

Kinetics of isotropic to string-like phase switching in electrorheological fluids of nanocubes

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Applying an electric field to polarisable colloidal particles, whose permittivity differs from that of the dispersing medium, generates induced dipoles that promote the formation of string-like clusters and ultimately alter the fluid mechanical and rheological properties. Complex systems of this kind, whose electric-field-induced rheology can be manipulated between that of viscous and elastic materials, are referred to as electrorheological fluids. By dynamic Monte Carlo simulations, we investigate the dynamics of self-assembly of dielectric nanocubes upon application of an electric field. Switching the field on induces in-particle dipoles and, at sufficiently large field intensity, leads to string-like clusters of variable length across a spectrum of volume fractions. The kinetics of switching from the isotropic to the string-like state suggests the existence of two mechanisms, the first related to the nucleation of chains and the second to the competition between further merging and separation. We characterise the transient unsteady state by following the chain length distribution and analysing the probability of transition of nanocubes from one chain to another over time. Additionally, we employ passive microrheology to gain an insight into the effect of the electric field on the viscoelastic response of our model fluid. Not only do we observe that it becomes more viscoelastic in the presence of the field, but also that its viscoelasticity assumes an anisotropic signature, with both viscous and elastic moduli in planes perpendicular to the external field being larger than those along it.

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I. INTRODUCTION

In his 1949 seminal paper, Winslow demonstrated that the application of an electric field to high-dielectric-constant particles dispersed in low-viscosity oils induces their self-assembly in fibrous filaments, with dramatic changes in the rheological properties (*e.g.* shear modulus, viscosity, yield stress) of the suspension¹. These systems, generally referred to as electrorheological (ER) fluids, are a class of smart soft materials that can adapt their viscoelasticity in response to an electric field of a given intensity. Due to their relatively simple manufacturing, significant responsiveness to external stimuli and reversible recovery, ER fluids are especially suitable for industry-relevant applications, such as damping systems, microfluidics, tactile displays, where an abrupt change in material rheology is required^{2–4}.

As originally predicted by Clausius⁵ and Mossotti⁶, the application of an external electric field generates an induced dipole in non-conducting suspended particles when their dielectric constant differs from that of the dispersing medium. Under these circumstances, particles polarise and tend to align with each other and with the direction of the electric field⁷. The effect of external fields on suspensions of spherical particles has been extensively investigated by experiments^{8–12} and simulations^{13–18}. Thanks to recent advances in chemical¹⁹, physical²⁰ and biosynthetic²¹ techniques for the synthesis of anisotropic particles^{22–28}, which were key to discover new

phases either driven by simple excluded-volume effects^{29–39} or induced by external stimuli^{40–44}, electrorheology has been extended to more exotic colloidal suspensions^{45–47}. Polarisation has then been employed to explore the fabrication of an intriguing family of novel materials, termed colloidal polymers, where a field-induced alignment of particles in polymer-like chains of tunable flexibility is subsequently made permanent even when the field is switched off^{48,49}. Most of the work on colloidal polymers and, more generally, on ER fluids has so far explored suspensions of spherical particles, with very few exceptions. One of these exceptions is the very recent experimental work by Cai and co-workers who prepared colloidal polymers of micron-sized α -Fe₂O₃ cubes combining dipolar-directed assembly and in situ hydrolysis-condensation of tetraethylorthosilicate⁵⁰. Despite the widespread interest in ER fluids of colloidal spheres, particle shape definitely plays a crucial role in the kinetics of clustering as well as in the resulting rheology of the suspension, thus opening the path to novel materials with tunable properties.

We have recently developed a stochastic method to mimic the dynamics of Brownian particles *via* standard Markov Chain Monte Carlo (MC) simulations with specific settings on the particle elementary moves. This method, referred to as dynamic Monte Carlo (DMC), allows one to implement discontinuous interaction potentials and generate time trajectories in equilibrium or over transitory unsteady states^{51–57}. In this work, we apply a novel DMC technique to assess the response of a suspension of perfect hard dielectric nanocubes under the application of an electric field. At sufficiently low volume fraction and moderate field strength, colloidal hard nanocubes are expected to assemble into string-like clusters,

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as predicted by equilibrium MC simulations and observed experimentally⁵⁸. While the phase behaviour of these ER fluids has been well documented, very little attention has been given to the kinetics of such an isotropic to string-like phase switching and to its impact on the viscoelastic properties of the material. To bridge this gap, here we investigate the responsiveness of nanocubes to the application of an electric field and compute the time scales associated to the formation of these chains and their length distribution. Additionally, we apply passive microrheology (MR) to infer, from the computation of the mean square displacement of a free-diffusing tracer, the elastic and viscous moduli of this model ER fluid for both the field-off and field-on cases. While dilute suspensions only exhibit negligible changes in their viscoelastic response to an electric field, denser suspensions, where the presence of fibrous structures is more significant, show an evident increase of the viscous and elastic moduli and the occurrence of a strong space-dependent rheology.

II. COMPUTATIONAL METHODOLOGY

A. Model

We set the length of a cube edge σ , the reciprocal of the thermal energy $\beta \equiv 1/k_B T$, with k_B the Boltzmann constant and T the absolute temperature, and the solvent viscosity μ as system units. It follows that time has units $\tau \equiv \beta \mu \sigma^3$. Polarised cubes are modeled *via* hard core interactions, and the induced dipole-dipole interaction between their centers of mass is considered only in the presence of an electric field. We apply an algorithm based on the separating axis theorem to detect overlaps between two nanocubes⁵⁹. Hard core models neglect more complex phenomena of anisotropic interactions, observed in simulations and experiments of dielectric nanocubes with electric double layers, where the type of the solvent and the salt concentration proved to have a role in the preferential relative orientation as they get closer to each other⁶⁰.

