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Using hydrodynamic simulations we examine the behavior of single polymers in a confined colloidal suspension under flow. We study the conformations of both, collapsed and non-collapsed polymers. Our results show that the presence of the colloids has a pronounced effect on the unfolding/refolding cycles of collapsed polymers, but does not have a large effect for non-collapsed polymers. Further inspection of the conformations reveals that the strong flow around the colloids and the direct physical compressions exerted on a globular polymer diffusing in between colloidal shear bands largely facilitates the initiation and unraveling of the globular chains. These results are important for rheological studies of (bio)polymer-(bio)colloid mixtures.

Understanding the dynamic behavior of dilute polymers in flow has been an active research area during the last decades because of its direct relevance to the rheological properties of polymer solutions [1], as well as to the emerging technologies of single-chain analysis of DNA molecules [2]. More recently, it has also been discovered that the dynamics of globular (or collapsed) polymers directly correlates with the functionality of certain proteins in the blood that are crucial during the blood clotting cascade [3]. Theories [4] and experiments [2, 5] have shown that polymers in good or Θ-solvent undergo periodic unfolding/refolding cycles when subjected to shear flow. This stretch-and-tumble behavior begins to occur at relatively small shear rates as long as the strain rate is faster than the characteristic chain relaxation time. Also, it is found that the mean extension of non-collapsed polymers varies smoothly with the shear rate [2, 4], and no well-defined deformation transition has been observed. On the other hand, polymers under bad solvent conditions (i.e. collapsed polymers) display in shear flow a well-defined globule-stretch transition at a critical shear rate that is about two orders of magnitude higher than the shear rate needed to unfold polymers in good or Θ-solvent [6, 7]. To understand this behavior, a nucleation based mechanism similar to that found in the pioneering work of de Gennes for non-collapsed polymers [4] has been proposed, and the scaling laws derived from this model appear to be in excellent agreement with simulations results under the same conditions [6, 8].

The properties of very dilute polymer solutions are important to understand the physical origin of the dynamics of polymers in flow, but most applications one does not have single polymers. Instead, one would typically have a dense solution and in many cases a mixture with colloidal particles. Thus, it is of interest to understand how the dynamics of the single chains is modified under these conditions. In this Letter we study such scenario by exploring how polymers behave in sheared colloidal suspensions. Our particular motivation comes from recent studies on the protein von Willebrand factor (vWF), which is one of the largest soluble biomacromolecules known [9]. vWF plays an important role in the initial

stages of the blood clotting process, and there is strong evidence that its function is directly related to the local hydrodynamic conditions [3, 10, 11]. Simulations which consider a globular chain in shear flow have captured the key dynamics of vWF in the absence of other cells [6, 8], but it is desirable to understand if platelets or red blood cells, which occupy ∼40% of the volume in blood, have an effect in the unraveling of vWF as well. To attack this problem we consider the simplest model that we believe captures the essential physics of the problem, namely a monodisperse colloidal suspension with a homopolymer undergoing shear flow, and simulate it using hydrodynamic simulations. The particular question we address here is how the unfolding/refolding cycles of the polymers in shear flow are affected by the presence of the colloids. Interestingly, we find that the stretching of non-collapsed polymers is not affected by the presence of colloids (at least up to 30% volume fraction), except at very high shear rates. However, when considering collapsed polymers we find that the colloids strongly affect the globule-stretch transition in a non-trivial fashion. Particularly, we find that the shear rate at which unfolding occurs is reduced by fivefold in some cases when colloids are present. The mechanism responsible for this enhancement in unfolding is colloidal compression of the polymers when crossing bands, which lowers the free energy necessary to create protrusions that the flow can pull out. This is corroborated by looking at different colloidal sizes and noting that there is a non-monotonic behavior on the stretching depending if shear bands are well developed or not. In order for the bands to form, the width of the channel has to be commensurate with the size of the colloids. There are two different arrangements in which one can closepack the plane perpendicular to the shearing walls: a hexagonal and a cubic packing. The colloids are said to be commensurate if the width of the channel is an integer multiple of the distance between two colloidal planes in either the hexagonal or cubic arrangement [12]. If this is the case, fully developed shear bands typically appear and the polymers are more stable while for non-commensurate cases colloids tend to cross more often between bands and the probability of compressing

