

Field-induced alignment dynamics in suspensions of polarizable rods

I. M. Zerón ^{1,2,*}, A. Iturbe-Jabaloyes ^{1,*}, S. Escañuela-Copado ¹, A. Moncho-Jordá ^{1,3} and A. Patti ^{1,3,4,†}

¹*Biocolloid and Fluid Physics Group, Department of Applied Physics, University of Granada, 18071 Granada, Spain*

²*TERMOCAL Research Group, Research Institute on Bioeconomy, University of Valladolid, 47011 Valladolid, Spain*

³*Carlos I Institute of Theoretical and Computational Physics, 18071 Granada, Spain*

⁴*Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom*



(Received 30 July 2025; accepted 26 March 2026; published 12 May 2026)

Fluids composed of polarizable particles exhibit tunable structural and functional properties when subjected to external electric fields, as the particles tend to reorient and align along the field direction. This field-induced anisotropy leads to pronounced changes in macroscopic properties, rendering these systems highly relevant for applications in nanotechnology. Understanding the dynamics of their response to external fields is crucial for designing responsive materials with fast and controllable actuation. In this work, we employ molecular simulation to study the behavior of suspensions of polarizable rodlike particles under the action of a uniform electric field, with particular attention given to the transient dynamics associated with the switching on and off of the field. Induced dipoles are modeled by independently varying charge magnitude and field strength, yielding a variable effective polarizability. The induced dipole moment of each rod is treated as an effective, externally controlled parameter, and collective polarization effects arising from local electric fields generated by neighboring particles are not explicitly included. The system is studied in a dense regime, where interparticle interactions play a significant role and are implicitly controlled via pressure. We investigate how the characteristic response time depends on the competition between thermal motion and electric forces across a range of temperatures and field strengths. Our results reveal a rich dynamical behavior: at low to moderate field intensities, increasing the temperature significantly reduces the response time, as thermal agitation facilitates reorientation. However, beyond a critical field strength, the response time plateaus, becoming effectively temperature-independent. This saturation indicates a regime where the aligning torque from the field dominates over thermal fluctuations, setting a lower bound for how fast the system can respond. More specifically, we show that the alignment dynamics cannot be inferred from single-particle behavior alone, but emerges from a nontrivial interplay of field-induced dipolar torques, thermal fluctuations, and steric interactions at finite density, producing strongly temperature-dependent and nonlinear trends in both the nematic order parameter and response times.

DOI: [10.1103/6xfz-s9q9](https://doi.org/10.1103/6xfz-s9q9)

I. INTRODUCTION

Over the past few decades, nanomaterials capable of adapting their physical properties in response to external stimuli, commonly known as stimuli-responsive or *smart* nanomaterials, have attracted considerable attention. These materials exhibit reversible and controllable changes when exposed to external factors such as temperature, mechanical stress, light, or electric and magnetic fields. Among them, particularly well-studied systems are composed of either soft or rigid nanoparticles (NPs), each exhibiting distinct response mechanisms. Soft, deformable particles such as microgels undergo complex swelling and structural transitions governed by the interplay between elastic and osmotic forces [1]. Rigid nondeformable NPs can be responsive, for instance by adapting to external

fields through induced polarization, as seen in electrorheological fluids (ERFs). In these systems, polarizable NPs align and reorient along the direction of an applied electric field [2–4], enabling dynamic control over macroscopic properties. ERFs, in particular, consist of suspensions of polarizable particles in an insulating medium and display significant and tunable changes in rheological behavior in the presence of an electric field. These include variations in viscosity, yield stress, and viscoelastic moduli, which make ERFs promising candidates for applications that demand fast, reversible, and externally controlled mechanical responses [5]. The phenomenon whereby nonconducting particles suspended in a fluid become polarized under an external electric field has its roots in the classical predictions of Clausius [6] and Mossotti [7]. When the dielectric constant of the particles differs from that of the surrounding medium, an electric field induces dipole moments in the particles. These induced dipoles experience torques that promote alignment with the applied field and generate dipole-dipole interactions between particles.

The influence of external electric fields on suspensions of spherical dielectric particles has been extensively studied through experiments [8–12], simulation [13–18], and theory [19–22]. However, such particles typically exhibit lower

*These authors contributed equally to this work.

†Contact author: apatti@ugr.es

electrorheological (ER) performance than anisotropic ones, such as rods, tubes, or fibrous particles [23]. This disparity is mainly attributed to the higher length-to-diameter (L/σ) ratio of anisotropic particles, which promotes stronger alignment under an applied field. Particles with larger L/σ ratios tend to form more stable field-induced structures due to their increased specific surface area and enhanced interparticle friction during reorientation. Although experimental methods for synthesizing anisotropic particles have advanced considerably, most studies on ERFs have continued to focus primarily on suspensions of nanospheres, with comparatively limited exploration of alternative shapes, including rodlike [24–26], platelike [27–29], or cubic [30–34] particles.

Molecular simulations of hard and soft rodlike particles have been extensively pursued over the past three decades, addressing a wide range of phenomena in both isotropic and structured phases, including crystalline and liquid-crystalline states. These investigations have provided valuable insights into phase behavior [35–42], dynamics [43–45], and microrheological properties [46,47], all of which have also been explored in the presence of external fields [48–51]. Understanding the structural and dynamical changes induced by such fields is particularly important in the context of responsive systems, whose properties are inherently time-dependent. A key concept in this framework is the *response time*, namely the characteristic timescale over which a system adjusts following the onset or removal of a stimulus. Quantifying response times is essential, as the practical utility of responsive materials often depends on their ability to react promptly.

In this work, we investigate both the equilibrium orientational order and the alignment dynamics of suspensions composed of soft, polarizable colloidal rods initially in isotropic configurations. Upon application of a uniform electric field, the particles progressively align along the field direction. To capture the interplay between thermal fluctuations, steric constraints, and field-induced torques, we employ Langevin dynamics simulations. By systematically varying field strength, temperature, and effective dipole moment, we analyze how finite-density interactions influence both the magnitude of orientational order and the characteristic response times associated with field-driven alignment. Instead of assuming a fixed intrinsic polarizability, we independently vary the induced charge and field strength at constant charge separation, treating the effective dipole moment as a controlled model parameter.

II. MODEL

To explore the phase behavior and response dynamics of fluids of rodlike colloidal particles subjected to a continuous electric field, we adopt a coarse-grained model based on chains of partially overlapping spherical beads. Following our earlier work [52], each rod is constructed from eight aligned beads of diameter σ , evenly spaced along the particle's main axis to achieve an aspect ratio of $L/\sigma = 5$, where L denotes the total length of the rod (see Fig. 1). While increasing the number of constituent beads would yield a more faithful geometric representation of a spherocylinder, the choice of eight beads strikes a practical balance between computational tractability and morphological accuracy. Given

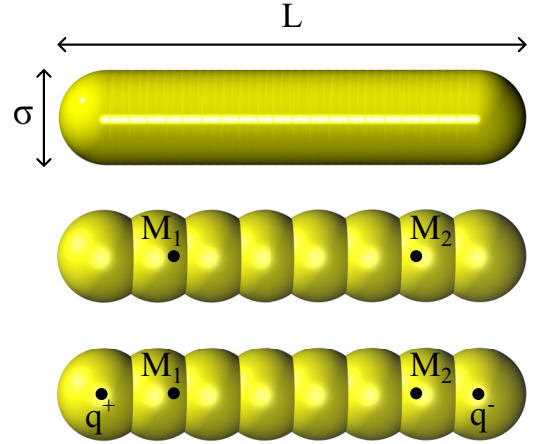


FIG. 1. Geometric representation of the rodlike particle model: Top: Ideal spherocylinder characterized by diameter σ , length L , and total mass M . Middle: Approximate model consisting of equally spaced, overlapping spherical beads aligned along the main axis. The total mass is distributed into two mass sites positioned to preserve the spherocylinder's moment of inertia. Bottom: Polarized rod model with positive and negative charges, q^+ and q^- , located at the centers of the terminal beads.

the length of the NRs, maintaining their rigidity using commonly employed harmonic bonds is inefficient and prone to numerical instability, even when large spring constants are used. To overcome this, we employ virtual sites that constrain the constituent beads to fixed positions, effectively ensuring structural rigidity without resorting to excessively strong bonding interactions. The total mass of each rod, M , is distributed across two noninteracting mass sites, $M_1 = M_2 = M/2$, placed symmetrically along the rod axis at a fixed distance from the center of mass. This setup preserves both translational invariance and the correct moment of inertia for a uniformly distributed mass. Further details on the placement of the mass sites and the calculation of the effective particle volume are available in our previous work [52].

In the absence of an external electric field, the NRs are treated as electrically neutral, and their intermolecular interactions are modeled as purely dispersive. Specifically, nonbonded interactions between beads belonging to different rods are described by a Lennard-Jones (LJ) potential:

$$U_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where r_{ij} is the distance between the centers of beads i and j , and ϵ sets the interaction strength and defines the system's energy unit. The implementation of soft effective interactions in colloidal suspensions allows us to capture the behavior of real systems such as microgels, deformable polymer-based colloids, or emulsion-stabilizing particles. In these systems, the softness typically arises from steric coronas, electrostatic repulsion, and intrinsic particle deformability [53]. Moreover, such soft interactions provide a useful conceptual framework to understand dense assemblies and aggregation phenomena [54].