We modelled the induced polarisation of the cubic particles using a point-dipole approximation, *i.e.* $\mathbf{p}_i = \alpha E_0 \hat{\mathbf{E}} = p \hat{\mathbf{E}}$, where p is the magnitude of the dipole moment, α the particle polarizability and $E_0 \hat{\mathbf{E}}$ the external field. The point dipole approximation has been proven to successfully mimic the phase behaviour of polarised cubes at different densities and strengths of the external electric fields. The Clausius-Mossotti relationship is used to express the particle polarizability:

$$\alpha = 3V_p \epsilon_o \epsilon_s \left(\frac{\epsilon_p - \epsilon_s}{\epsilon_p + 2\epsilon_s} \right) = \frac{3V_p \epsilon_s}{4\pi k} \left(\frac{a-1}{a+2} \right) \quad (1)$$

where $k \equiv 1/(4\pi\epsilon_0)$ is the Coulomb constant, set as unit in our simulations, $V_p = \sigma^3$ is the volume of one cubic particle, ϵ_0 is the vacuum permittivity and $a = \epsilon_p/\epsilon_s$ the ratio between permittivities of the particles and the solvent^{5,6,61}. The dipolar interaction between two dipoles is:

$$u_{ij,dip} = -\frac{k}{\epsilon_s} \frac{3(\mathbf{p}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{p}_j \cdot \hat{\mathbf{r}}_{ij}) - \mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}^3}, \quad (2)$$

TABLE I. List of units used in this work.

Quantity	Units
Length of cube edge	σ
Solvent viscosity	μ
Thermodynamic beta	$\beta \equiv 1/(k_B T)$
Time	$\tau \equiv \beta \mu \sigma^3$
Frequency	$1/\tau$
Translational diffusivity	σ^2/τ
Rotational diffusivity	rad^2/τ
Pressure	$1/(\beta \sigma^3)$
Coulomb constant	$k \equiv 1/(4\pi\epsilon_0)$
Magnitude of dipole moment	$\sqrt{\sigma^3/(\beta k)}$
Polarizability	σ^3/k
Intensity of external field	$\sqrt{k/(\beta \sigma^3)}$

where $r_{ij} \hat{\mathbf{r}}_{ij}$ is the distance vector between particles i and j . One can simplify Eq. 2 considering that $\mathbf{p}_i \cdot \mathbf{p}_j = p^2$ and $\mathbf{p}_i \cdot \hat{\mathbf{r}}_{ij} = \mathbf{p}_i \cdot \hat{\mathbf{r}}_{ij} = p^2 \cos(\theta_{ij})$, where $\cos(\theta_{ij}) = \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}_{ij}$. We can finally express Eq. 2 as a function of a dimensionless interaction parameter γ , as already defined in the work by Vutukuri *et al.*⁵⁸:

$$\beta u_{ij,dip}(r_{ij}, \theta_{ij}) = \frac{\gamma}{2} \left(\frac{\sigma}{r_{ij}} \right)^3 [1 - 3\cos^2(\theta_{ij})], \quad (3)$$

where

$$\gamma = \frac{2k\beta p^2}{\epsilon_s \sigma^3}. \quad (4)$$

Figure 1 shows a schematic representation of the model dipolar interaction described by Eq. 3, while Table I lists the units of the physical quantities used in this work.

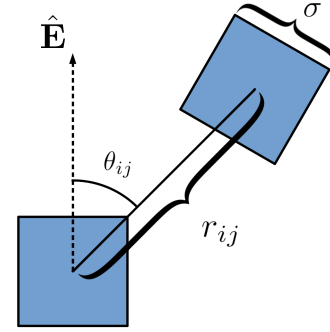


FIG. 1. Model of dipolar interactions between nanocubes. The interaction potential $u_{ij,dip}(r_{ij}, \theta_{ij})$ depends on the module of the vector \mathbf{r}_{ij} between the centers of mass of particle i and j , and θ_{ij} , *i.e.* the angle between \mathbf{r}_{ij} and the external field with orientation $\hat{\mathbf{E}}$.

Since simulations are performed in boxes with periodic boundaries, we employ the Ewald summation method for dipolar interactions to compute the long range contributions to the system's energy⁶². In all simulations with field on, γ is set equal to 13. At this field intensity, one can observe the

formation of isolated strings that do not percolate through the simulation box and do not cluster. For this value of the dipole-dipole interaction strength, Vutukuri *et al.*⁵⁸ determined that no phase transition has been observed within the packing fractions we investigated.

For simulations of passive microrheology, where a spherical probe is added to the suspension of nanocubes, the tracer is assumed to be unaffected by the presence of the external field, and only hard-core interactions between the tracer and the cubic particles are considered. For each trial move of the tracer, collisions between the sphere and the cubes are checked by using the OCSI algorithm⁶³.

B. Dynamic Monte Carlo simulations

We perform simulations in the NVT ensemble using the dynamic Monte Carlo (DMC) technique to investigate the Brownian motion of nanocubes. Each trial consists of one translation of the center of mass and one body-centered rotation of a randomly selected particle. Random moves are sampled uniformly over $[-\delta\xi_k : \delta\xi_k]$, where $\delta\xi_k$ are defined by the Einstein relation

$$\delta\xi_k^2 = 2D_{kk}\delta t_{MC}, \quad (5)$$

being D_{kk} the diagonal element of the diffusion tensor of the particle, and δt_{MC} the MC timescale of the particle. One time step in our simulations corresponds to 1 MC cycle (N attempts to displace particles). In out-of-equilibrium DMC simulations, the physical time is recovered using Eq. 6

$$t_{BD} = \delta t_{MC} \sum_{c=0}^{\mathcal{C}_{MC}} \frac{\mathcal{A}_c}{3}, \quad (6)$$

where \mathcal{A}_c indicates the average acceptance of trial moves in one MC cycle, and \mathcal{C}_{MC} the total number of MC cycles simulated⁵³. We note that if the system is at equilibrium, the acceptance rate is constant over the the entire simulation and Eq. 6 can be further simplified to

$$t_{BD} = \frac{\mathcal{A}}{3} \delta t_{MC} \mathcal{C}_{MC}, \quad (7)$$

Particles with different sizes and shapes exhibit different diffusivities and acceptance rates. Accordingly, since every particle holds its own MC timescale, they all have to be balanced with their respective acceptance rates to recover a unique timescale. In our microrheology simulations, $\delta t_{MC,sphere}$ and $\delta t_{MC,cube}$ are balanced using Eq. 8

$$\mathcal{A}_{sphere} \delta t_{MC,sphere} = \mathcal{A}_{cube} \delta t_{MC,cube}. \quad (8)$$

As in this case the systems are in equilibrium, \mathcal{A}_{sphere} and \mathcal{A}_{cube} will be constant over time. The validity of Eq. 8 is ensured before running the DMC simulations by fixing one timescale and recalculating the other one using the estimated acceptance rate in a preliminary trial-and-error simulation^{52,64}.