a polymer is strongly enhanced. Finally, we must say that although our motivation comes from blood clotting, analogous systems are ubiquitous in our world and found in everyday items such as ink, milk, and paint. However, present research has mainly focused on the microstructures or the phase behavior of the colloids, and the internal degrees of freedom of the polymer chains have usually been ignored [13]. We believe that the dynamics of the polymer chains is as important as that of the colloids, especially in the driven systems.

Our model system consists of purely repulsive spheres (colloids) of size r_c with a no-slip boundary condition at the surface [14]. The colloid volume fraction, which is denoted by ϕ, is defined as the total volume occupied by the colloids divided by the volume of the simulation box. The polymer consists of $N = 50$ beads of radius a interacting through the intrinsic potential $U = U_s + U_{LJ}$. The first term accounts for the connectivity of the chain, $U_s = \frac{\kappa}{2} k_B T \Sigma_{i=1}^{N-1} (r_{i+1,i} - 2a)^2$, where $r_{i+1,i}$ is the distance between adjacent beads along the chain, and the spring constant is taken to be $\kappa = 800/a^2$ that ensures the average bond length is not bigger than 10% the equilibrium bond length for all the shear rates considered. The second term is a Lennard-Jones (LJ) potential $U_{LJ} = \tilde{\epsilon} k_B T \Sigma_{ij}[(2a/r_{i,j})^{12} - 2(2a/r_{i,j})^6]$, where $\tilde{\epsilon}$ determines the depth of the potential, and $r_{i,j}$ is the distance between the ith and the jth bead. In this work, we use a Θ-solvent for which $\tilde{\epsilon} = 0.41$ and a bad solvent with $\tilde{\epsilon} = 2.08$ that strongly collapses the chains [6]. Except for the intra-polymer interactions that were described above, every other interaction (i.e. polymer-colloid, colloid-colloid, polymer-wall, and colloid-wall) in the system is purely repulsive. To implement this repulsive force, we also use a stiff Hookean interaction that is only present if the distance between two particles is less than the sum of their radii [15]. The simulation box is bounded in the z-direction by no-slip walls separated by a distance $H = 33$, and periodic boundaries are used in the other two directions. The implicit fluid inside the simulation box is simulated on a three dimensional grid by the fluctuating lattice-Boltzmann (LB) equation [16], which accounts quantitatively for the dissipative and fluctuating hydrodynamic interactions. For simplicity, we set the grid spacing Δx and the LB time step Δt equal to unity. Other parameters for the fluid are the density $\rho = 1$, the kinematic viscosity $\nu = 1/6$, and the temperature $k_B T = 10^{-4}$. The polymer beads couple to the fluid in a dissipative manner [17]; in the LB units, the effective radius of the polymer beads is $a = 0.5$, and the characteristic monomer diffusion time is $\tau = 6\pi\eta a^3/k_B T \cong 4\times 10^3$, where η is the dynamic viscosity of the fluid that $\eta = \nu\rho$. A detailed descriptions of the simulation methods for the polymers and the colloids can be found in reference [18].