The characteristic time unit is defined as $\tau = \sigma \sqrt{m/\epsilon}$, where $m = M/8$ is the mass of a single bead. The potential is truncated at a cutoff radius of $r_c = 2.4\sigma$, with long-range corrections applied to account for interactions beyond this distance. We employ the parameters $\sigma = 0.63$ nm and $\epsilon \approx 2.49$ kJ/mol, consistent with our previous work. With this choice of parameters, a temperature of $T = 300$ K corresponds to a reduced temperature $T^* = k_B T / \epsilon = 1$, while a pressure of $P = 165$ bar corresponds to $P^* = 1$. Considering the rod length $L = 5\sigma$ and the arrangement of eight beads, the interbead spacing is approximately 0.57σ . This configuration yields a particle volume $V_{\text{rod}} \simeq 3.323 \sigma^3$ and a mass site separation of about 2.62σ . We notice that this volume underestimates that of a corresponding spherocylinder by roughly 9%. When an external electric field is applied, the rods become polarized as their electron clouds distort along the particle's main axis, inducing a dipole moment. This is modeled by assigning two opposite charges, $\pm q$, at the centers of the terminal beads, resulting in a dipole moment of magnitude $\vec{\mu} = q\vec{d}$, where $\|\vec{d}\| = 4\sigma$ denotes the separation distance, and q is varied from 0 to 1e.

In the present model, the induced dipole moment of each rod is treated as an effective quantity that captures the average polarization response to the applied external field. A fully self-consistent description of polarization would require accounting for both the external field and the local electric fields generated by neighboring particles, such that the dipole of particle i could be written as $\mathbf{p}_i = \alpha(\mathbf{E} + \sum_{j \neq i} \mathbf{E}_j)$. Implementing such approaches typically involves solving large coupled systems or iterative self-consistent schemes [55–57]. In this work, collective polarization effects are neglected and the induced dipole moment is treated as an effective quantity determined solely by the external field. This approximation allows us to focus on the orientational dynamics governed by dipolar torques, thermal fluctuations, and steric constraints at finite density, while keeping the computational model tractable and consistent with commonly used approaches in simulations of dipolar colloidal systems.

Importantly, instead of fixing the intrinsic polarizability associated with a given material, we vary the induced charge magnitude and the applied field strength independently, maintaining a constant charge separation. This approach enables us to treat the effective dipole moment as a key control parameter, allowing for a more general interpretation of the observed behavior beyond specific material systems. We note that double-charge models based on the Clausius-Mossotti approximation have also been proposed for anisotropic particles such as ellipsoids and rods [48,49,58,59]. This approach reproduces adequately the electric-field interaction energy in the case of spherocylinders [60]. Like the present effective dipole description, these models do not explicitly account for local field effects arising from neighboring particles, and therefore operate at a comparable level of approximation with respect to collective polarization.

Although more sophisticated techniques such as fluctuating charges, Drude oscillators, reaction-field methods, or induced point dipoles could be used to explicitly capture local polarization contributions [61–64], their implementation is beyond the scope of the present work. Under the assumptions of our effective-polarization model, the total particle interac-

tions are described as the sum of the LJ potential, the rod-field interaction,

$$U_{\text{field}} = -\vec{\mu} \cdot \vec{E}, \quad (2)$$

and the Coulombic interaction,

$$U_{\text{el}}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{q_i q_j}{r_{ij}}, \quad (3)$$

where the sum runs over all charges q_i belonging to different molecules, r_{ij} is the separation between charge sites i and j , and ϵ_0 is the vacuum permittivity.

III. SIMULATION METHODOLOGY

As a first step toward understanding how the physical properties of fluids of polarizable rodlike particles vary under an external electric field, we established the phase diagram of the proposed model system. To this end, we performed Langevin dynamics simulations in both the NVT and NPT ensembles using the GROMACS software package [65]. The equations of motion were integrated with the leap-frog stochastic dynamics algorithm, which serves as both integrator and thermostat, enabling efficient temperature control. The integration time step and inverse friction coefficient were set to approximately $3.8 \times 10^{-4}\tau$ and $3.8 \times 10^{-1}\tau$, respectively. Pressure was maintained constant via the Parrinello-Rahman barostat [66], employing a relaxation time of $\sim 3.6 \times 10^{-1}\tau$. The rod internal geometry was maintained using the LINCS algorithm [67]. To investigate the phase behavior, simulations were initialized with 1250 rods randomly placed within a cubic box of side length approximately 22σ , under periodic boundary conditions in all directions. The phase space was explored up to reduced pressures $P^* = 5$ and temperatures $T^* = 8$. For each thermodynamic state point, an initial equilibration phase was conducted until both pressure and temperature stabilized. Production runs were then carried out for $t/\tau \simeq 9.4 \times 10^3$, saving system configurations approximately every 3.8τ . All thermodynamic and structural properties were computed from the equilibrated portion of the trajectory, identified from the stability of the total energy profile.

To distinguish between the different phases (isotropic, nematic, smectic, crystalline solid), we evaluated the orientational ordering of the system using the nematic order parameter S_2 , defined as the largest eigenvalue of the ordering tensor:

$$Q_{\alpha\beta} = \frac{1}{2N} \sum_{i=1}^N (3\hat{u}_{i\alpha}\hat{u}_{i\beta} - \delta_{\alpha\beta}), \quad (4)$$

where $\hat{u}_i$ is the unit vector along the axis of the i th rod, $\delta_{\alpha\beta}$ is the Kronecker delta, and the indices $\alpha, \beta \in \{x, y, z\}$. The summation runs over all N rods in the system. The parameter S_2 ranges from values close to zero in the isotropic phase to values approaching unity in highly aligned phases. While S_2 quantifies the global orientational order, additional structural information was obtained by analyzing the spatial distribution of neighboring rods through the radial, parallel, and perpendicular pair distribution functions. These are defined as

$$g(\mathbf{d}) = \frac{N_p}{\rho N N_c V(\mathbf{d})}, \quad (5)$$

where $\mathbf{d} = \{\mathbf{r}, \mathbf{r}_{\parallel}, \mathbf{r}_{\perp}\}$, with $\mathbf{r}$ the center-to-center distance vector between two rods, and $\mathbf{r}_{\parallel}$ and $\mathbf{r}_{\perp}$ its projections along and perpendicular to the nematic director $\hat{\mathbf{n}}$, respectively. Here, N_p is the number of particle pairs found within the volume element $V(\mathbf{d})$, ρ is the number density, N is the total number of rods, and N_c is the number of sampled configurations. Once the thermodynamic conditions corresponding to a stable isotropic phase were identified, a uniform electric field was applied along the z -axis to investigate the system's response to the external stimulus. To enhance statistical reliability, the final equilibrated configuration at a given pressure and temperature was replicated four times along the z -direction, while maintaining the same average density. A short NVT equilibration run was then performed to ensure isotropic conditions prior to the application of the field.

A continuous electric field of reduced magnitude $E^* = \mu E / k_B T$, ranging from 0 to approximately 800, was applied along the z -axis, parallel to the long axis of the simulation box. This field induces a dipolar polarization in the rodlike particles, modeled by assigning opposite charges $\pm q$ at the centers of the outermost beads. The reduced charge magnitude $q^* \equiv q/e$ was varied from 0 to 1. By maintaining a fixed charge separation while independently adjusting the charge magnitude and field strength, the effective dipole moment is treated as a tunable parameter, allowing us to investigate a broad spectrum of dipolar interactions beyond those constrained by fixed material polarizabilities. Although values smaller than the elementary charge may initially appear unphysical, this practice is well established in coarse-grained simulations, where q serves as an effective interaction parameter and may also be viewed as a statistical average of partial charge accumulation at the rod ends that characterizes tunneling effects in conducting materials separated by a potential barrier. Consequently, it enables continuous adjustment of the dipolar coupling strength without modifying the particle geometry or imposing discrete charge quantization. Upon deactivation of the electric field, the rods naturally return to a neutral state. Electrostatic interactions were computed using the Coulomb potential between charged sites belonging to different rods only. Long-range electrostatics were handled using the particle mesh Ewald (PME) method [68].

The structural and dynamic response of the system to the applied electric field was investigated through NVT simulations comprising 10 alternating cycles of field activation and deactivation. To characterize potential metastable states, we measured the nematic order parameter, pair distribution functions, and diffusion coefficient across various field strengths and charge magnitudes, under different pressure and temperature conditions. The response times τ^{on} and τ^{off} were defined as the times required for the system to reach 95% of the corresponding equilibrium values of the nematic order parameter after the field is switched on or off, denoted as $\langle S_2^{\text{on}} \rangle$ and $\langle S_2^{\text{off}} \rangle$, respectively. Specifically, τ^{on} is the time at which $S_2 = 0.95 \times \langle S_2^{\text{on}} \rangle$ is reached following field application, while τ^{off} is defined by the condition $S_2 = 1 - 0.95 \times \langle S_2^{\text{off}} \rangle$ after the field is removed.