The dynamics and kinetics of string formation are investigated by performing simulations of a system of $N_{cube} = 1500$ nanocubes in cubic simulation boxes with periodic boundary conditions, at packing a fraction $\eta = 0.02$. We perform 30 independent simulations, setting $\delta t_{MC,cube} = 10^{-3} \tau$. The diffusion tensor of the cube is estimated using the software Hydro++⁶⁵, from which we obtain translational and rotational diffusivities, $D_{t,cube} = 8.35 \times 10^{-2} \sigma^2 \tau^{-1}$, and $D_{r,cube} = 1.48 \times 10^{-1} \text{rad}^2 \tau^{-1}$. We simulate 3 consecutive sequences where the external electric field is turned on and off. In a single sequence, starting from a perfect isotropic phase (field off), the external field is switched on for 2×10^6 time steps and then turned off for 3×10^5 time steps.

The study of microrheology is performed in suspensions of $N_{cube} = 1500$ cubes of side σ and 1 spherical tracer with diameter $d_{sphere} = 3\sigma$ at a packing fraction $\eta = 0.2$, at equilibrium states when the external field is on and off. The diffusivity of the tracer at infinite dilution is $D_{t,sphere} = (1/9\pi) \sigma^2 \tau^{-1}$, and attempted moves to displace it are sampled through trial translations in all the three spatial directions. We set the nanocubes time step to $\delta t_{MC,cube} = 5.0 \times 10^{-3} \tau$ and perform preliminary equilibration runs to recover $\delta t_{MC,sphere}$ according to Eq. 8. While in isotropic phases (field off) $\delta t_{MC,sphere,OFF} = 5.307 \times 10^{-3} \tau$, in string-like phases (field on) $\delta t_{MC,sphere,ON} = 3.516 \times 10^{-3} \tau$. We compute the rheological properties of the host phase from 1000 independent trajectories of the system.

C. Structural properties

The positional pair correlation functions are employed to investigate the structural properties of the suspension. Due to the system's anisotropy, we decompose the analysis in the direction parallel and perpendicular to the external field. We define $r_{ij} = \|\mathbf{r}_{ij}\|$, $r_{ij,\parallel} = |\mathbf{r}_{ij} \cdot \hat{\mathbf{E}}|$ and $r_{ij,\perp} = \|\mathbf{r}_{ij} - (\mathbf{r}_{ij} \cdot \hat{\mathbf{E}})\hat{\mathbf{E}}\|$ as the moduli of the relative distance between particles i and j for the total, parallel and perpendicular directions to the field, respectively. In isotropic phases, we compute the classical radial distribution function⁶⁶

$$g(r) = \frac{1}{Nv_r\rho} \sum_{i \neq j} \left\langle \delta(r - r_{ij}) \right\rangle, \quad (9)$$

where $v_r = 4\pi[(r + \Delta r)^3 - r^3]/3$ is the volume of a hollow sphere of radii r and $r + \Delta r$. By contrast, for the field-induced string-like phase, we compute the parallel and perpendicular pair correlation functions, defined as follows

$$g_{\parallel}(r) = \frac{\sum_{i \neq j} \left\langle H(R_{\parallel} - r_{ij,\perp}) \delta(r - r_{ij,\parallel}) \right\rangle}{Nv_{\parallel}\rho} \quad (10)$$

$$g_{\perp}(r) = \frac{\sum_{i \neq j} \left\langle H(h_{\perp} - r_{ij,\parallel}) \delta(r - r_{ij,\perp}) \right\rangle}{Nv_{\perp}\rho}, \quad (11)$$

where H is the Heaviside step function, $v_{\parallel} = \pi R_{\parallel}^2 \Delta r$ is the volume of a cylinder of radius R_{\parallel} and height Δr , and $v_{\perp} = \pi[(r + \Delta r)^2 - r^2]h_{\perp}$ is the volume of a cylindrical annulus of height h_{\perp} and thickness Δr ^{67,68}.

We assess the degree of orientational order with respect to the field by computing a specific uniaxial order parameter for each particle i , that takes into account the cubic symmetry of the particles

$$S_i = \frac{\pi \left(3 \max_k ((\hat{\mathbf{E}} \cdot \hat{\mathbf{e}}_{k,i})^2) - 1 \right) - 2\sqrt{3}}{2\pi - 2\sqrt{3}}, \quad (12)$$

where $\hat{\mathbf{e}}_{k,i}$ are the three axes of orientation of particle i , for $k = 1, 2, 3$. A detailed proof for the normalisation of the order parameter is reported in Section S2 of the Supplementary Information. Since, by definition, each S_i does not depend on the orientation of particles $j \neq i$, we could compute different order parameters depending on the set of particles considered for the average: the total order parameter is obtained by averaging over all the cubes in the system, *i.e.* $S^{(tot)} = \langle S_i \rangle_{\forall i}$; the average order parameter of cubes that belong to chains is $S^{(c)} = \langle S_i \rangle_{\forall i \in c}$, for c the set of cubes in clusters.