A representative snapshot of our simulation results is presented in Fig. 1(a), where we show a stretched chain (blue beads) in a sea of colloids (red spheres) undergoing
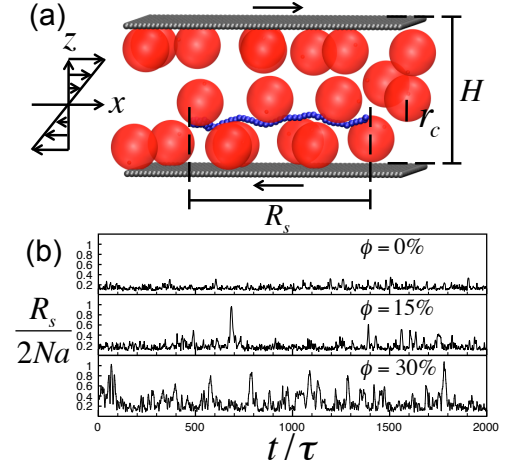

FIG. 1. (a) Snapshot of a single-chain (blue beads) with a cohesive energy $\tilde{\epsilon} = 2.08$ unfolding in a sheared colloidal suspension (red spheres) with $\phi = 15\%$ and $r_c = 5$. (b) Typical extension sequences as a function of time for a collapsed polymer at different colloid volume fractions $\phi = 0\%$, 15%, and 30%. The other parameters are $\dot{\gamma}\tau = 2$ and $r_c = 5$.
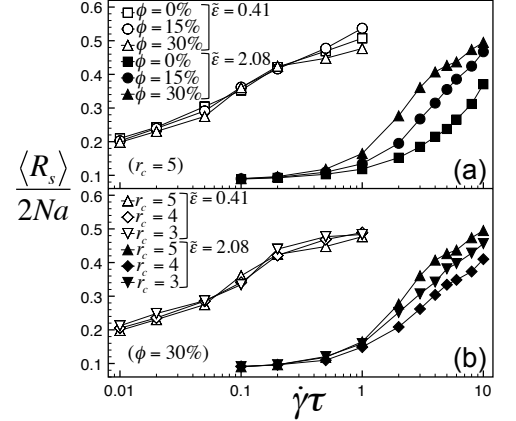

FIG. 2. Rescaled chain extension $\langle R_s \rangle/2Na$ for non-collapsed (open symbols) and collapsed polymers (filled symbols) as a function of the shear rate $\dot{\gamma}\tau$ for (a) different colloid volume fractions ($\phi = 0\%$, 15%, and 30%) with fixed radius $r_c = 5$, and (b) fixed volume fraction $\phi = 30\%$ with different radiuses: $r_c = 3$, 4, and 5.

shear flow. The polymer extension R_s is defined as the projected polymer length along the flow direction as illustrated. In Fig. 1(b) we present three time sequences of the extension of the collapsed polymers (with $\tilde{\epsilon} = 2.08$) at the same shear rate $\dot{\gamma}\tau = 2$ but with different colloid volume fractions. Clearly, the presence of the colloids has an important effect on the unfolding of the collapsed polymers since for $\phi = 0\%$ the chain remains collapsed, while at higher volume fractions the chain starts exhibiting pronounced and repeated elongation and folding events.

Interestingly, the enhancement observed for collapsed polymers is not seen in Θ-chains, as can be appreciated in Fig. 2(a), where we show the mean extension $\langle R_s \rangle$ for both the non-collapsed and collapsed polymers as a function of the dimensionless shear rate $\dot{\gamma}\tau$ for different ϕ's.
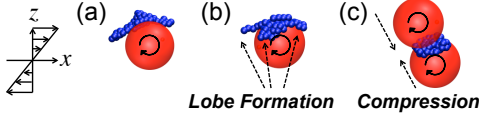
FIG. 3. Isolated snapshots of a collapsed polymer globule (blue) encountering one (a and b) or two (c) colloids (red) in flow ($\dot{\gamma}\tau = 2$ and $r_c = 5$). See text for details.

As can be seen in this plot, the effect of the colloids is minimal for non-collapsed chains and can only be visible at large shear rates (to be discussed in a future publication), while for collapsed polymers the unfolding is clearly enhanced and is correlated with the volume fraction. In spite of the fact that in confined channels the size of the colloids is important to determine the structure of the fluid, we have also used three different colloid sizes $r_c = 3$, 4, and 5, and fixed ϕ. As in the previous scenario, we do not find any differences in the average stretching of Θ-polymers. However, we observe that $\langle R_s \rangle$ has a non-monotonic dependence on r_c in the case of globular chains. When $r_c = 5$ we observe the strongest enhancement, while for $r_c = 4$ we observe the smallest enhancement with $r_c = 3$ being somewhat in the middle.

