct part: $G(r,t) = G_s(r,t) + G_d(r,t)$, where

$$G_s(r,t) = \frac{1}{M} \sum_{i=1}^{M} \langle \delta[r - r_i(t) + r_i(0)] \rangle$$  \hspace{0.5cm} (S5)

and

$$G_d(r,t) = \frac{1}{M} \sum_{\substack{i=1 \atop j \neq i}}^{M} \langle \delta[r - r_j(t) + r_i(0)] \rangle.$$  \hspace{0.5cm} (S6)

The self part of the van Hove function represents the time-dependent spatial autocorrelation of a particle, while the distinct part represents the time-dependent spatial pair correlation. As usual, we will consider the spherical average of these two quantities: $G_s(r,t)$ and $G_d(r,t)$. The function $4\pi r^2 G_s(r,t)$ represents the probability to find a particle at time $t$ a distance $r$ from its original position. We note that $G_s(r,0) = \delta(r)$ and $G_d(r,0) = \rho g(r)$, where $g(r)$ is the pair correlation function [61].

For both small and large values of $t$, the self part of the van Hove function is a Gaussian [61]:

$$G_s(r,t) = \Gamma_s(r,t) = \left( \frac{3}{2\pi \langle r^2(t) \rangle} \right)^{3/2} \exp \left( -\frac{3r^2}{2\langle r^2(t) \rangle} \right).$$  \hspace{0.5cm} (S7)

We can therefore define a rescaled self van Hove function which also preserves the probability with the following change of variables:

$$r \to r' = r \cdot \left( \frac{3}{2\langle r^2(t) \rangle} \right)^{1/2} \left( \frac{3}{2\langle r^2(t) \rangle} \right)^{-3/2}$$  \hspace{0.5cm} (S8)

$$G_s \to G'_s = G_s \cdot \left( \frac{3}{2\langle r^2(t) \rangle} \right)^{-3/2}$$

If $G_s$ is Gaussian, the result of the transformation (S8) is

$$\Gamma'_s(r') = \pi^{-3/2} e^{-r'^2},$$  \hspace{0.5cm} (S9)

i.e., the distribution is independent of time.

In Fig. S3a, we show the rescaled van Hove function for the case $\sigma_N = 1, \phi_N = 0.05$ (but for other parameters we
find the same qualitative behavior). In Fig. S3b, we report the ratio between the rescaled self van Hove function $G_s'(r,t)$ of the NPs and the same quantity in the Gaussian approximation $\Gamma_s'(r,t)$, for the same system. We observe that the shape of $G_s'(r,t)$ at short and long times is indeed very close to a Gaussian ($G_s'(r,t) = \Gamma_s'(r,t)$), and that the largest deviation from Gaussian behavior occurs when the dynamics of the NPs starts to be diffusive (in this case, at $t \approx 1$). These deviations are found to be most pronounced at large $r$, i.e., the NPs move a bit further than expected from a Gaussian approximation.

To better quantify how dissimilar $G_s(r,t)$ is from a Gaussian, it is customary to define a non-Gaussian parameter [71],

$$\alpha_2(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1,$$

(S10)

where

$$\langle r^n(t) \rangle = \frac{1}{M} \sum_i \langle |r_i(t) - r_i(0)|^n \rangle$$

(S11)

$$= 4\pi \int_0^\infty G_s(r,t) r^{2+n} dr.$$

If $G_s(r,t)$ is Gaussian, Eq. (S7), we have $\alpha_2 = 0$. Therefore, high values of $|\alpha_2|$ indicate a significant non-Gaussian behavior.

In Fig. S4, we show $\alpha_2(t)$ of the NPs for several values of the NP diameter $\sigma_N$ and of the NP volume fraction $\phi_N$. The largest departure from Gaussian behavior happens when the dynamics of the NPs starts to be diffusive, in agreement with what is observed from $G_s(r,t)$. Both at short and long times $\alpha_2 \approx 0$, as expected. We notice that the maximum deviation from Gaussian behavior (the maximum of the curves in Fig. S4) becomes larger when $\phi_N$ is increased. This trend shows that the structure of the surrounding polymer mesh and the presence of nearby NPs both contribute to the non-Gaussian behavior. Moreover, increasing the NP size at fixed $\phi_N$ generally reduces the magnitude of $\alpha_2$. This is reasonable, since a large NP interacts with a large number of monomers and other NPs and thus “feels” an averaged interaction, which results in a reduction of the dynamical fluctuations and therefore of $\alpha_2$. One exception to this trend is $\sigma_N = 7$ at high NP volume fraction (Fig. S4d). The reason for this is likely that the system is approaching crystallization. Apart from the case $\sigma_N = 7, \phi_N = 0.467$, we always have $|\alpha_2| < 0.2$, and we can therefore state that the dynamics of the NPs is, to a good approximation, Gaussian. The non-Gaussian parameter of the polymer chains (not shown) always satisfies $|\alpha_2| < 0.1$, therefore also the dynamics of the polymers is approximately Gaussian.

Finally, in Fig. S5 we show the distinct part of the van Hove function, $G_d(r,t)$, of the NPs for some selected systems. The relaxation happens in a way which is very similar to that observed in simple, non-supercooled liquids [71], in that we observe that in all cases the correlation hole at $r = 0$ is slowly filled as $t$ is increased. Since there is no evidence for the presence of a peak at $r = 0$, we conclude that hopping dynamics is absent in the studied systems [80].