To investigate the formation of string-like structures we perform a cluster analysis on the simulated trajectories. Given that βu_{max} is our choice of the threshold energy for the cluster definition, two polarised cubes i and j are considered to form a cluster if $u_{ij,dip} \leq u_{max}$. The cluster analysis of the trajectories is performed following the algorithm described by Sevick and co-workers⁶⁹. To properly optimize the threshold parameter βu_{max} , we apply a density-based clustering algorithm to independent configurations of cubes in the string-like state. A detailed description of the method is reported in Section S1 of the Supplementary Information. From the cluster analysis, we estimate the number of clusters of size l at time t , $N(l, t)$. The molar fraction of strings of size l (free cubes are labeled as $l = 1$) reads

$$X(l, t) = \frac{N(l, t)}{N_{cube}}. \quad (13)$$

From the above expression we can recover the molar fraction of cubes that belong to strings as $X_c = \sum_{l=2}^{\infty} lX(l, t)$. Numerical and weighted average chain lengths read

$$\langle l \rangle_n(t) = \frac{\sum_{l=2}^{\infty} lN(l, t)}{\sum_{l=2}^{\infty} N(l, t)} \quad (14)$$

$$\langle l \rangle_w(t) = \frac{\sum_{l=2}^{\infty} l^2 N(l, t)}{\sum_{l=2}^{\infty} lN(l, t)}. \quad (15)$$

D. Microrheological properties

In passive microrheology, the viscoelastic properties of complex systems can be computed from the MSD of a tracer

particle embedded in the host phase^{70–74}. More specifically, according to Mason⁷², the complex shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$, where $G'(\omega)$ and $G''(\omega)$ are the elastic and viscous moduli, respectively, can be written as

$$|G^*(\omega)| = \frac{2\sigma^3}{\pi d_{sphere} \langle \Delta r_t^2(1/\omega) \rangle \Gamma[1 + \chi(\omega)] \beta \sigma^3}, \quad (16)$$

where $\chi(\omega) = d \ln(\Delta r_t^2(t)) / d \ln(t)|_{t=\omega^{-1}}$ indicates the local exponent of tracer's MSD, Γ is the gamma function and the modulus is in units of pressure, expressed as $1/(\beta \sigma^3)$. Consequently, the elastic and viscous moduli are computed as follows

$$G'(\omega) = |G^*(\omega)| \cos\left(\frac{\pi\chi(\omega)}{2}\right) \quad (17)$$

$$G''(\omega) = |G^*(\omega)| \sin\left(\frac{\pi\chi(\omega)}{2}\right). \quad (18)$$

While in a viscous system the motion of the particles is mainly diffusive ($\chi(\omega) \approx 1$) and $G''(\omega)$ is larger than $G'(\omega)$, in an elastic system the tracer motion is hindered by the local distribution of surrounding bath particles ($\chi(\omega) \ll 1$) and $G'(\omega)$ dominates over $G''(\omega)$. It should be pointed out that in addition to the Fourier approximation, other methods have been proposed to calculate the viscoelastic response of the bath from the tracer dynamics, including Laplace transform⁷⁰ and compliance-based^{73,74} methods among others. In Fig. 7 of the Supplementary Information, we compare the viscoelastic moduli calculated from the Fourier-based method (Eqs. 16–18) and the compliance approach proposed by Evans *et al.*⁷³ and show that they are in excellent quantitative agreement.

III. RESULTS AND DISCUSSION

In the following, we first discuss the effect of applying an electric field to a suspension of polarisable nanocubes and what structural changes it determines. Then, we analyse the nanocubes' dynamics in the transitory unsteady state to gain an insight into the mechanisms underpinning the process of formation of chains. Finally, we employ passive MR to infer the local viscoelastic behaviour of our model ER fluid and compare it to the case where no external stimuli are applied. As a reference system, we consider a suspension of hard nanocubes, whose packing fraction vs field intensity phase diagram has been calculated by MC simulations by Dijkstra and co-workers⁵⁸.

A. Effect of external field on system conformation

Figure 2 shows the time evolution of the molar fraction X_c of nanocubes in string-like clusters, and the uniaxial order parameter $S^{(tot)}$ averaged over all nanocubes, for three on/off field-switching cycles, at $\eta = 0.02$ and $\gamma = 13$. This order parameter is specifically proposed for particles with cubic symmetry (see Eq. 12). To identify the nanocubes belonging to

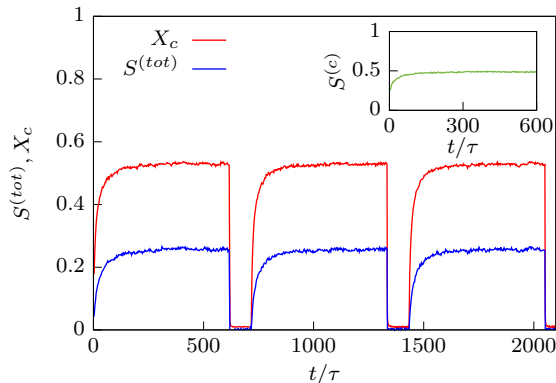


FIG. 2. Average molar fraction of nanocubes in chains (X_c) and uniaxial order parameter ($S^{(tot)}$) over three on/off switching cycles. The inset depicts the average uniaxial order parameter that only considers the nanocubes in chains ($S^{(c)}$), for the first on/off cycle (from $t = 0$ to 600τ). The packing fraction and field strength are $\eta = 0.02$ and $\gamma = 13$, respectively.

the same cluster, we define an energy-based cluster criterion whose optimal parameterisation was achieved *via* a density-based cluster analysis (see Methods and Section S1 of Supplementary Information). When the external field is switched on, X_c increases up to ~ 0.50 , indicating that nearly half of the nanocubes are assembled in strings. The clustering is completed at a response time $t_r \approx 150\tau$. We notice that, when the field is off, nanocubes displace an average distance approximately equal to 9σ over the same period of time. This suggests that, in terms of the nanocubes' ability to diffuse in an isotropic phase, the response time t_r is relatively long.

Figure 3 shows a typical snapshot of the system in the string-like state, with the strings of nanocubes oriented along $\hat{\mathbf{E}}$. Most string-like clusters comprise between 2 and 4 nanocubes, while longer chains are less likely to be observed. Our simulation results also reveal the presence of isolated nanocubes (reduced in size for clarity in Figure 3) that are free to assume random orientations with respect to the field direction, in agreement with former experiments and simulations⁵⁸. In Figure 2, we compare the total uniaxial order parameter $S^{(tot)}$ with the same parameter averaged exclusively over particles that belong to strings $S^{(c)}$ (see inset). In particular, $S^{(c)} = \langle S_i \rangle_{i \in c}$ is defined as the average contribution of particles in chains to $S^{(tot)}$, while $S^{(free)} = \langle S_i \rangle_{i \in free}$ is the contribution of free nanocubes. According to Figure 2, during the switching on, the nanocubes in chains ($X_c \sim 50\%$) lead to $S^{(c)} \sim 0.50$ whereas $S^{(tot)} \sim 0.25$. Thereby, the contribution of free particles ($S^{(free)}$) to $S^{(tot)}$ is negligible since $S^{(tot)} \approx (S^{(c)} + S^{(free)})/2 \approx S^{(c)}/2$. One should notice that the dipolar interaction only depends on the distance between nanocubes and not on their space orientation. However, this interaction becomes very attractive when the nanocubes are face-to-face piled, minimizing their mutual distance and thus forming strings aligned with \mathbf{E} as shown in Figure 3.