IV. RESULTS

This study is structured in two main parts. First, we investigated the phase behavior of a system of neutral rodlike

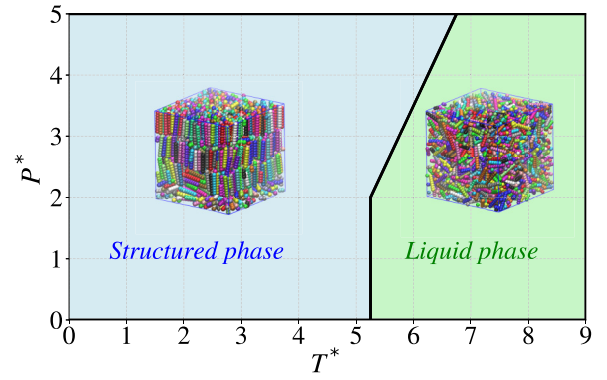


FIG. 2. P^* vs T^* phase diagram for a system of rods with aspect ratio $L/\sigma = 5$. The light blue region corresponds to the structured phase (nematic, smectic, or crystalline), while the light green region represents the liquid (isotropic) phase. Representative snapshots of typical configurations are shown for each region.

particles with an aspect ratio of $L/\sigma = 5$ across a wide range of temperatures and pressures, with the goal of identifying the thermodynamic conditions under which the isotropic phase is stable. It is important to note that for neutral rods, orientational correlations and partially aligned local structures may be observed even at zero applied field ($E = 0$), highlighting that packing effects alone can induce local alignment without any external electric field. Once these conditions were established, we applied a constant electric field of varying strength to the system of polarizable rods in order to characterize both the resulting disorder-order phase transition and the timescales associated with the system's response to the external stimulus.

A. Phase diagram of neutral rods

The phase diagram of similar rigid bead-necklace prolate particles has been previously investigated by Tian and Smith [69], who considered rods with an aspect ratio of 7 interacting via the LJ potential. They identified an isotropic phase at packing fractions $\eta < 0.420$, a nematic phase in the intermediate range $0.420 < \eta < 0.514$, and smectic A and crystalline phases at higher densities. We first analyze the phase behavior of a system composed of neutral rodlike particles with aspect ratio $L/\sigma = 5$, interacting exclusively via the LJ potential, as described in Sec. II. To this end, NPT simulations were carried out for 1250 uncharged rods over a range of reduced pressures $0 < P^* < 5$ and temperatures $0 < T^* < 8$. Rods were initially placed at random positions within the simulation box, and the system was equilibrated under the desired thermodynamic conditions. Production runs were then performed for a total simulation time of $t/\tau \simeq 9.4 \times 10^3$, during which the density, nematic order parameter, and pair distribution functions were computed to characterize the emerging phases. As shown in Fig. 2, the phase diagram reveals two predominant regions: a low-density isotropic (fluidlike) phase and a high-density structured phase.

In the present work, our interest is specifically restricted to the field-induced transition between disordered and ordered states. Therefore, we focus on thermodynamic conditions where the equilibrium state at zero field is isotropic, and a de-

tailed characterization of the structured region in equilibrium is not pursued. The isotropic phase emerges at temperatures above $T^* \approx 5$, with the transition temperature increasing with pressure. This region is characterized by a low orientational order parameter ($S_2 \lesssim 0.1$), moderate packing fraction ($\eta \lesssim 0.5$), and relatively high mobility, as indicated by diffusion coefficients $D^* = D\tau/\sigma^2 \gtrsim 0.01$. In contrast, the structured phase exhibits pronounced orientational order ($S_2 \gtrsim 0.4$), higher density ($\eta \gtrsim 0.5$), and significantly reduced diffusion ($D^* \ll 0.01$), indicating the emergence of positional and orientational correlations characteristic of ordered phases. Representative snapshots of the system at $(P^*, T^*) = (1, 5)$ and $(1, 6)$ are shown in Fig. 2, illustrating the distinct structural features of each phase.

Further structural insight is provided by the analysis of the pair distribution functions (PDFs) defined in Eq. (5). Figure 3 displays the radial distribution $g(r)$, along with its parallel $g_{\parallel}(r_{\parallel})$ and perpendicular $g_{\perp}(r_{\perp})$ components relative to the nematic director. These functions are calculated by considering the center-of-mass distance vector $\mathbf{r}$ between each pair of rods and projecting it onto directions parallel and perpendicular to the director. For the representative isotropic state at $(P^*, T^*) = (1, 6)$ (blue curves), both $g(r)$ and $g_{\perp}(r_{\perp})$ exhibit a pronounced peak near $r^* \equiv r/\sigma \approx 1.1$, with the first coordination shell extending up to $r^* \approx 3$. Beyond this range, the functions rapidly decay to unity, as expected for a disordered, low-density fluid. In contrast, the parallel component $g_{\parallel}(r_{\parallel})$ remains flat across all distances, confirming the absence of positional correlations or layering along the nematic director, being consistent with a fully isotropic arrangement. At $(P^*, T^*) = (1, 5)$, the system exhibits pronounced positional and orientational correlations indicative of an ordered equilibrium state. As shown by the red curves in Fig. 3, the pair distribution functions display a sequence of well-defined peaks and troughs, reflecting the presence of short- and medium-range positional order. In particular, the parallel distribution function $g_{\parallel}(r_{\parallel})$ reveals a layered structure, with a periodicity of approximately 5.5σ , slightly exceeding the rod length, being consistent with smecticlike organization.

B. Effect of an electric field on polarizable rods

Having established the conditions for the isotropic phase, we proceeded to investigate the response of polarizable rods to an external electric field. Systems with rod charges $q^* = \pm 0.1, \pm 0.3$, and ± 0.5 were studied at a fixed pressure $P^* = 1$ and temperatures $T^* = 6, 7$, and 8 . To enhance statistical accuracy and reduce finite-size effects, the final equilibrated configuration under each set of conditions was replicated four-fold along the z -axis, yielding systems of 5000 rods. A short equilibration run followed each replication to ensure structural and thermodynamic consistency before applying the electric field. NVT simulations were conducted using cyclic protocols where a constant electric field E^* , ranging from 0 to approximately 800, was periodically switched on and off along the z -axis. When the field is applied, we assume that the polarization of the rods, arising from electron cloud distortions along the particle axis, occurs on a timescale much shorter than their mechanical reorientation or translational response. This assumption is standard in modeling colloidal particles

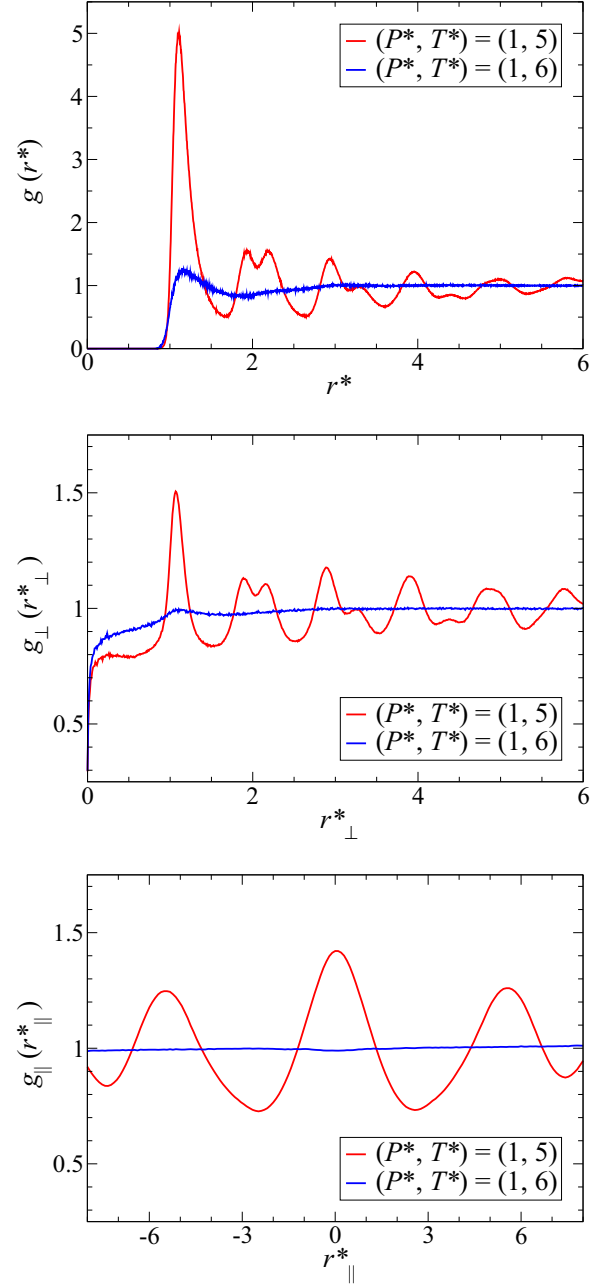


FIG. 3. Radial (top), perpendicular (middle), and parallel (bottom) pair distribution functions of a structured phase (red line) and an isotropic phase (blue line) at $(P^*, T^*) = (1, 5)$ and $(1, 6)$, respectively. The corresponding nematic order parameters are $S_2 = 0.72$ for the structured phase and $S_2 = 0.04$ for the isotropic phase. Here $r^* = r/\sigma$ is the reduced distance.

where electronic polarization is treated as quasi-instantaneous compared to particle-scale dynamics. Therefore, rods are considered instantaneously polarized, and the charged rod model, with opposite charges localized at the ends, is employed to capture the resulting dipolar interactions. Within this effective description, the induced dipole moment represents the dominant response to the externally applied field, while collective polarization effects arising from local fields generated by neighboring particles are not treated explicitly.