In order to understand the origin of the enhancement observed in collapsed polymers, we show isolated snapshots of a polymer globule encountering one or more colloids in Fig. 3. These snapshots elucidate how the colloids help to unravel the collapsed polymers. The reason is because one can clearly see that when a polymer collides with one (Fig. 3(a) and (b)) or two (Fig. 3(c)) colloids the chain becomes compressed due to the shear stress applied on the system, as well as the hydrodynamic conditions around the colloid. As the polymers become flattened or elongated on the surface of the colloids, chain protrusions have a higher probability of appearing because the free energy per protrusion in the quasi two dimensional pancake globule is much lower than in the spherical case. In some circumstances we even see star like shapes on the surface of colloids as shown in Fig. 3(b) where we note that we only have repulsive interactions between the polymers and the colloids, so this effect can only be ascribed to hydrodynamics. To make our argument more precise, we first consider the free energy F (in units of $k_B T$) in the strongly collapsed case necessary to pull out a filament of length l in 2D and 3D which is proportional to $F \sim l\Delta\tilde{\epsilon} = l(\tilde{\epsilon} - \tilde{\epsilon}_c^{(2D/3D)})$, where $\tilde{\epsilon}_c$ is the collapse transition point of the polymer chains [6, 8]. It is well known that $\tilde{\epsilon}_c^{(2D)} > \tilde{\epsilon}_c^{(3D)}$ because of the reduced number of contacts possible in 2D [19, 20]. Previous studies have predicted a nucleation type mechanism for the unfolding of collapsed polymer chains in flow that relies on these thermally excited protrusions [6, 8, 21]. The main idea behind this argument is that one needs a protruding polymer segment that is long enough so that the hydrodynamic drag force can pull the segment out and eventually unfold the whole chain. If the segment is too
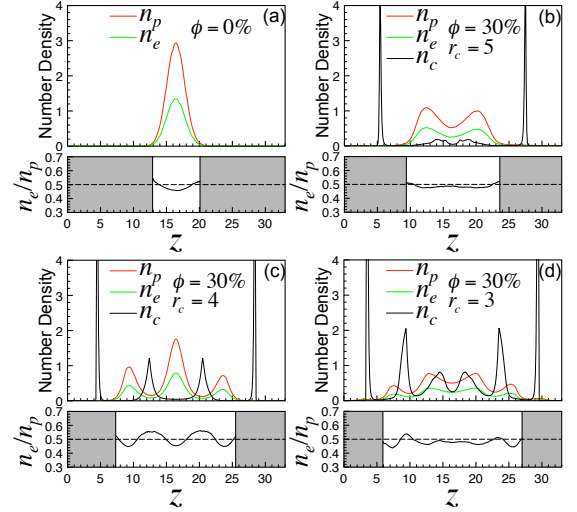

FIG. 4. Top panels: Number density of polymer beads n_p (red line), extended polymer beads n_e (green line), and colloids n_c (black line) as a function of the z position within the channels. The extended polymer beads are defined by the condition $dR_s(t)/dt > 0$. Bottom panels: Number density of the extended polymer beads divided by the total number density of the polymer beads. The different parts correspond to: (a) $\phi = 0\%$, (b) $\phi = 30\%$ ($r_c = 5$), (c) $\phi = 30\%$ ($r_c = 4$), and (d) $\phi = 30\%$ ($r_c = 3$). Other parameters are $\tilde{\epsilon} = 2.08$, $\dot{\gamma}\tau = 10$. Note: the data in the gray areas has been deleted because the density of polymer is negligible.

small, the drag force will not be able to overcome the cohesive energy $\sim \Delta\epsilon$. Thus, the presence of the colloids effectively enhances the probability for creating large protrusions due to the formation of these deformed pancakes, as explained above. On the other hand, the stretching of non-collapsed polymers occurs at lower shear rates and is characterized by a smoother deformation. Instantaneous perturbations by the colloids on the shape of the non-collapsed coils do not have any obvious effect on the average extension for the non-collapsed case.