When the field is switched off the system relaxes nearly instantaneously from the string-like state. At equilibrium, the isotropic configurations where both $X_c \approx 0$ and $S_c \approx 0$ are fully

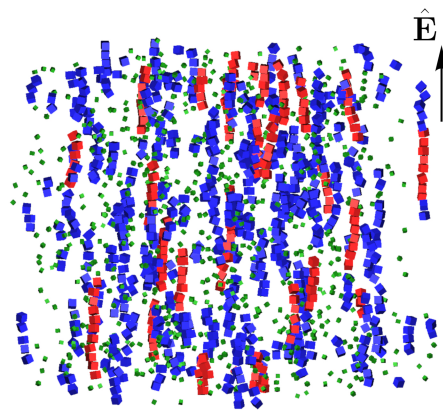


FIG. 3. Suspensions of $N_{cube} = 1500$ nanocubes upon the application of an external electric field. The orientation of the field $\hat{\mathbf{E}}$ is shown with a black arrow on the top right of the Figure. Blue chains contain less than 6 nanocubes, while red chains contain at least 6 of them. Isolated nanocubes are shown in green and reduced in size for clarity. Packing fraction and field strength are $\eta = 0.02$ and $\gamma = 13$, respectively.

recovered. Their sudden decay is due to the approximations in our model, where the particle polarisation is assumed to be exclusively triggered by the external field. It is worth noting that a more general definition of particle polarisation should involve the contributions of both the external field and the particle-particle polarisation i.e. $\mathbf{p}_i = \alpha(\mathbf{E} + \sum_{i \neq j} \mathbf{E}_j)$. Nevertheless, the approximation $\mathbf{p} = \alpha\mathbf{E}$ is often found in simulations of ER fluids^{12,14,15,75}. Incorporating both local and external fields into the particles' dynamics would require either the inversion of a $3N \times 3N$ matrix or the use of iterative procedures⁷⁶⁻⁷⁸, resulting in very demanding calculations. However, we notice that, for moderate electric fields, simulations of dilute ER fluids of spheres reveal that the particle-particle polarisation may contribute up to 5% of the total dipole moment, and no tangible effects on dynamics are reported¹⁸.

One may suggest that point-dipole approximations play a role in determining the dynamics of cubes when an electric field is applied. Vutukuri *et al.* estimated the energy differences for pairs of aligned and misaligned cubes at face-to-face contact, being discretized in smaller cubes each containing one point dipole⁵⁸. These authors found that energy differences level off to a limiting value of $0.01\gamma k_B T$ and, when comparing simulation results on single point-dipole cubes to those on multiple point-dipole cubes, they did not observe any notable difference in cubes alignment for field intensities below $\gamma = 30$. Moreover, Kwaadgras *et al.* applied the Couple Dipole Method to estimate the exact self-consistent dipolar interaction between two axis-aligned cubes polarised by an external field, as a function of their relative position in space, and compared it to the two aforementioned models⁷⁹. Both single and multiple point-dipole approximations showed similar discrepancies with respect to the exact model of interaction, underestimating attractions and overestimating repulsion. In conclusion, according to the findings reported in

these works, the point-dipole approximation used here is not expected to be determinant in the formation of chains, at least for the field strength investigated in this work. Nonetheless, a more detailed description of the potential may highlight intriguing anisotropic phenomena occurring in the dynamics of cubes, especially at short distances, that cannot be observed when modelling the polarisation as a point-dipole.

B. Structural properties at equilibrium

The structural organisation of nanocubes in suspension is inferred from the pair correlation functions parallel ($g_{\parallel}(r)$, see Eq. 10) and perpendicular ($g_{\perp}(r)$, see Eq. 11) to the electric field. In Figure 4, we present $g_{\parallel}(r)$ and $g_{\perp}(r)$. For comparison, we also include the radial distribution function, $g(r)$, of the nanocubes in the isotropic phase, that is when the electric field is off. The peaks observed in $g_{\parallel}(r)$ indicate a strong or-

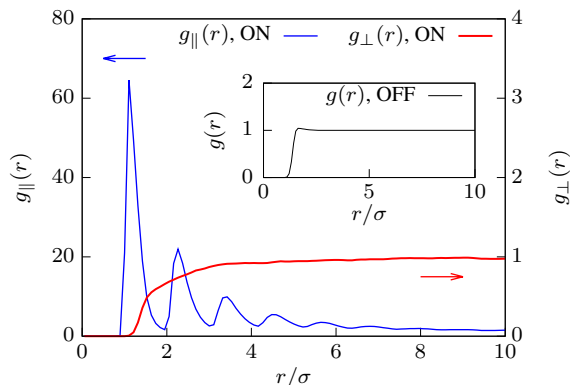


FIG. 4. Pair correlation functions of nanocubes in the presence of an external field, in the direction parallel (blue line) and perpendicular (red line) to the field. For comparison, the radial distribution function when the field is off is also shown in the inset.

dering of particles at short distances, arising from the piling of nanocubes on top of each other and the subsequent formation of string-like structures oriented along $\hat{\mathbf{E}}$. This order vanishes for $r > 6\sigma$, suggesting that the occurrence of strings comprising more than 6 nanocubes is very unlikely. Moreover, we confirm that the string-like clusters do not percolate through the box boundaries, as $g_{\parallel}(r)$ decays at distances $r < l_{box}/2$, with $l_{box} \sim 42.2\sigma$ the box length. By contrast, no structural order is observed in the perpendicular direction. Since $g_{\perp}(r) < 1$ at short distances, the chains are usually separated from each other and from isolated nanocubes by a long distance. Consequently, at $\eta = 0.02$ and $\gamma = 13$ the suspension is characterised by strong density heterogeneities that are not found in the isotropic phase, as illustrated by $g(r)$ in the inset of Figure 4.