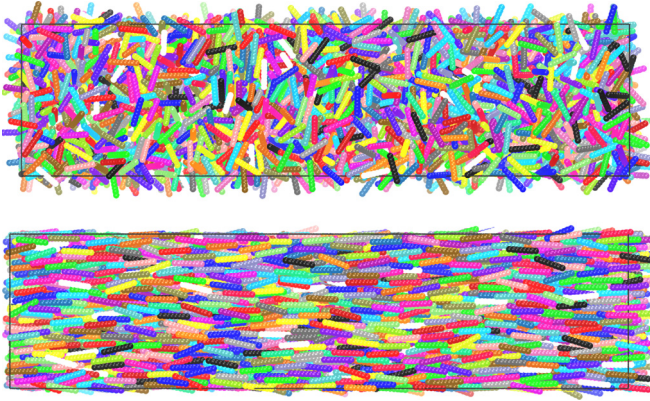


FIG. 4. Equilibrium snapshots of a system of 5000 rods with $q^* = \pm 0.5$ at $P^* = 1$ and $T^* = 7$. The top panel shows the configuration with the electric field switched off ($E^* = 0$), while the bottom panel corresponds to the field switched on ($E^* = 7$) along the z -direction.

Upon removal of the field, the charges are assumed to rapidly redistribute along the rod backbone, restoring electrical neutrality and effectively switching back to the neutral rod model. This approach allows us to isolate and investigate the rods' structural and dynamic responses to the external field under realistic assumptions about polarization kinetics.

Figure 4 displays two representative configurations of the system with the electric field switched off and on, respectively. Upon application of the field, the rods exhibit strong alignment along the field direction (the z -axis), resulting in a nematiclike ordered state. Under the conditions indicated in the figure, the system reaches a nematic order parameter of $S_2 = 0.8$. The dynamical response to repeated switching of the electric field is illustrated in Fig. 5, where the evolution of S_2 is tracked over several on/off cycles. When the field is turned on, the system rapidly responds, with S_2 rising sharply and stabilizing at a characteristic value determined by the

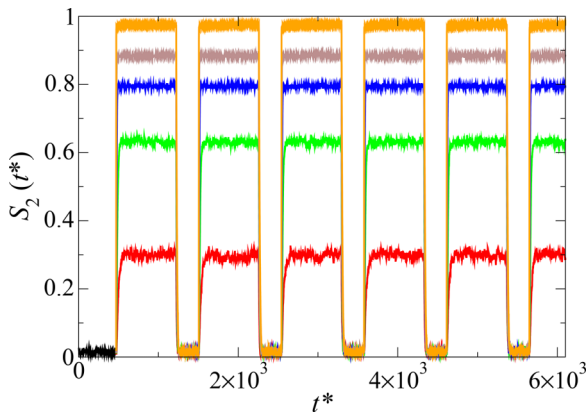


FIG. 5. Time evolution of the nematic order parameter S_2 for a system of 5000 rods with charge $q^* = \pm 0.5$, at $P^* = 1$ and $T^* = 7$, subjected to periodic cycles of a constant electric field applied along the z -axis. Curves correspond to different field strengths: $E^* = 0$ (black), 1.8 (red), 3.5 (green), 7.0 (blue), 13.9 (brown), and 69.6 (orange). The degree of alignment increases with field strength, as reflected in the rise of S_2 during the active phase of each cycle.

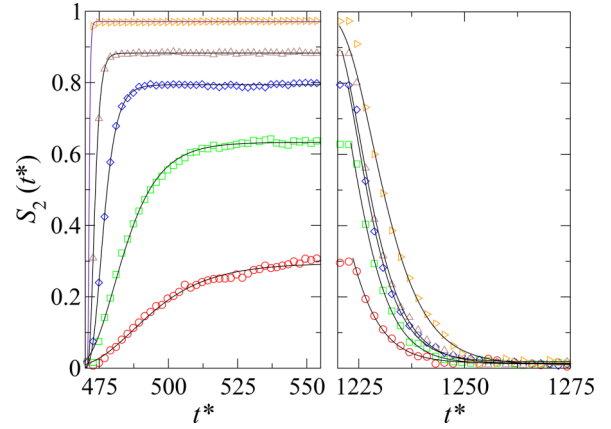


FIG. 6. Short-time evolution of the nematic order parameter S_2 during the initial stages field application (left) and removal (right) for polarizable rods under a constant electric field along the z -axis. Symbols indicate different field strengths: $E^* = 1.8$ ($\circ$), $E^* = 3.5$ ($\square$), $E^* = 7.0$ ($\diamond$), $E^* = 13.9$ ($\triangle$), $E^* = 69.6$ ($\triangleright$). Solid lines represent exponential fits of the form $S_2(t) \propto 1 - \exp[-b(t/t_0)^c]$ (left) and $S_2(t) \propto \exp[-b(t/t_0)^c]$ (right), where t_0 is a characteristic relaxation time, and b and c are fitting parameters, whose values are, respectively, ($\circ$) (1186.08, 350.55, 221.32), ($\square$) (1190.63, 476.1, 229.59), ($\diamond$) (1192.18, 476.87, 228.63), ($\triangle$) (1190.64, 553.61, 219.63), and ($\triangleright$) (1187.8, 472.57, 184.12) for the cycles with the field turned off, and ($\circ$) (464.41, 4.97, 33.03), ($\square$) (460.02, 11.26, 55.47), ($\diamond$) (468.95, 8.37, 153.44), ($\triangle$) (466.18, 141.71, 346.15), and ($\triangleright$) (470.30, 19.37, 1415.82) for the cycles when the field is turned on.

field strength and system parameters. At low field strengths (e.g., $E^* = 1.8$), thermal fluctuations dominate over dipolar interactions, resulting in weak alignment. In this regime, the order parameter remains relatively low, with $S_2 \approx 0.3$ for rods bearing charges $q^* = \pm 0.5$ at $P^* = 1$ and $T^* = 7$. As the field strength increases, the influence of the electric torque on the polarized rods grows, progressively suppressing rotational motion. At high field intensities, such as $E^* = 69.6$, the system approaches near perfect alignment, with the order parameter reaching $S_2 \approx 0.97$.

To further assess the dynamical response of the system to external electric fields, we analyzed the short-time evolution of the nematic order parameter S_2 immediately following the switching on and off of the field. The results, shown in Fig. 6 for the first on/off cycle, reveal a clear asymmetry between the ordering and disordering processes. Upon field application, S_2 rises rapidly as the rods align along the field direction. In contrast, when the field is removed, the loss of orientational order proceeds more gradually, particularly at high field strengths. Interestingly, for weaker fields, this trend is reversed: the disordering kinetics is faster than the ordering, suggesting a subtle interplay between dipolar coupling and thermal fluctuations in the system's relaxation behavior. Both processes are well described by exponential functions of the form $S_2^{\text{on}}(t) \propto 1 - \exp[-b(t/t_0)^c]$ (switching on) and $S_2^{\text{off}}(t) \propto \exp[-b(t/t_0)^c]$ (switching off), where t_0 is a characteristic relaxation time, which is inversely proportional to the particle average rotational diffusion coefficient [70], while b and c are fitting parameters.

This exponential behavior is reminiscent of the optical Kerr effect, wherein an initially isotropic medium develops birefringence upon application of an external electric field. According to Kerr's law, the induced birefringence Δn increases with time and, in the case of dilute suspensions of particles without intrinsic dipole moments and under weak electric fields, scales with the square of the field strength: $\Delta n(t) = KE^2[1 - \exp(-(t/\tau_K)^\alpha)]$. Here, K is the Kerr constant, τ_K is a characteristic optical relaxation time, and α is an empirical exponent [71–73]. When the field is switched off, the birefringence decays in a manner closely linked to the distribution of the particles' rotational diffusion coefficients. This decay generally follows a similar exponential function, although alternative forms, based on the Watson-Jennings and multiexponential methods, have also been proposed [70]. Since birefringence originates from orientational anisotropy, it is directly proportional to the nematic order parameter $S_2(t)$, particularly in the weak-alignment regime. Accordingly, the exponential form used to fit our simulation data reflects a kinetic process closely related to the buildup and decay of Kerr birefringence, highlighting the connection between microscopic orientational ordering and macroscopic optical responses. The fitting parameters t_0 and c capture the influence of dipolar interactions and thermal fluctuations on the system's relaxation dynamics, with the characteristic timescale primarily set by rotational diffusion and modulated by the applied field strength. Experimental studies report that the alignment of rod- and platelike particles follows stretched-exponential birefringence dynamics consistent with Kerr's law, with relaxation times ranging from milliseconds to seconds [27,70,74]. Although our study focuses on rodlike particles, analogous field-dependent response times have also been observed in electrorheological suspensions of spherical particles, where viscosity, yield stress, and dielectric properties evolve over comparable timescales and typically decrease with increasing field strength as $t \sim E^{-\alpha}$, with $\alpha < 2$ [75–78].

