

## Rhythmic Cluster Generation in Strongly Driven Colloidal Dispersions

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We study the response of a nematic colloidal dispersion of rods to a driven probe particle which is dragged with high speed through the dispersion perpendicular to the nematic director. In front of the dragged particle, clusters of rods are generated which rhythmically grow and dissolve by rotational motion. We find evidence for a mesoscopic cluster-cluster correlation length, *independent* of the imposed drag speed. Our results are based on nonequilibrium Brownian dynamics computer simulations and in line with a dynamical scaling theory.

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In recent years particle tracking techniques have been developed to determine the viscoelasticity of soft materials on a microscale [1]. Optical or magnetic tweezers can be used to drag a bead particle through the material in a controlled way. The system's response to the tracer particle reveals its microrheology and provides insight into the viscoelastic response of biological matter [2], colloidal dispersions [3,4], polymer solutions [5], and wormlike micelles [6]. Microrheological measurements are usually based on linear response, employing the intrinsic thermal motion of the probe particle. Much less is known about nonlinear effects that occur when soft materials are subject to strongly driven probe colloids as expressed by a high Péclet number. The best studied examples are colloidal suspensions owing to their model character and direct accessibility by real-space techniques [7]. Striking novel effects in strongly driven colloidal dispersions include force thinning of the microviscosity [8], local jamming in front of the dragged particle [9], and rhythmic bursting of colloids driven through channels [10].

In this Letter we propose a new effect of *colloid cluster generation* by a spherical probe particle which is dragged through the suspension with a high velocity. In contrast to static colloid clustering which was recently observed under equilibrium conditions [11,12], the cluster generation is rhythmic here; i.e., particle clusters grow and dissolve with a characteristic frequency. Correspondingly, along the trace of the moving probe particle, a characteristic cluster-cluster correlation length occurs. While the average cluster size increases monotonically as a function of the drag velocity, the correlation length is found to be *independent* of the velocity for strong drags.

Our results are obtained by Brownian dynamics computer simulations of a two-dimensional (2D) suspension of rodlike colloidal solute particles. The rods are in the nematic phase, and the probe particle is dragged perpendicular to the nematic director and cannot penetrate the rods. We observe the following cluster generation process at high drag speeds: the moving probe particle will touch a rod which is then taken up to its speed forming a particle-

rod complex. This complex successively sweeps together further rods such that a cluster grows in front of the dragged particle. Forcing a collective rotation of the whole cluster, the tracer particle is rushing over the cluster, the cluster slowly dissolves, and the process starts again. In order to quantify and predict the statistics of this process of dynamical cluster generation, we propose a simple dynamical scaling theory. The simulation results for the cluster size distribution, the time-averaged cluster size, and the characteristic cluster correlation length are in agreement with the theory.

The rhythmic cluster generation effect is very general. It is also expected in three dimensions and for tracer and colloidal particles of different shapes. The only condition is that the interaction between the particles possesses an excluded volume region, i.e., a region of impenetrability. Therefore, rhythmic clustering should be observable in many different experimental setups. However, cluster formation is absent for a soft spherical tracer particle in a suspension of soft colloids as simulated in Ref. [13].

The present mechanism of cluster formation may be important for dispersions that coagulate once the interparticle distance drops below a critical distance. Since the average cluster size is governed by the drag speed it is possible to generate rod aggregates with tunable size.

In our simulations, we consider a 2D system of  $N$  charged rodlike particles kept at constant temperature  $T$  via the solvent. The simulation involves a numerical solution of the overdamped Langevin equations using the (short-time) rotational diffusion constant  $D_0^r$  and translational ones  $D_0^{\parallel}$  and  $D_0^{\perp}$ , parallel and perpendicular to the rod axis, for a single noninteracting rod with length  $L_0$  and thickness  $d_0$  [14]. The mutual rod interaction is represented by a segment model in which the total rod charge is equally partitioned over  $n = 13$  equidistant segments located on the rod axis. The interaction potential between two segments  $a$  and  $b$  on rods  $i$  and  $j$  ( $j \neq i$ ) is of the Yukawa type,  $U = U_0 \exp(-\kappa r_{ab}^{ij}) / \kappa r_{ab}^{ij}$  with  $\kappa$  the Debye screening constant and  $r_{ab}^{ij}$  the segment-segment distance. The amplitude is  $U_0 = 6.5 \times 10^{-2} k_B T$  (with  $k_B T$  the thermal