**SIV. POLYMER DIFFUSION COEFFICIENT AS A FUNCTION OF NP VOLUME FRACTION**

In Sec. IV B of the main text we have seen how, in the regime of good NP dispersion, the decrease of the polymer diffusion coefficient $D_p$ relative to the diffusion coefficient in the pure polymer solution $D_{p0}$ can be empirically described by the function $D_p = D_{p0}[1-(\phi_N/\phi_{p0})^{-\eta}]$ (see Fig. 10a in the main text). In Table S1, we report...
the fit parameters for this empirical relation.

| $\sigma_N$ | $\phi_0$ | $\alpha$ |
|------------|----------|----------|
| 1          | 0.194    | 0.763    |
| 2          | 0.231    | 0.768    |
| 3          | 0.364    | 0.812    |
| 4          | 0.471    | 0.851    |
| 5          | 0.519    | 1.006    |
| 7          | 0.594    | 1.150    |

**SV. COMPARISON OF POLYMER AND NP DIFFUSIVITIES**

In Fig. S6a, we compare the diffusion coefficient of the NPs, $D_N$, and of the CM of the polymers, $D_p$. One sees that, in almost all the systems we considered, $D_N > D_p$, i.e. the NPs move faster than the polymer chains. An exception is $\sigma_N = 7$ at high densities; however, we know that at higher NP volume fraction the NPs form in this case a crystal and therefore $D_N$ becomes very small.

Figure S6b shows the NP diffusion coefficient $D_N$ as a function of the polymer center of mass diffusion coefficient $D_p$. One can observe that there is a strong correlation between $D_N$ and $D_p$, which can be empirically described via a power law: $D_N \propto D_p^\alpha$, where $\alpha$ increases with increasing NP diameter (inset of Fig. S6b). This correlation suggests that there is a coupling between the long time diffusivities of NPs and the centers of mass of the polymers, as it was recently proposed by Chen et al. [70].

**SVI. ADDITIONAL DETAILS ON THE SIMULATED SYSTEMS**

In Table S2 we report some additional details on the simulated systems. $N_N$: number of NPs; $\sigma_N$: NP diameter; $L$: side of the cubic simulation box; $\phi_{m}$: monomer volume fraction; $\phi_N$: NP volume fraction; $R_g$: average radius of gyration of the polymers; $h$: interparticle distance (Eq. (7) in the main text).
FIG. S5. (color online) Distinct part of the van Hove function, Eq. (S6), for some selected systems. The curves are equally spaced in logarithmic time ($t$). In (a) and (c), we have indicated some of the $t$ values associated to the curves. The minimum value of $t$ is for all the figures $t_{\text{min}} = \delta t = 0.003$ (integration time step), while the maximum value, $t_{\text{max}}$, is reported in the legend.

FIG. S6. (a) Ratio between the NP and polymer diffusion coefficients as a function of the NP volume fraction and for different values of the NP diameter $\sigma_N$. (b) NP diffusion coefficient $D_N$ versus the chain CM diffusion coefficient $D_p$. The correlation between $D_N$ and $D_p$ takes the form of a power law, $D_N \propto D_p^\alpha$, where $\alpha$ increases with the NP diameter. Inset: $\alpha$ as a function of the NP diameter.
TABLE S2. Details of the simulated systems. Systems in which there is poor NP dispersion (p.d.) are denoted by an asterisk in the last column.

| $N_N$ | $\sigma_N$ | $L$ | $\phi_N$ | $D_N$ | $D_p$ | $R_q$ | $h$ | p.d. |
|-------|-------------|-----|-----------|-------|-------|-------|-----|------|
| 0     |             | 56.32 | 0.1466  | 0.0000 | -     | 0.0114 | 6.282| -    |
| 30000 | 1           | 57.08 | 0.1408  | 0.0845 | 0.2793 | 0.0046 | 6.468| 0.961* |
| 15000 | 1           | 54.03 | 0.1660  | 0.0498 | 0.2824 | 0.0050 | 6.213| 1.338 |
| 7500  | 1           | 54.57 | 0.1611  | 0.0242 | 0.3477 | 0.0072 | 6.236| 1.975 |
| 3000  | 1           | 55.64 | 0.1520  | 0.0091 | 0.3949 | 0.0096 | 6.245| 3.118 |
| 1000  | 1           | 56.11 | 0.1482  | 0.0030 | 0.4221 | 0.0111 | 6.269| 4.988 |
| 300   | 1           | 56.28 | 0.1468  | 0.0009 | 0.4199 | 0.0114 | 6.253| 7.974 |
| 100   | 1           | 56.11 | 0.1482  | 0.0003 | 0.4380 | 0.0111 | 6.262| 11.903|
| 50    | 1           | 56.18 | 0.1476  | 0.0001 | 0.4400 | 0.0109 | 6.264| 15.278|
As a first approximation, if $\phi_N$ is low, the excluded volume can be estimated as $V_{ex} = \pi N N (\sigma_N + 1)^3 / 6 V = \phi_N (1 + \sigma_N^{-3} + 3 \sigma_N^{-2} + 3 \sigma_N^{-1})$.

This functional form would imply that $D_p$ becomes zero at $\phi_N = \phi_{N0}$, i.e., that the dynamics of the polymers is completely arrested. However, for larger values of $\phi_N$ the dependence of $D_p$ on $\phi_N$ changes (see Sec. V) and thus this dynamical transition is avoided.