C. Dynamics of chain formation in transitory state

In this section, we study the kinetics of string formation. To this end, we estimate the 2-particle connectivity with the

aid of an energy threshold parameter, $\beta u_{max} = -3.2$. More specifically, two nanocubes i and j are considered to be connected if $\beta u_{ij,dip} < \beta u_{max}$. The cluster parameter βu_{max} has been calculated by applying a density-based cluster analysis (DBSCAN)^{80,81} on equilibrated configurations of strings of nanocubes. Details of these calculations are given in Section S1 of Supplementary Information.

Figure 5 reports the results obtained from the cluster analysis in suspensions of nanocubes at $\eta = 0.02$ starting from an isotropic phase (field off) and ending into a phase of string-like clusters (field on). Numerical (Eq. 14) and weighted (Eq. 15) averaged chain lengths are reported in Figure 5(a). Similarly, Figure 5(b) presents the time dependence of the molar fraction of chains whose length ranges between $l = 2$ and $l = 7$. At short times ($t/\tau < 1$), strings of sizes 2 and 3 are more likely to form. While the concentration of these short strings displays a local maximum at intermediate times ($10 < t/\tau < 50$), that of longer strings, with $l \geq 4$, is smoothly increasing until a plateau at times $t > t_r$ is achieved. Interestingly, although the molar fraction, X_c , of cubes in chains reaches a steady value at $t_r \sim 150\tau$, numerical ($\langle l \rangle_n$) and weighted ($\langle l \rangle_w$) lengths are still relaxing at this time. This suggests that strings of different sizes are continuously breaking and merging while reaching the equilibrium distribution regardless the fact that the percentage of nanocubes in chains remains basically constant for $t > t_r$ (see Figure 2).

Figure 5(c) contains the resulting equilibrium distribution of molar fractions $X_{eq}(t)$ for the different sizes of the string-like clusters. Our simulation results (red circles) are compared to a fitting model (black line) that assumes an exponential decay of $X_{eq}(t)$. According to the first-order Wertheim's perturbation theory of associating fluids, if the probability of two particles to be connected is constant and equal to p_b , a probability distribution of clusters at equilibrium can be defined as follows^{43,82–84}

$$X_{eq}(l) = (1 - p_b)^2 p_b^{l-1}. \quad (19)$$

From Eq. 19, the linear dependence $\ln(X_{eq}) \propto l$ can be recovered. In our case, however, concentrations of free nanocubes and chains of 2 and 3 particles are significantly larger than those predicted by Wertheim's theory. We hypothesise that this discrepancy may arise from the crucial assumption underlying Wertheim's theory that considers particle connectivity to be independent from the cluster size. This approximation is not directly applicable to our system as dipolar interactions are long-ranged. Indeed, the mechanisms involved in the formation of string-like clusters of polarised particles are more complex than those in simple associating fluids. More specifically, the kinetics of formation of chains consisting of polarised nanoparticles is governed by the dipole moment of each particle, excluded-volume interactions and thermal fluctuations.

To gain better insights into the kinetics of formation of string-like clusters of nanocubes, we compute the transition probability matrix of a cubic particle to belong to chain c of size $l(c)$ at time t_1 and be in chain c' of size $l(c')$ at time $t_2 = t_1 + \delta t$, where δt is set to 0.3τ ⁸⁵. Figure 5(d) and (e) present the transition matrices computed at times $t = 16\tau$