energy) comparable to that of tobacco mosaic virus particles in a salt-free solution under standard conditions for which  $L_0 = 300$  nm,  $d_0 = 18$  nm, and  $\kappa^{-1} \approx 50$  nm [15]. A starting configuration was generated by randomly putting  $N = 900$  rods in a parallel, nonoverlapping configuration such that the nematic director is parallel to the  $y$  axis of a rectangular simulation box of lengths  $L_x$  and  $L_y$ . In all simulations the reduced number density of the nematic system was fixed at  $\rho^* = NL_0^2/L_x L_y = 3.0$ . Equilibration typically required  $10^5$  Brownian time steps of magnitude  $\Delta t = 0.002\tau_0^T$ , measured in units of the typical translational Brownian relaxation time of a free rod  $\tau_0^T = L_0^2/D_0^T$ , with  $D_0^T = (D_0^{\parallel} + 2D_0^{\perp})/3$ . We confirmed that this system is in a 2D nematic phase [16] with a director along the  $y$  axis of the simulation box.

The next step in our simulation is to drag a small sphere through the nematic host structure along the  $x$  axis of the frame. The probe particle is a small repulsive sphere interacting with the rod segments via a truncated and shifted Lennard-Jones potential (setting the Lennard-Jones parameters to  $\sigma_{LJ} = \kappa^{-1}$  and  $\epsilon_{LJ} = k_B T$ ) and a cutoff distance  $2^{1/6}\sigma_{LJ}$ . The particle is trapped in a parabolic potential well which is displaced through the system along  $\hat{x}$  at a constant speed  $v$ . The external potential for the sphere located at position  $\mathbf{r}$  can be written as  $U_{\text{ext}}(\mathbf{r}, t) = A_0|\mathbf{r} - v t \hat{x}|^2$  with a large amplitude  $A_0 = 10^6 k_B T/L_0^2$  for the trapping potential. The particle is dragged until it has traversed the horizontal box size  $L_x$ . Henceforth, we will use a reduced drag speed  $v^* = vL_0/D_0^T$  which expresses  $v$  in units of the Brownian speed of a freely diffusing rod.

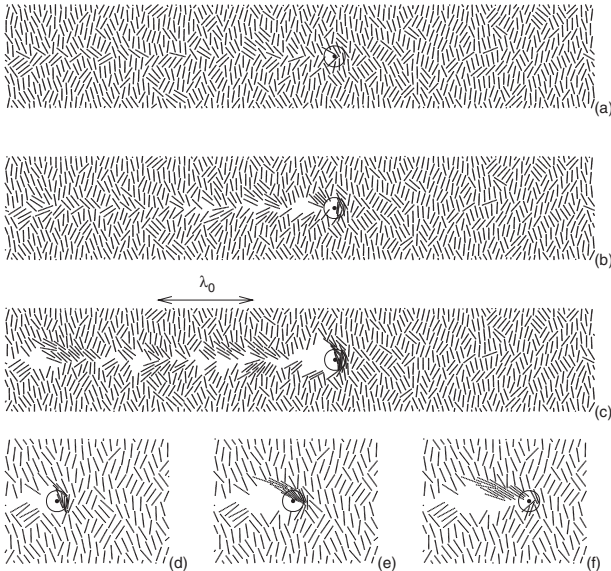


FIG. 1. Snapshots of the nematic structure at (a)  $v^* = 100$ , (b)  $v^* = 1000$ , and (c)  $v^* = 4000$ . The driven sphere is indicated by the encircled dot. The sequence (d)–(f) depicts the growth and rotation of a single cluster at  $v^* = 4000$ . The arrow indicates a cluster-cluster correlation length of  $\lambda_0 = 5L_0$ .

Quantitative results were collected by averaging over consecutive independent initial configurations for the nematic state.

In Figs. 1(a)–1(c) three simulation snapshots are depicted corresponding to a dragging event at increasing drag speeds. At high drag speeds a rhythmic clustering effect is observed, as reflected in Figs. 1(b) and 1(c), in which rods are pushed together into an anisometric cluster which subsequently dissolves by collective rotation under the influence of the force exerted by the dragged sphere. This process is depicted explicitly in a time series of snapshots shown in Figs. 1(d)–1(f). In all snapshots, voids can be observed in the wake of the dragged particle which slowly dissolve over time. The length of the void trail grows continuously with drag speed. The same holds for the void size, indicating that the time needed for the system to relax back to equilibrium also increases with drag speed.