To investigate the influence of thermal energy on field-induced ordering, we examined the nematic response at three different temperatures: $T^* = 6, 7$, and 8 . For each case, the average nematic order parameter S_2 was computed over 10 complete cycles of field switching. The results, shown in the top panel of Fig. 7, display the equilibrium values of S_2 as a function of the applied electric field strength E^* for a system of 5000 rods with charge $q^* = \pm 0.5$ at fixed pressure $P^* = 1$. At low field strengths ($E^* < 2$), rod alignment remains weak, and the system retains its isotropic character. Beyond this threshold, the order parameter increases markedly with field strength, indicating progressive alignment along the field direction. Notably, at high fields ($E^* > 100$), the system reaches nearly perfect nematic order irrespective of temperature. However, at intermediate field strengths, thermal fluctuations play a more prominent role, and higher temperatures lead to reduced alignment, as evidenced by the lower values of $\langle S_2^{\text{on}} \rangle$. In this regime, the system approaches the behavior expected for an ideal ensemble of noninteracting dipoles, as represented by the dashed reference curve in the figure. These results highlight the competition between thermal agitation and field-induced orientational ordering in determining the system's macroscopic response.

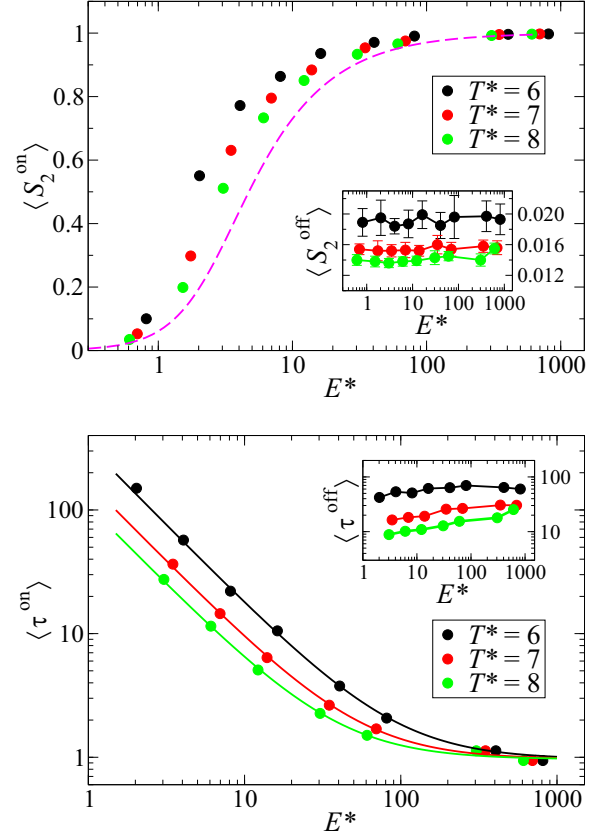


FIG. 7. Equilibrium nematic order parameter (top) and corresponding response times (bottom) as a function of electric field strength for a system of 5000 rods at pressure $P^* = 1$ and temperatures $T^* = 6, 7$, and 8 . Ten cycles of a constant electric field being switched on and off (illustrated in the inset) were applied. Upon field application, the rods acquire a charge $q^* = \pm 0.5$, whereas they become neutral ($q^* = 0$) when the field is removed. The dashed curve represents the equilibrium S_2 value for an ideal dipolar system (see text for details), while the solid lines are fits to the response time data. Error bars are smaller than the symbol size unless otherwise specified.

To relate our results to real systems, we consider experiments on silica rods [58]. The goal is to capture a physically meaningful range of dipole moments and field strengths that are consistent with the general alignment trends observed experimentally, without attempting to replicate collective phase behavior. Nanorods with a diameter of 550 nm and aspect ratio 5 exhibit a para-nematic phase at $E = 0.05$ V/ μm and a highly oriented phase at $E = 0.1$ V/ μm (see Fig. 3 in Ref. [58]). At $T = 300$ K and a dipolar charge $q = \pm 0.5e$, these fields correspond to $E^* = 2$ and $E^* = 4$, for which simulations predict a weakly nematic phase ($S_2 \approx 0.4$) and a highly oriented phase ($S_2 \approx 0.8$), respectively (Figs. 7 and 8). At higher fields, the maximum torque remains within physically realistic limits, showing that the model spans a relevant range of dipole strengths and field conditions.

When the field is switched off, the average order parameter S_2^{off} relaxes to the value observed during the preequilibration stage, as shown in the inset of Fig. 7. The slight differences between datasets reflect the temperature-dependent equilibrium

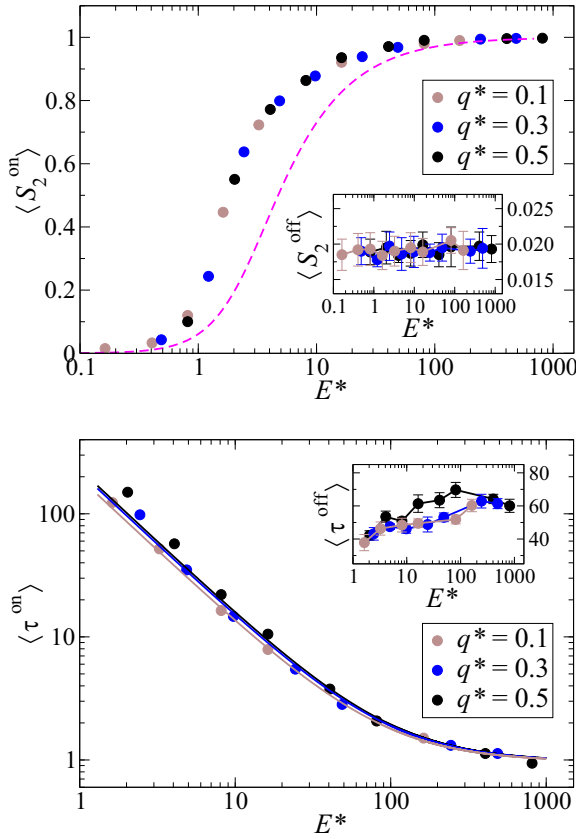


FIG. 8. Average nematic order parameter (top) and corresponding response times (bottom) as a function of electric field strength for a system of 5000 rods at $P^* = 1$, $T^* = 6$, and charges $q^* = \pm 0.1, \pm 0.3$, and ± 0.5 . Ten cycles of a constant electric field being switched on and off (illustrated in the inset) were applied. Upon field application, the rods acquire a charge $q^* = \pm 0.5$, whereas they become neutral ($q^* = 0$) when the field is removed. The dashed curve represents the equilibrium S_2 value for an ideal dipolar system (see text for details), while the solid lines are fits to the response time data. Error bars are smaller than the symbol size unless otherwise specified.

values. Based on this behavior, and following the definition of the response times introduced in the previous section, we computed the average switching times τ^{on} and τ^{off} for each condition. The bottom panel of Fig. 7 shows the dependence of the response times τ^{on} and τ^{off} (inset) on the applied electric field. As observed, τ^{on} decreases with both increasing temperature and field strength. At very high field values, the switching-on time approaches a constant value, $\tau^{\text{on}}_{\infty} \approx 0.96$. In contrast, τ^{off} increases with field strength, reflecting the fact that a higher degree of alignment requires more time for the system to relax back to a disordered state once the field is removed. However, beyond a certain threshold, both S_2 and τ^{off} saturate, becoming independent of further increases in field intensity. This insensitivity of τ^{off} to the field is primarily due to the relaxation being fundamentally dominated by the rotational diffusion of the rods. The residual dependence of τ^{off} on the field strength can be attributed to the system's nondilute nature, which imposes constraints on particle mo-

tion that are more pronounced when starting from a higher initial alignment at larger E^* .

Finally, we examine the effect of varying dipole charges on the nematic order parameter S_2 and the response times τ^{on} and τ^{off} at fixed pressure $P^* = 1$ and temperature $T^* = 6$. As shown in Fig. 8, when the electric field is applied, both the order parameter S_2^{on} and the response time τ^{on} exhibit a universal trend that is largely independent of the specific dipole charge assigned to the rods. The observed collapse of the nematic order parameter and response time in reduced units indicates that the alignment dynamics are governed by underlying dimensionless ratios of relevant physical quantities, such as the field strength relative to thermal energy and the dipole magnitude, rather than by absolute values alone. Importantly, our simulations reveal that at finite density, excluded volume, steric repulsion, and local dipolar interactions introduce collective orientational correlations that modify the single-particle response. This shows that the observed trends reflect both single-particle physics and finite-density collective effects, providing insight into robust trends in field-induced alignment dynamics in dense suspensions of interacting polarizable rods. While a systematic exploration across a broader range of pressures, temperatures, and material polarizations is needed to fully establish the generality of this behavior, the current results already highlight the coupled role of thermal fluctuations, interparticle interactions, and dipolar torques in shaping the collective response.