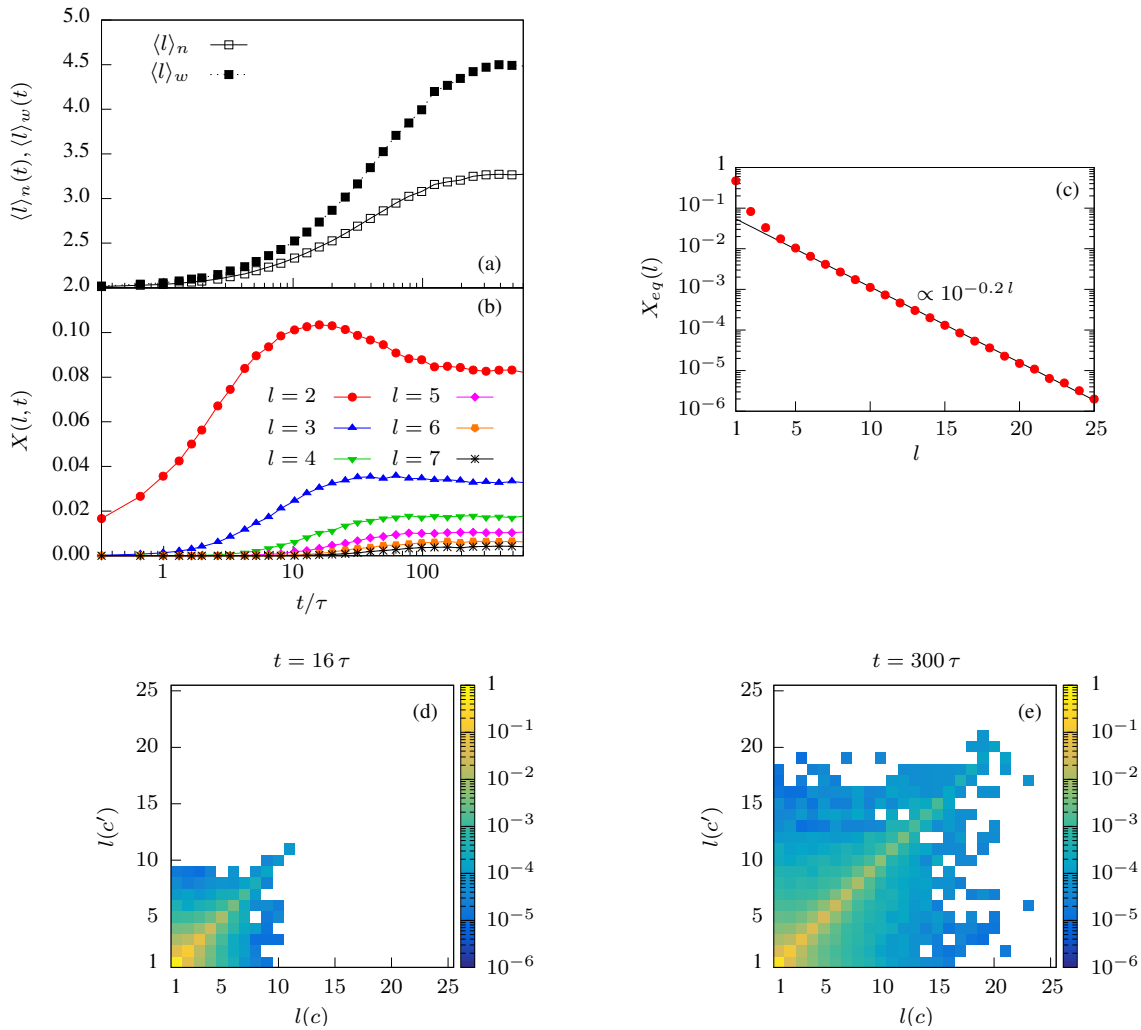


FIG. 5. (a) Profiles of numerical ($\langle l \rangle_n(t)$) and weighted ($\langle l \rangle_w(t)$) average chain lengths over time, for the isotropic (field off) to string-like (field on) phase. (b) Time dependent profiles of molar fractions of chains of length $2 \leq l \leq 7$, starting from the isotropic phase and switching the field on. (c) Equilibrium distribution of molar fraction of chain lengths in the string-like state from simulations (red points), together with the exponential decay obtained by nonlinear regression of data (black solid line). (d, e) Probability transition matrix of a nanocube moving from an initial cluster c of size $l(c)$ to a cluster c' of size $l(c')$ after 0.3τ , (d) at time 16τ , corresponding to the maximum of $X(2, t)$ and (e) at 300τ , when the system reaches the string-like state. Transition probabilities lower than 10^{-6} are in white.

and $t = 300\tau$, corresponding, respectively, to the maximum and stationary values of $X(2, t)$ in Figure 5(b). Since the largest probabilities have a tendency to lie on the diagonal ($l(c) = l(c')$), at long and short times most nanocubes prefer to remain in chain c rather than diffusing to chain c' . At short times, strings contain no more than 10 nanocubes, while they grow up to $l \sim 20$ at longer times. Nonetheless, at the stationary state ($t = 300\tau$), clusters with more than 25 nanocubes have been occasionally seen, with $X_{eq}(l \geq 25) < 10^{-6}$ (Figure 5(c)). It is interesting to note that, at both short and long time scales, a smooth decay of the transition probabilities is observed from short to long strings along the diagonal elements of the matrix, *i.e.* where $l(c) = l(c')$, and also where $|l(c) - l(c')|$ gradually becomes larger. It has to be pointed out, however, that the transition matrices are not weighted by the size of the chains since their individual elements are

computed tracking the single nanocubes rather than the cluster themselves. Nevertheless, a wide variety of transitions between chains of different lengths is still observed. We would expect that the kinetic rates characterising these transitions were string-size dependent and, what we actually observe is that aggregation and disaggregation mechanisms involving individual cubes or small clusters are more likely to occur rather than those involving larger strings. Equally interesting is the change of the mechanical properties of ER fluids upon switching the electric field on/off. The change in the viscoelastic behaviour of nanocubes in the presence of the external field is analysed in the following section by applying passive microrheology.

D. DMC Microrheology of ER fluids

In passive MR, one can obtain the viscoelastic response of a soft material from the mean square displacement (MSD) of a tracer particle embedded in it. By estimating the complex shear modulus G^* , where ω is the frequency of interest, it is possible to identify the viscous (G'') and elastic (G') moduli of the system from $G^*(\omega) = G'(\omega) + iG''(\omega)$. A number of methods have been proposed to determine G^* from the dynamics of a tracer particle^{70–74}. In this work, we apply the method developed by Mason⁷² where the Fourier transform of tracer's MSD serves to estimate the viscoelastic properties of the bath.

A preliminary MR analysis of a bath of nanocubes at a packing fraction $\eta = 0.02$ revealed no visible differences in the viscoelastic properties of the system when the external field is either on or off. Essentially, the very low concentration of bath particles does not affect the mobility of the tracer even when field-induced strings are formed, as the full equivalence of the MSDs reported in the Supplementary Information (Fig. 5, top frame) suggests. It follows that both viscous and elastic moduli in the presence of the field are the same as those calculated with no field applied. Consequently, to shed light on how the formation of chains affects the viscoelastic properties of the bath of nanocubes, we have increased the system packing by one order of magnitude. In Fig. 6, we report the viscous and elastic moduli for a system of nanocubes containing a spherical tracer of size 3σ at packing fraction $\eta = 0.20$. The top frame reports G' and G'' calculated from the tracer's total MSD when the field is on and off. In both scenarios, the system exhibits a dominant viscous response, which becomes more viscoelastic at low and intermediate frequencies upon switching the field on (solid blue curve vs solid red curve). Figure 6(a) shows the system's viscous and elastic moduli calculated from the total MSD of the tracer. While G'' is substantially unaffected by the presence of the electric field, G' increases at short to intermediate frequencies ($\omega\tau < 1$) when the field is switched on. The increase in G' , sparked by the presence of oriented strings that slow down the tracer's mobility at relatively long times (see Fig. 6(a) in the Supplementary Information), indicates that the material is significantly more viscoelastic compared to the field-off scenario. More intriguing is the viscoelastic response of the system in the directions parallel and perpendicular to the applied field, reported in Fig. 6(b). In particular, the perpendicular components of both G' and G'' are larger than their counterparts along the direction of the field. This difference has its origin in the anisotropic diffusion of the tracer when the field is on (see the MSDs in Fig. 6(b) of the Supplementary Information). More specifically, the formation of chains redistributes the nanocubes in space by creating low-density vertical channels for the tracer diffusion in the direction of $\hat{\mathbf{E}}$ and consequently an increase in density perpendicularly to $\hat{\mathbf{E}}$. This particle redistribution, resulting into a density anisotropy, can be appreciated in the top and bottom frames of Fig. 7. Accordingly, the viscoelastic properties assume an anisotropic behaviour with $G''_{\perp} > G''_{\parallel}$ and $G'_{\perp} > G'_{\parallel}$, as indicated in Figure 6(b). It follows that string-