The instantaneous cluster size can be monitored using a simple cluster criterion based on the distance of closest approach of rod pairs located in front of the drag sphere. A rod pair is assigned to a cluster if this distance is smaller than 0.5 times the average distance of closest approach in the equilibrium nematic phase. The rhythmic nature of the clustering is clearly reflected in the cluster time series depicted in Fig. 2. Intermittent behavior is evident from the sudden outburst of a big clustering event after a sequence of smaller ones. We verified that  $N_c(vt)$  does not significantly change upon small variations of the cluster selection criterion. Defining  $\langle \dots \rangle$  as an average over time  $t$ , we observe that  $\langle N_c(vt) \rangle$  increases smoothly as a function of the drag speed, implying that the transition towards a state of rhythmic clustering occurs continuously. To investigate correlations between the cluster events, we have carried out a spectral analysis of the cluster time series. The power spectrum  $S(q)$  represents the Fourier transform of the cluster-cluster autocorrelation function via

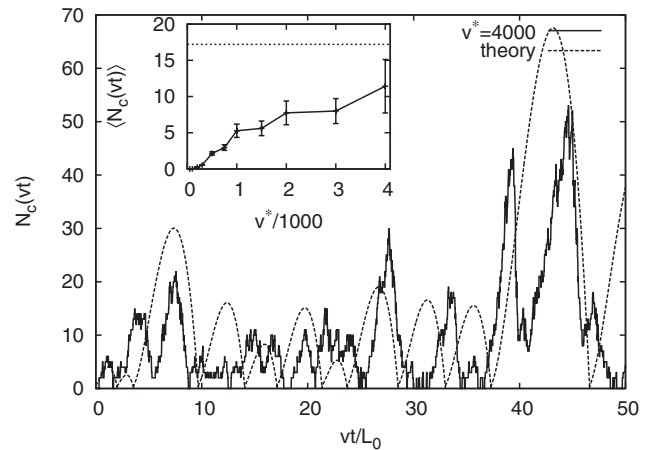


FIG. 2. Time series for the cluster size  $N_c$  for a single drag event. Inset: Time-averaged cluster size  $\langle N_c(vt) \rangle$  versus drag speed. The dashed line  $\langle N_c \rangle = 17.2$  follows from theory.

$$S(q) = \int_{-\infty}^{\infty} dt' \exp[-iqvt'] \langle N_c(vt) N_c[v(t+t')] \rangle$$

with  $q$  the wave number. In the relevant spectral range, all spectra show a dominant peak [see Fig. 3(a)] which we can identify with a typical cluster-cluster *correlation length*  $\lambda_0$ . Whereas the dominant peak is blurred somewhat by the high noise level in the spectra at low speeds, it becomes much more pronounced at  $v^* > 1000$ ; see Fig. 3(a). The location of the dominant peak for various  $v$  is presented in Fig. 3(b). A striking effect is that  $\lambda_0$  does not increase with speed but remains at constant value of roughly  $5-6L_0$ . This result suggests the existence of a typical cluster-cluster correlation length scale for the nonlinear response of a driven system of colloidal rods. The length scale has also been indicated in Fig. 1.

Given the generic character of the clustering mechanism, we expect this length scale to be insensitive to the details of rod pair interactions and to depend only on the concentration  $\rho^*$  of the nematic phase [17]. Moreover, we anticipate dynamic clustering to be *unique* for rodlike systems and do not expect it to occur in dense systems of soft spheres. The reason for this is that two charged rods in 2D have a finite core excluded volume in the limit  $\kappa^{-1} \searrow 0$ , namely,  $V_{\text{ex}} = 2L_0^2 \sin \gamma$  (with  $\gamma$  the angle between the rods), unlike soft Yukawa spheres for which  $V_{\text{ex}} = 0$ . A finite exclusion zone around each particle is a necessary condition for the formation of large force chains that are associated with the clustered particles. To verify this statement we have performed similar drag experiments for dense 2D fluids of Yukawa spheres close to the glass transition using various Lennard-Jones parameters for the sphere-rod interactions. In all cases, no evidence for rhythmic clustering was found up to drag speeds exceeding the present range by several orders of magnitude.