At high field strengths, the system approaches the behavior of an ideal dipolar fluid, and the response time asymptotically approaches $\tau^{\text{on}}_{\infty} \approx 0.96$. When the field is switched off, S_2^{off} returns to the equilibrium value corresponding to $P^* = 1$ and $T^* = 6$, as expected. The response time τ^{off} follows a general increasing trend with electric field strength and ultimately reaches a plateau at approximately $\tau^{\text{off}}_{\infty} \approx 65$ under these conditions. While our simulations provide quantitative insights into the dependence of the nematic order parameter and the response time on temperature, electric field, and dipole moment, the results remain limited to the parameter space explored in this study. A more extensive analysis covering broader thermodynamic and dipolar conditions would be necessary to establish general trends and formulate comprehensive rules.

To rationalize the asymptotic alignment behavior observed at high field strengths, we now present an analytical treatment of the equilibrium order parameter for a dilute ideal gas of dipolar rods under an external electric field. Consider a system of N identical dipolar rods in a volume V , in the highly dilute limit such that interparticle interactions are negligible. In this regime, the system behaves as a classical ideal gas. Upon application of an external field, the interaction energy of a single dipole is given by

$$\varepsilon = -\mu E \cos \theta, \quad (6)$$

where θ denotes the angle between the dipole axis and the field. The canonical partition function of the system is $Z = (Z_1)^N / N!$, where Z_1 is the single-particle partition function. For a classical particle with center-of-mass coordinates x, y, z and orientation specified by the Euler angles ϕ, θ, ψ ,

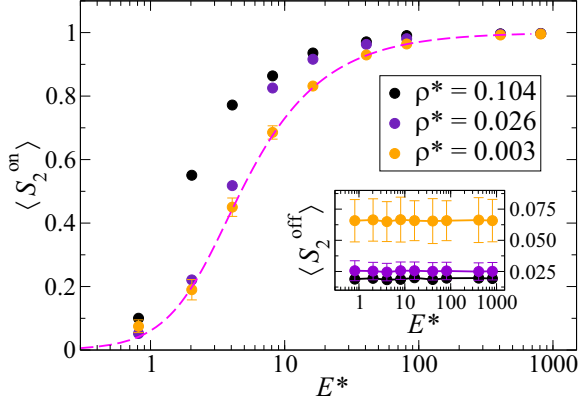


FIG. 9. Average nematic order parameter as a function of electric field strength at pressure $P^* = 1$ and temperature $T^* = 6$ for three systems of 5000 ($\rho^* = 0.104$), 1250 ($\rho^* = 0.026$), and 156 ($\rho^* = 0.003$) rods carrying a dipolar electric charge $q^* = \pm 0.5$ when the electric field is on and $q^* = 0$ when the field is off. The dashed curve represents the equilibrium S_2 value for an ideal dipolar system.

the Hamiltonian reads

$$H_1 = \frac{p_x^2}{2M} + \frac{p_y^2}{2M} + \frac{p_z^2}{2M} + \frac{(p_\phi - p_\psi \cos \theta)^2}{2I_1 \sin^2 \theta} + \frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} - \mu E \cos \theta, \quad (7)$$

where I_1 and I_3 are the principal moments of inertia of the rod. Integrating over all phase-space variables yields the single-particle partition function:

$$Z_1 = \frac{1}{h^6} \int e^{-H_1/k_B T} d\mathbf{q} d\mathbf{p} = \frac{8\pi^2 V}{h^6} (2\pi k_B T)^3 M^{3/2} I_1^{1/2} \frac{\sinh(E^*)}{E^*}, \quad (8)$$

where the dimensionless parameter $E^* = \mu E / k_B T$ quantifies the relative strength of field-induced alignment versus thermal agitation. The corresponding equilibrium order parameter, $\langle S_2(E^*) \rangle = \langle P_2(\cos \theta) \rangle$, reads

$$\langle S_2(E^*) \rangle = \frac{1}{h^6 Z_1} \int e^{-H_1/k_B T} P_2(\cos \theta) d\mathbf{q} d\mathbf{p} = 1 - \frac{3 \coth(E^*)}{E^*} + \frac{3}{(E^*)^2}, \quad (9)$$

which is plotted as a dashed line in Figs. 7 and 8. This function satisfies the expected limiting behavior: $\langle S_2(0) \rangle = 0$ (isotropic state), monotonic increase with E^* , and $\lim_{E^* \rightarrow \infty} \langle S_2 \rangle = 1$, corresponding to perfect alignment. The lack of universal scaling in the simulation data stems from the system's inherent nonideality. Unlike an ideal gas, the simulated dipolar rods interact via excluded volume and attractive LJ forces, breaking the ideal scaling with E^* . These interactions induce many-body effects, including spontaneous alignment at finite density and zero field, leading to a finite baseline order parameter and increased temperature sensitivity. Such collective phenomena account for the deviations from ideal behavior and preclude collapse onto a single master curve. This phenomenon is illustrated in Fig. 9, where for a system at very low

density ($\rho^* = 0.003$) the average alignment closely follows the ideal behavior (dashed curve), except for low electric fields ($E^* < 1$), where the system approaches the equilibrium value in the absence of a field ($S_2 = 0.065$). As the free volume decreases, the rods become more confined, leading to stronger interactions with neighboring rods and promoting greater alignment. Consequently, the nematic order parameter deviates from the ideal trend, except at very high electric field strengths.

V. CONCLUSION

We have investigated the orientational response of dipolar rodlike particles to an external electric field by combining Langevin dynamics simulations with analytical theory. As a first step, we characterized the phase behavior of our bead-necklace model in the absence of external fields to identify the thermodynamic conditions under which isotropic and structurally ordered phases emerge. This preliminary mapping allowed us to select state points within the stability region of the isotropic phase, ensuring that field-induced alignment could be unambiguously distinguished from spontaneous ordering due to interparticle interactions. Using cyclic field-switching protocols, we then quantified the system's nonequilibrium response by measuring the nematic order parameter and the corresponding response times during the field-on and field-off periods. Our model does not assume a fixed intrinsic polarizability characteristic of a specific material. Instead, by varying the charge magnitude and electric field independently while keeping the charge separation constant, we treat the effective dipole moment as a tunable parameter. This allows us to explore a broader response landscape and to account for potential nonlinearities in the polarization response at high field strengths.

We observe a rich interplay between dipolar coupling, thermal fluctuations, and interparticle interactions. At sufficiently strong fields, the system exhibits an asymptotic alignment response that becomes weakly dependent on the specific dipole moment, characterized by a plateau in the order parameter and a saturation of the alignment time. To rationalize this high-field behavior, we developed an analytical treatment based on a classical ideal gas of dipolar rods. In the dilute limit, we derived a closed-form expression for the equilibrium order parameter as a function of the dimensionless field strength $E^* = \mu E / k_B T$. This model accurately reproduces the observed high-field trend, predicting full alignment in the limit $E^* \rightarrow \infty$ and isotropic behavior at zero field. The analytical expression serves as a useful benchmark for interpreting simulation results and for exploring the response in regimes not easily accessible computationally.

An important outcome of this work is that the alignment response cannot be understood solely from the well-known single-particle picture of a rod aligning with an external field. Our simulations demonstrate that the observed trends in both nematic order parameter and response times result from a complex interplay of dipolar torques, thermal fluctuations, and steric interactions at finite density. The pronounced temperature dependence of the response highlights the competition between thermal agitation and field-induced forces, while local packing constraints induce orientational correla-

tions that underpin collective alignment. These finite-density effects, including dipole-dipole interactions, play a central role in shaping both equilibrium and dynamical behavior in dense suspensions and dipolar nematic phases.

In summary, our study provides a detailed particle-level understanding of field-induced ordering in dipolar fluids. It establishes connections between idealized analytical predictions and the complex behavior observed in simulations, offering both theoretical insight and practical guidance for the design of responsive anisotropic materials under external stimuli. Finally, we notice that a more comprehensive study could explicitly incorporate hydrodynamic interactions, which are known to significantly influence the rheological response at different shear rates as well as the diffusive properties [79–82]. Although such effects are neglected in the present work, they represent an important aspect to be addressed in future investigations, particularly in the context of rheological properties.

ACKNOWLEDGMENTS

I.M.Z. and A.P. acknowledge Grant No. P21_00015 funded by Junta de Andalucía, Consejería de Universi-

dad, Investigación e Innovación. A.J.I. was supported by Banco Santander and the University of Granada through the P5A: Research Initiation Scholarship Program for Students (Grant No. ACG265/6a). A.P. and A.M.-J. acknowledge project Grant No. PID2022-136540NB-I00 awarded by MICIU/AEI/10.13039/501100011033 and ERDF, A Way of Making Europe. S.E.-C. and A.P. acknowledge Grant No. W911NF-23-1-0099 awarded by the U.S. Army Research Office. A.P. has been supported by a María Zambrano Senior fellowship, financed by the European Union within the NextGenerationEU program and the Spanish Ministry of Universities. All authors gratefully acknowledge the UGR Servicio de Supercomputación and PROTEUS, the supercomputing center of the Institute Carlos I for Theoretical and Computational Physics, for providing computational resources. Valuable discussions with María L. Jiménez and Miguel Ibáñez, both from the University of Granada, are also sincerely appreciated.

DATA AVAILABILITY

The data that support the findings of this article are openly available [83].