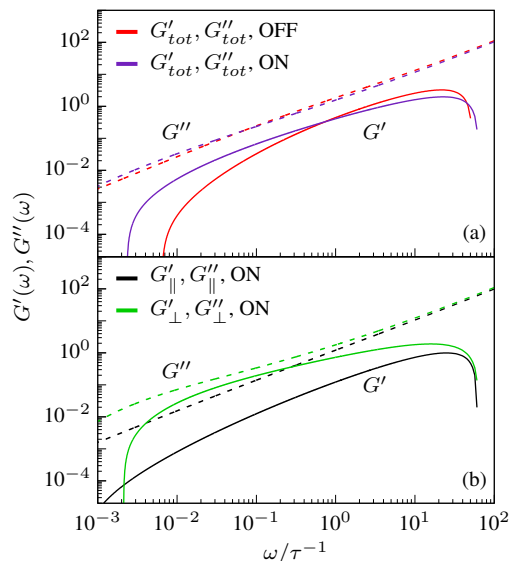


FIG. 6. Viscous G'' (dashed lines) and elastic G' (solid lines) moduli of a suspension of hard cubes at a packing fraction $\eta = 0.2$ containing a spherical tracer of diameter 3σ . (a) Viscous and elastic moduli calculated in the three spatial coordinates with fields off (red curves) and on (blue curves). (b) Viscous and elastic moduli with the field on in the direction parallel (black curves) and perpendicular (green curves) to the field.

like phases of nanocubes exhibit a viscoelastic response in planes perpendicular to the field, but are substantially viscous along the field direction.

IV. CONCLUSIONS

In summary, we employed DMC simulation to model the behaviour of colloidal suspensions of dielectric nanocubes upon application of an electric field. We also applied machine learning techniques to define a robust cluster criterion for the study of strings aggregation and breaking over time. Our results show that, at a volume fraction $\eta = 0.02$ and field strength $\gamma = 13$, the suspension reaches a steady state where $\sim 50\%$ of particles are organized in aligned string-like clusters, with steady lengths and dispersity, or in individual cubes with no preferential orientation. Over the isotropic-to-string-like transition, one first observes the formation of relatively short strings, comprising 2 or 3 nanocubes. Subsequently, while clusters are still breaking and merging, the fraction of particles in chains converges to a steady-state value, which is fully achieved at $t_r \sim 150\tau$. By contrast, the concentration of chains with more than 3 nanocubes increases monotonically until equilibrium is reached.

The kinetics of formation of clusters has been further investigated by analysing the transition probability of a nanocube to move from one cluster to another. Most nanocubes remain attached to a string over times shorter than the elementary time step and only a few of them move to clusters of different sizes. In fact, the larger the difference in size between the

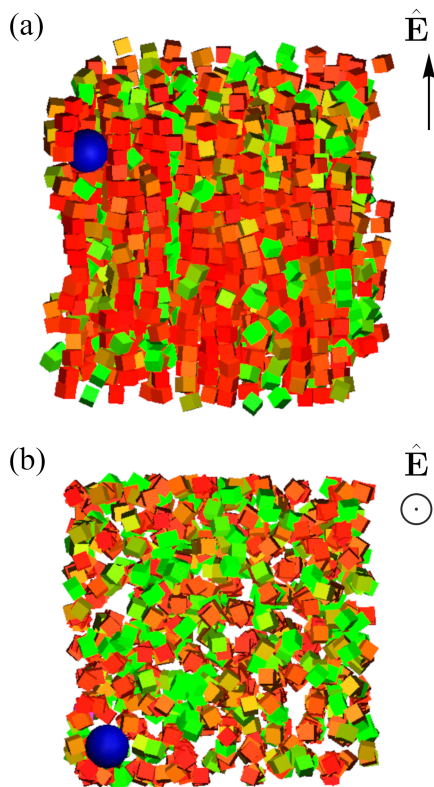


FIG. 7. (Color on-line). (a) Side and (b) top view of a typical configuration of $N_{cube} = 1500$ nanocubes of edge σ and one spherical tracer of diameter $d_{sphere} = 3\sigma$, under the application of the external field. The orientation of the field $\hat{\mathbf{E}}$ is shown at the top right of each panel. Nanocubes are coloured with a gradient from green to red, depending on their orientation with respect to the external field. Packing fraction and field strength are $\eta = 0.20$ and $\gamma = 13$, respectively.

cluster a nanocube leaves and the cluster it joins, the lower the transition probability. This suggests that any aggregation and fragmentation mechanism can potentially occur, with larger probabilities for mechanisms that involve string-like clusters of similar sizes.

Finally, we have investigated how the viscoelastic response of our model suspensions is affected by the field-driven assembly of nanocubes in strings. To this end, we incorporated a spherical tracer into the system, calculate its total and directional MSDs and thus obtain the viscous and elastic moduli of the fluid. While very dilute ER fluids display the same viscoelastic response regardless of whether an electric field is applied or not, sufficiently dense ER fluids exhibit an increase in their viscoelasticity due to the field-induced string-like clusters. Such an enhanced viscoelastic response has an intriguing anisotropic signature with the viscous and elastic moduli significantly larger in the direction perpendicular to the electric field than parallel to it.

All the simulation results reported in this work have been obtained neglecting the fluid-mediated hydrodynamic interactions (HI) between the nanocubes in suspension. Different works investigating the dynamics of colloids have shown

quantitative discrepancies between simulations with and without HI, while retaining similar qualitative features^{86–88}. The same characteristics have been observed in the analysis of rheological properties of electrorheological⁸⁹ and magnetorheological⁷⁵ fluids of spherical particles. HI have also been found to play a non-negligible role in active microrheology^{90,91} and their inclusion in simulation generally results into a better agreement with experiments⁹². Currently, a study on how HI can be incorporated into DMC simulation is in progress. Models of ER fluids can be further improved also by (i) incorporating mutual polarisation of bath particles and (ii) studying their behaviour under confinement to better reproduce an experimental setup.

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