We now propose a simple dynamical scaling theory for the observed behavior. At high drag speeds the external forces exerted by the dragged sphere are much larger than the Brownian forces and the system is governed by overdamped, deterministic motion. The rotational motion of a *single* rodlike cluster with length  $\ell$  under an external torque  $\mathcal{T}$  is then given by  $\xi_r(\ell)\dot{\varphi}(t) = \mathcal{T}$ , with  $\dot{\varphi}$  the

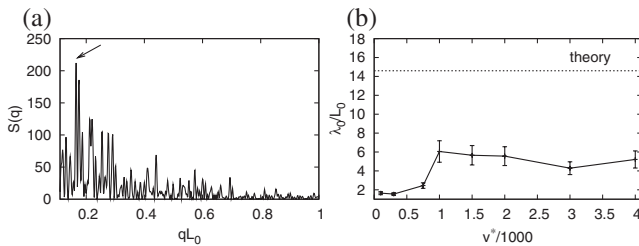


FIG. 3. (a) Power spectrum for  $v^* = 1000$ . The correlation peak is indicated by the arrow. (b) Dominant cluster-cluster correlation length  $\lambda_0$  corresponding to the maximum amplitude of the power spectrum versus speed. The horizontal line is the theoretical result  $\lambda_0 \approx 14.6L_0$ .

time derivative of the angle between the rod axis and  $\hat{y}$  and  $\xi_r = \ell^3 \mathcal{F}(p)$  the rotational friction coefficient of the cluster, with  $\mathcal{F}$  a function of the *cluster* aspect ratio  $p$  [18]. The force  $F$  directed along the  $x$  axis is proportional to  $\ell \cos \varphi$  and the velocity, so we write  $F = v \xi_{\perp}^0 \ell \cos \varphi$ , with  $\xi_{\perp}^0$  the translational friction coefficient of an individual rod. The torque is then given by the force times the vertical component of the arm length  $d$ . We consider  $d$  to be a *dynamical* angle-dependent variable proportional to speed, i.e.,  $\dot{d} = v \sin \varphi$ . Finally, we assume the growth of the cluster length to be proportional to the speed while an increased inhibition is expected as the cluster rotates towards the  $x$  direction. This gives  $\dot{\ell} = v L_0 a^{-1} \cos \varphi$ , where the additional length scale  $a$  pertains to the nearest neighbor distance in the nematic phase. It can be quantified from a simple cell description as sketched in Fig. 4(a). If we assume each rod to be confined to a rectangular cage, we can directly obtain  $a^* = a/L_0$  from the concentration of the nematic phase, via  $2a^* = (1 + 4/\rho^*)^{1/2} - 1$ , giving  $a^* = 0.264$  for  $\rho^* = 3$ . We also assume the cluster aspect ratio  $p$  to be a constant inversely proportional to  $a^*$ , i.e.,  $p = 1/a^*$ . Gathering all contributions gives a set of three coupled dynamical nonlinear equations:

$$\begin{aligned} v^{-1} \dot{\varphi} &= \Theta(x) \xi_{\perp}^0 \mathcal{F}^{-1} \ell^{-2} d \cos \varphi, \\ v^{-1} \dot{d} &= \sin \varphi, \\ v^{-1} \dot{\ell} &= a^{*-1} \cos \varphi, \end{aligned} \quad (1)$$

with initial values  $\{\varphi_0, d_0, L_0\}$  at  $t = 0$ . It is important to note that the velocity can be *scaled out* of Eq. (1) using the total drag distance  $vt$  as the independent variable. A step function  $\Theta(x)$  with  $x = (\ell/2) \cos \varphi - d$  has been included for consistency reasons to stop the rotation and growth process once the arm length exceeds  $\ell/2$ .