- [1] P. J. Flory and J. Rehner Jr., Statistical mechanics of cross-linked polymer networks II. Swelling, *J. Chem. Phys.* **11**, 521 (1943).
- [2] W. M. Winslow, Induced fibrillation of suspensions, *J. Appl. Phys.* **20**, 1137 (1949).
- [3] Z. G. Wei, R. Sandström, and S. Miyazaki, Shape-memory materials and hybrid composites for smart systems: Part I shape-memory materials, *J. Mater. Sci.* **33**, 3743 (1998).
- [4] N. Kuznetsov, V. Kovaleva, S. Belousov, and S. Chvalun, Electrorheological fluids: From historical retrospective to recent trends, *Mater. Today Chem.* **26**, 101066 (2022).
- [5] L. Munteanu, A. Munteanu, and M. Sedlacik, Electrorheological fluids: A living review, *Prog. Mater. Sci.* **151**, 101421 (2025).
- [6] R. Clausius, Behandlung dielectricischer medien, in *Die Mechanische Behandlung der Electricität* (Springer, New York, 1879), pp. 62–97.
- [7] O. F. Mossotti, *Discussione analitica sull'influenza che l'azione di un mezzo dielettrico ha sulla distribuzione dell'elettricità alla superficie di più corpi elettrici disseminati in esso* (Dai Tipi della RD Camera, 1846), Vol. 22.
- [8] J. E. Martin, J. Odinek, and T. C. Halsey, Evolution of structure in a quiescent electrorheological fluid, *Phys. Rev. Lett.* **69**, 1524 (1992).
- [9] J. E. Martin, J. Odinek, T. C. Halsey, and R. Kamien, Structure and dynamics of electrorheological fluids, *Phys. Rev. E* **57**, 756 (1998).
- [10] J. G. Cao, J. P. Huang, and L. W. Zhou, Structure of electrorheological fluids under an electric field and a shear flow: Experiment and computer simulation, *J. Phys. Chem. B* **110**, 11635 (2006).
- [11] B. Horváth and I. Szalai, Structure of electrorheological fluids: A dielectric study of chain formation, *Phys. Rev. E* **86**, 061403 (2012).
- [12] G. Belijar, Z. Valdez-Nava, S. Diaham, L. Laudebat, T. B. Jones, and T. Lebey, Dynamics of particle chain formation in a liquid polymer under AC electric field: Modeling and experiments, *J. Phys. D* **50**, 025303 (2017).
- [13] K. C. Hass, Computer simulations of nonequilibrium structure formation in electrorheological fluids, *Phys. Rev. E* **47**, 3362 (1993).
- [14] Y. Baxter-Drayton and J. F. Brady, Brownian electrorheological fluids as a model for flocculated dispersions, *J. Rheol.* **40**, 1027 (1996).
- [15] D. J. Klingenberg, F. van Swol, and C. F. Zukoski, Dynamic simulation of electrorheological suspensions, *J. Chem. Phys.* **91**, 7888 (1989).
- [16] M. Whittle, Computer simulation of an electrorheological fluid, *J. Non-Newtonian Fluid Mech.* **37**, 233 (1990).
- [17] D. Fertig, D. Boda, and I. Szalai, A systematic study of the dynamics of chain formation in electrorheological fluids, *AIP Adv.* **11**, 025243 (2021).
- [18] D. Fertig, D. m. H. Boda, and I. Szalai, Induced permittivity increment of electrorheological fluids in an applied electric field in association with chain formation: A Brownian dynamics simulation study, *Phys. Rev. E* **103**, 062608 (2021).
- [19] W. Y. Tam, G. H. Yi, W. Wen, H. Ma, M. M. T. Loy, and P. Sheng, New electrorheological fluid: Theory and experiment, *Phys. Rev. Lett.* **78**, 2987 (1997).
- [20] X. Li, X. Gao, G. Sun, and D. Huang, Giant electrostatic interaction between two neutral conducting spheres in a uniform electric field: A theoretical study via the multiple-image method, *Mod. Phys. Lett. B* **36**, 2250085 (2022).
- [21] X. Li, C. Li, X. Gao, and D. Huang, Like-charge attraction between two identical dielectric spheres in a uniform electric field: A theoretical study via a multiple-image method and an effective-dipole approach, *J. Mater. Chem. A* **12**, 6896 (2024).

- [22] A. Bhattacharya and S. Chakraborty, Modulating the selective enrichment and depletion of ions using electrorheological fluids in variable-area microchannels, *Langmuir* **41**, 2347 (2025).
- [23] J.-Y. Hong, M. Choi, C. Kim, and J. Jang, Geometrical study of electrorheological activity with shape-controlled titania-coated silica nanomaterials, *J. Colloid Interface Sci.* **347**, 177 (2010).
- [24] M. L. Jiménez, T. Bellini, The electrokinetic behavior of charged non-spherical colloids, *Curr. Opin. Colloid Interface Sci.* **15**, 131 (2010).
- [25] S. Almajdalawi, V. Pavlinek, M. Mrlik, Q. Cheng, and M. Sedlacik, Synthesis and electrorheological effect of Cr doped TiO₂ nanorods with nanocavities in silicone oil suspensions, *J. Phys.: Conf. Ser.* **412**, 012003 (2013).
- [26] V. Kovaleva, N. Kuznetsov, A. Istomina, O. Bogdanova, A. Vdovichenko, D. Streltsov, S. Malakhov, R. Kamysinsky, and S. Chvalun, Low-filled suspensions of α -chitin nanorods for electrorheological applications, *Carbohydr. Polym.* **277**, 118792 (2022).
- [27] P. Arenas-Guerrero, G. R. Iglesias, Á. V. Delgado, and M. L. Jiménez, Electric birefringence spectroscopy of montmorillonite particles, *Soft Matter* **12**, 4923 (2016).
- [28] J. Yuan, Y. Wang, L. Xiang, X. Zhao, and J. Yin, Understanding the enhanced electrorheological effect of reduced graphene oxide-supported polyaniline dielectric nanoplates by a comparative study with graphene oxide as the support core, *IET Nanodielectrics* **4**, 143 (2021).
- [29] J. Noh, S. Jekal, J. Kim, H.-Y. Kim, Y.-R. Chu, C.-G. Kim, W.-C. Oh, S. Song, H. Sub Sim, and C.-M. Yoon, Vivid-colored electrorheological fluids with simultaneous enhancements in color clarity and electro-responsivity, *J. Colloid Interface Sci.* **657**, 373 (2024).
- [30] H. R. Vutukuri, F. Smalenburg, S. Badaire, A. Imhof, M. Dijkstra, and A. Van Blaaderen, An experimental and simulation study on the self-assembly of colloidal cubes in external electric fields, *Soft Matter* **10**, 9110 (2014).
- [31] C. Li, K. He, W. Sun, B. Wang, S. Yu, C. Hao, and K. Chen, Synthesis of hollow TiO₂ nanobox with enhanced electrorheological activity, *Ceram. Int.* **46**, 14573 (2020).
- [32] C. Li, Z. Wang, L. Wang, Q. Bai, B. Wang, and C. Hao, Synthesis and electrorheological properties of TiOF₂@SiO₂ cubic-like core/shell nanocomposite, *J. Mol. Liq.* **366**, 120335 (2022).
- [33] S. Huang, Z. Li, L. Gao, H. Gao, Z. Xu, J. Lin, and C. Cai, Colloidal polymers of iron oxide cubes prepared by dipolar-driven assembly and in situ welding with silica, *Giant* **9**, 100083 (2022).
- [34] L. Tonti, F. García Daza, and A. Patti, Kinetics of isotropic to string-like phase switching in electrorheological fluids of nanocubes, *J. Chem. Phys.* **157**, 224906 (2022).
- [35] S. C. McGrother, D. C. Williamson, and G. Jackson, A re-examination of the phase diagram of hard spherocylinders, *J. Chem. Phys.* **104**, 6755 (1996).
- [36] P. Bolhuis and D. Frenkel, Tracing the phase boundaries of hard spherocylinders, *J. Chem. Phys.* **106**, 666 (1997).
- [37] D. J. Earl, J. Ilnytskyi, and M. R. Wilson, Computer simulations of soft repulsive spherocylinders, *Mol. Phys.* **99**, 1719 (2001).
- [38] A. Cuetos and M. Dijkstra, Kinetic pathways for the isotropic-nematic phase transition in a system of colloidal hard rods: A simulation study, *Phys. Rev. Lett.* **98**, 095701 (2007).
- [39] A. Patti and M. Dijkstra, Do multilayer crystals nucleate in suspensions of colloidal rods? *Phys. Rev. Lett.* **102**, 128301 (2009).
- [40] R. Ni, S. Belli, R. van Roij, and M. Dijkstra, Glassy dynamics, spinodal fluctuations, and the kinetic limit of nucleation in suspensions of colloidal hard rods, *Phys. Rev. Lett.* **105**, 088302 (2010).
- [41] G. Campos-Villalobos, M. Dijkstra, and A. Patti, Nonconventional phases of colloidal nanorods with a soft corona, *Phys. Rev. Lett.* **126**, 158001 (2021).
- [42] J. A. Wood, Y. Liu, and A. Widmer-Cooper, Crystal nucleation in colloidal rod suspensions: The effect of depletant size, *J. Chem. Phys.* **154**, 244505 (2021).
- [43] A. Patti, D. El Masri, R. Van Roij, and M. Dijkstra, Stringlike clusters and cooperative interlayer permeation in smectic liquid crystals formed by colloidal rods, *Phys. Rev. Lett.* **103**, 248304 (2009).
- [44] M. Piedrahita, A. Cuetos, and B. Martínez-Haya, Transport of spherical colloids in layered phases of binary mixtures with rod-like particles, *Soft Matter* **11**, 3432 (2015).
- [45] Y. Liu and A. Widmer-Cooper, A dissipative particle dynamics model for studying dynamic phenomena in colloidal rod suspensions, *J. Chem. Phys.* **154**, 104120 (2021).
- [46] F. A. García Daza, A. M. Puertas, A. Cuetos, and A. Patti, Microrheology of isotropic and liquid-crystalline phases of hard rods by dynamic Monte Carlo simulations, *J. Mol. Liq.* **365**, 120146 (2022).
- [47] F. A. García Daza, A. M. Puertas, A. Cuetos, and A. Patti, Insight into the viscoelasticity of self-assembling smectic liquid crystals of colloidal rods from active microrheology simulations, *J. Chem. Theor. Comput.* **20**, 1579 (2024).
- [48] M. Rotunno, T. Bellini, Y. Lansac, and M. A. Glaser, Phase behavior of polarizable spherocylinders in external fields, *J. Chem. Phys.* **121**, 5541 (2004).
- [49] T. Troppenz, L. Fillion, R. Van Roij, and M. Dijkstra, Phase behaviour of polarizable colloidal hard rods in an external electric field: A simulation study, *J. Chem. Phys.* **141**, 154903 (2014).
- [50] A. P. Antonov, S. Schweers, A. Ryabov, and P. Maass, Brownian dynamics simulations of hard rods in external fields and with contact interactions, *Phys. Rev. E* **106**, 054606 (2022).
- [51] M. A. Dorsey and C. K. Hall, Directed assembly of magnetic colloidal rods in an external field, *Langmuir* **41**, 3938 (2025).
- [52] S. Escañuela-Copado, A. Martín-Molina, and A. Patti, Molecular simulation of hybrid polymer nanocomposites with organic nanodimers and inorganic nanorods: From structure and dynamics to viscosity, *J. Chem. Phys.* **162**, 174906 (2025).
- [53] A. Moncho-Jordá, A. Cuetos, M. A. Fernandez-Rodríguez, J. Dzubielia, and A. Patti, Capturing structure and morphology in responsive microgels: From intrinsic free energy to collective behavior, *Macromolecules* **58**, 10659 (2025).
- [54] S. V. Nikolov, A. Fernández-Nieves, and A. Alexeev, Behavior and mechanics of dense microgel suspensions, *Proc. Natl. Acad. Sci. USA* **117**, 27096 (2020).
- [55] W. Xie, J. Pu, and J. Gao, A coupled polarization-matrix inversion and iteration approach for accelerating the dipole convergence in a polarizable potential function, *J. Phys. Chem. A* **113**, 2109 (2009).
- [56] D. N. Bernardo, Y. Ding, K. Krogh-Jespersen, and R. M. Levy, An anisotropic polarizable water model: Incorporation of