The aforementioned mechanism of unfolding that corresponds to an effective local confinement effect in space and time is important to understand the origin of the enhanced unfolding rate, yet cannot account for the non-monotonic character on the size of the colloids. In this respect, one needs to analyze how the size affects the overall hydrodynamics. A particularly useful method is to look at the band structure formed by the colloids in response to the shear flow. Literature has shown that confined colloidal suspensions exhibit complex ordering transitions under shear, and the transitions highly depend on commensurability between the particle radius and density with the dimensions of the channel [12]. In Fig. 4 we show the number density of polymers (red line), and colloids (black line) as a function of the z position within the channels (see the figure legend for detailed simulation parameters). The green line corresponds to those polymers in the extended state and will be discussed later. The first observation is that for polymers without col-

loids, Fig. 4(a), the polymers accumulate in the center of the channel. This behavior is due to the hydrodynamic lift force exerted on the stretched conformations [22–24]. Secondly, it is observed that for $r_c = 5$ and $r_c = 3$ (Fig. 4(b) and (d)) only diffuse colloidal shear bands appear in the middle. In contrast, the band structure in the case of $r_c = 4$ seems to be fully developed (clear high peaks in Fig. 4(c)). More importantly, the distribution of the polymer beads is highly regulated by the colloidal bands, as can be seen more clearly for $r_c = 4$, where the polymer beads almost always reside between the bands of the colloids, seen as alternating peaks of black and red lines on Fig. 4(c). On the contrary, it is more probable for the polymers to reside within the diffuse bands for the $r_c = 3$ and $r_c = 5$ cases, which can be observed from the large overlaps of the black and the red lines in the middle of the channels in Fig. 4(b) and (d). The ratios of the number density of the extended polymer beads n_e (green line; see the figure legend for the definition) and the total number density of the polymer beads n_p (red line) are shown in the bottom panels of Fig. 4. This ratio (n_e/n_p) shows the relative probability for the polymers to be extending in the channel. As can be clearly seen in the bottom panel of Fig. 4(c), the unfolding of the polymers is largely enhanced within the colloidal bands, and is suppressed between the bands. Since the polymer beads are mostly in between bands when $r_c = 4$, but mix more within the middle bands in the $r_c = 3$ and $r_c = 5$ cases, the average extension is non-monotonic depending on the size of the colloids.

In summary, we have presented a detailed analysis of the dynamics of polymers in colloidal suspensions, putting particular attention on the effect that colloids have on the stretching transition observed in shear flows. We found that the stretching of Θ-polymers is not affected by the presence of colloids up to a volume fraction of 30%, while in the case of globular polymers we see a clear enhancement. The underlying mechanism responsible for this behavior was shown to be the compression that the chains undergo while colliding with the colloids, which effectively places the polymers in a quasi 2D state that promotes the nucleation of polymeric protrusions and eventually leads to unfolding events. The effect of the colloid size on the average polymer extension was found to be important for the globular case, and this was traced back to the appearance of bands that could range from a fully developed state to a diffuse state depending on the commenssurability of the colloidal density and size with the channel dimensions. If the bands are fully developed we find that this stabilizes the collapsed polymers, while in the case of the diffuse bands polymer-colloid interactions are more prevalent that in turn destabilize the globules. Returning to our original motivation which was vWF, we believe that the results found here could po-

tentially be important in understanding the unfolding of vWF in blood since, as shown, the presence of colloids such as platelets of red blood cells could in principle enhance the unfolding of vWF. Nevertheless, the dynamics of these cells is far more complex than that of the colloids presented here which could lead to other behaviors not capture in the present work. Further experiments in this area are needed to validate our predictions.

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