Because of the external force the rod is pushed toward the edges of the cell, indicated in Fig. 4(b), and we may define a *typical* cage deflection angle given by  $\varphi_m = \sin^{-1} a^*$  and associated arm component  $d_m^* = (a^* + 1 - \cos \varphi_m)/2$ . If we use these as the initial values for Eq. (1) we numerically obtain a dominant cluster length scale of  $\lambda_0 = vt(\dot{\varphi} = 0) = 14.6L_0$  in qualitative agreement with the simulation data; see Fig. 3(b). The overestimation is

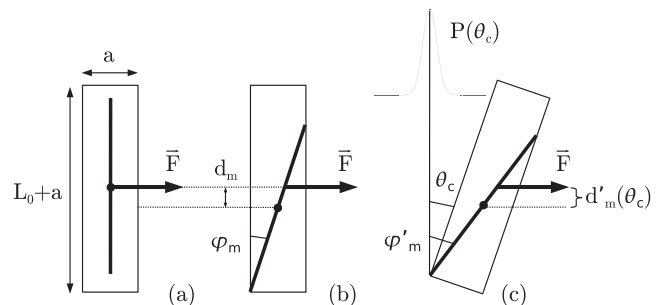


FIG. 4. Sketch of the cage model used in the scaling theory.



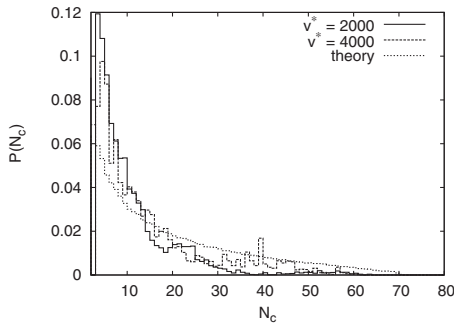


FIG. 5. Distribution of the cluster size  $N_c$  for large speeds.

probably due to the somewhat crude nature of the cage model and the neglect of Brownian fluctuations which are expected to play a role in the initial stages of cluster formation.

Fluctuations around the dominant length scale can be introduced by noting that the rods are not all parallel due to local orientational fluctuations around the nematic director  $\hat{y}$ . Therefore, we can introduce an angle  $\theta_c$  measuring the deflection angle of the cage from its parallel orientation  $\theta_c = 0$ . The fluctuation strength can be roughly quantified by a nematic order parameter  $0 \leq S_z \leq 1$ , defined as  $S_z = \langle \sum_i \cos 2\theta_i / N \rangle$  with  $0 \leq \theta_i \leq \pi/2$  the angle between rod  $i$  and  $\hat{y}$ . We measured  $S_z \approx 0.8$ . Assuming the cell orientation angle  $\theta_c$  to obey a Gaussian distribution  $P(\theta_c) \propto \exp[-\theta_c^2/2(1 - S_z)^2]$ , we can construct a series of cluster events by solving Eq. (1) for 1000 consecutive sets of initial values  $\{\varphi_m + \theta_c, d'_m(\theta_c), L_0\}$ , with  $0 \leq \theta_c \leq \pi/2$  sampled *randomly* from the Gaussian distribution [see also Fig. 4(c)]. The cluster size  $N_c$  can be obtained by multiplying the area fraction of the cluster rectangle located ahead of the sphere with the typical rod concentration  $\rho_c^*$  inside the cluster, which we estimate at  $\rho_c^* \approx 6.0$  from our simulations. From the time series (included in Fig. 2) we can extract the average cluster size  $\langle N_c \rangle$  (Fig. 2) and the distribution function of the cluster size shown in Fig. 5. It can be deduced from Fig. 5 that the strong tail of the distributions at large speeds is correctly reproduced by the theory.

In summary, we have studied the effect of a small colloidal sphere driven through a nematic background at various drag speeds. We observe the formation of rod clusters whose growth is inhibited by collective rotation of the cluster under the influence of the force exerted by the dragged sphere. The growth-inhibition mechanism gives rise to *rhythmic* clustering behavior, quantified by a typical cluster-cluster correlation length which is independent of the imposed drag speed. A simple dynamical model without adjustable parameters is proposed based on overdamped rotational motion of a single rod cluster. The theory predicts a velocity-independent scaling value for

the cluster-cluster correlation length in qualitative agreement with the simulation results.

The observations described in this Letter can be verified in experiments. Various experimental realizations are conceivable: one can confine suspensions of rodlike particles between two parallel glass plates and use an optical tweezer to drag a probe particle through the suspensions. Further setups to test our predictions are nematics anchored at interfaces [19], quasi-2D granular rods [20], or elongated dust rods levitated in a plasma sheath [21]. Qualitatively similar rhythmic clustering is expected in three-dimensional colloidal nematic systems when a thin transversely oriented rod is pulled perpendicular to the nematic director.

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