- all-atom polarizabilities into molecular mechanics force fields, *J. Phys. Chem.* **98**, 4180 (1994).
- [57] F. J. Vesely, *N*-particle dynamics of polarizable Stockmayer-type molecules, *J. Comput. Phys.* **24**, 361 (1977).
- [58] A. Kuijk, T. Troppenz, L. Filion, A. Imhof, R. Van Roij, M. Dijkstra, and A. Van Blaaderen, Effect of external electric fields on the phase behavior of colloidal silica rods, *Soft Matter* **10**, 6249 (2014).
- [59] A. Azari, J. J. Crassous, A. M. Mihut, E. Bialik, P. Schurtenberger, J. Stenhammar, and P. Linse, Directed self-assembly of polarizable ellipsoids in an external electric field, *Langmuir* **33**, 13834 (2017).
- [60] B. W. Kwaadgras, R. Van Roij, and M. Dijkstra, Self-consistent electric field-induced dipole interaction of colloidal spheres, cubes, rods, and dumbbells, *J. Chem. Phys.* **140**, 154901 (2014).
- [61] D. Bedrov, J. P. Piquemal, O. Borodin, A. D. M. Jr., B. Roux, and C. Schroder, Molecular dynamics simulations of ionic liquids and electrolytes using polarizable force fields, *Chem. Rev.* **119**, 7940 (2019).
- [62] P. Cieplak, F. Y. Dupradeau, Y. Duan, and J. Wang, Polarization effects in molecular mechanical force fields, *J. Phys.: Condens. Matter* **21**, 333102 (2009).
- [63] V. M. Anisimov, G. Lamoureux, I. V. Vorobyov, N. Huang, B. Roux, and A. D. MacKerell, Determination of electrostatic parameters for a polarizable force field based on the classical Drude oscillator, *J. Chem. Theor. Comput.* **1**, 153 (2005).
- [64] H. J. Bakker, Reaction-field model for the dielectric response of mixtures, *J. Chem. Phys.* **153**, 054503 (2020).
- [65] D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. Berendsen, Gromacs: Fast, flexible, and free, *J. Comput. Chem.* **26**, 1701 (2005).
- [66] M. Parrinello and A. Rahman, Polymorphic transitions in single crystals: A new molecular dynamics method, *J. Appl. Phys.* **52**, 7182 (1981).
- [67] B. Hess, H. Bekker, H. J. Berendsen, and J. G. Fraaije, LINCS: A linear constraint solver for molecular simulations, *J. Comput. Chem.* **18**, 1463 (1997).
- [68] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, A smooth particle mesh Ewald method, *J. Chem. Phys.* **103**, 8577 (1995).
- [69] P. Tian and G. D. Smith, A molecular-dynamics simulation study of the influence of attractive dispersion interactions on the phase behavior of rigid bead-necklace molecules, *J. Chem. Phys.* **116**, 9957 (2002).
- [70] P. Arenas-Guerrero, Á. V. Delgado, K. J. Donovan, K. Scott, T. Bellini, F. Mantegazza, and M. L. Jiménez, Determination of the size distribution of non-spherical nanoparticles by electric birefringence-based methods, *Sci. Rep.* **8**, 9502 (2018).
- [71] V. Degiorgio, R. Piazza, F. Mantegazza, and T. Bellini, Stretched-exponential relaxation of electric birefringence in complex liquids, *J. Phys.: Condens. Matter* **2**, SA69 (1990).
- [72] T. Bellini, F. Mantegazza, V. Degiorgio, R. Avallone, and D. A. Saville, Electric polarizability of polyelectrolytes: Maxwell-Wagner and electrokinetic relaxation, *Phys. Rev. Lett.* **82**, 5160 (1999).
- [73] P. Arenas-Guerrero, S. Ahualli, Á. V. Delgado, and M. L. Jiménez, Electric birefringence of gold nanorods: Effect of surfactant coating, *J. Phys. Chem. C* **123**, 26623 (2019).
- [74] S. Martín-Martín, Á. V. Delgado, P. Arenas-Guerrero, and M. L. Jiménez, Electro-orientation of Ag nanowires in viscoelastic fluids, *J. Colloid Interface Sci.* **622**, 700 (2022).
- [75] R. Nava, M. A. Ponce, L. Rejon, S. Viquez, and V. M. Castano, Response time and viscosity of electrorheological fluids, *Smart Mater. Struct.* **6**, 67 (1997).
- [76] B. Horváth and I. Szalai, Dynamic dielectric response of electrorheological fluids in drag flow, *Phys. Rev. E* **92**, 042308 (2015).
- [77] M. J. Espín, Á. V. Delgado, and F. González-Caballero, Structural explanation of the rheology of a colloidal suspension under high DC electric fields, *Phys. Rev. E* **73**, 041503 (2006).
- [78] M. J. Espín, Á. V. Delgado, and L. Rejon, Electrorheological properties of hematite/silicone oil suspensions under DC fields, *J. Non-Newtonian Fluid Mech.* **125**, 1 (2005).
- [79] D. Klingenberg, F. Van Swol, and C. Zukoski, The small shear rate response of electrorheological suspensions. I. Simulation in the point-dipole limit, *J. Chem. Phys.* **94**, 6160 (1991).
- [80] M. Lettinga, J. Dhont, Z. Zhang, S. Messlinger, and G. Gompper, Hydrodynamic interactions in rod suspensions with orientational ordering, *Soft Matter* **6**, 4556 (2010).
- [81] G. Kwon, B. J. Sung, and A. Yethiraj, Dynamics in crowded environments: Is non-Gaussian Brownian diffusion normal? *J. Phys. Chem. B* **118**, 8128 (2014).
- [82] V. Pryamitsyn and V. Ganesan, Screening of hydrodynamic interactions in Brownian rod suspensions, *J. Chem. Phys.* **128**, 134901 (2008).
- [83] I. M. Zerón Jiménez, A. J. I. Jabaloyes, A. E. Copado, A. M. Jordá, and A. Patti, Field-induced alignment dynamics in suspensions of polarizable rods, Zenodo (2025), doi:10.5281/zenodo.16603189.