Switching on high activity in a relatively dense system of active Janus colloids, we observe fast clustering, followed by cluster aggregation towards full phase separation. The phase separation process is however interrupted when large enough clusters start breaking apart. Following the cluster size distribution as a function of time, we identify three successive dynamical regimes. Tracking both the particle positions and orientations, we characterize the structural ordering and alignment in the growing clusters and thereby unveil the mechanisms at play in these regimes. In particular we identify how alignment between the neighboring particles is responsible for the interruption of the full phase separation. Our large scale quantification of the phase separation kinetics in active colloids points towards the new physics observed when both alignment and short-range repulsions are present.

Self-propelled particles show a strong tendency to phase separate or form clusters with various structural and dynamical properties [1–30]. Two limiting scenarios have been identified. When alignment dominates the interactions, a transition to polar or nematic order takes place following a phase separation between a disordered gas and an orientationally ordered liquid. At coexistence, polar bands or nematic lanes dominate the dynamics. This physics is captured in Vicsek-like models [31–34]. When excluded volume interactions dominate and crowding effects slow down the propulsion speed, a motility-induced phase separation (MIPS) takes place: coarsening leads to the formation of one large droplet surrounded by a disordered gas phase [9, 14, 16]. Both scenarios are well understood at the level of large-scale hydrodynamic equations [35–37].

In experimental situations, clustering results from the interplay of several factors such as self-propulsion, excluded volume, alignment and noise, in addition to usual attractive, repulsive and hydrodynamic interactions. Disentangling these effects is a truly challenging task [38], which has motivated a large number of numerical studies [17, 22, 23, 25, 26, 28, 29]. Of particular interest, is the case where alignment and excluded volume are simultaneously present. These are the minimal ingredients at play in the population dynamics of elongated micro-organisms [4, 24, 39–42]. On one hand, it was argued that alignment reduces the rotational diffusion and therefore favors MIPS [28, 29]. On the other hand, recent simulations of self-propelled rods suggest that steric alignment reduces MIPS to a minor part of the phase diagram [30], in agreement with earlier simulations [5, 21].

In this letter, we take advantage of a 2D experimental system of induced-charge electrophoretic self-propelled Janus colloids [43, 44] to study the clustering and coarsening processes (Fig. 1). We specifically focus on the aggregation kinetics and demonstrate that (i) initially, single particles aggregate into clusters, the size of which rapidly increases, first exponentially with alignment playing no role, then following a power law with an exponent prescribed by the Cahn-Hilliard equation; (ii) later, a second regime of aggregation-fragmentation takes place, during which cluster dynamics, composed of rigid body translation and rotation, is dominated by the orientational ordering of the colloids inside the clusters; (iii) finally, the phase separation is eventually interrupted when fragmentation events dominate. It is the intricate interdependence of the structural and polar ordering growth which control the kinetics. In particular in the last regime, the largest clusters break up along grain boundaries, which were formed during their aggregation. These regions populated with defects cannot resist the active stresses
resulting from the partial alignment within the grains.

The experimental system, following [44], is composed of tens of thousands of Janus colloids (silica particles with a diameter \( d \) of 4.28 \( \mu \)m half-coated in 35 nm of titanium followed by 15 nm of silica) in an aqueous solution of 0.1mM NaCl, sandwiched between two ITO coverslips (Diamond Coatings) that were coated with 25 nm of silica, separated by \( \sim 95 \mu \)m thick spacers. The particles form a monolayer, with a surface fraction \( \phi \approx 0.25 \), on the bottom electrode. When a square wave with a frequency of 10 kHz and an amplitude of 10 V is applied, the particles self-propel with their silica side facing forward, as prescribed by induced-charge electrophoresis (ICEP) [45]. We record the dynamics at 50 fps using an Olympus Plan N 20x/0.40 objective and 2048x2048 pixels camera. This allows us to capture the large scale dynamics, while simultaneously tracking the particles positions \( r_k(t) \) and orientations \( n_k(t) \). The nominal velocity of an individual particle is \( v_0 \approx 20d/s \). For such large particles, the rotational diffusion constant \( D_\psi \approx 10^{-2}s^{-1} \) so that the persistent length of the trajectories \( l_p = v_0D_\psi^{-1} \approx 2000d \).

At the working frequency, the dielectric dipole-dipole interactions are weak [44]. A visual inspection of pairwise interactions (see Movie 5 to 8 in Supp. Mat.) however reveals a short-range repulsion (particles never strictly collide), together with some head-to-tail attraction. As a result particles incoming sideways align their directions almost perfectly, while particles colliding head-on don’t align. The total number of particles \( M \) inside the field of view remains approximately constant (\( M = 5500 \)).

In a typical run [46], clustering starts right at the onset of self-propulsion. Clusters are defined using a nearest neighbor criteria, with a cut-off distance \( 1.2d \). Figure 2-(a,b) display the average cluster size, defined as \( \langle s \rangle = \frac{1}{n(t)} \sum_j s_j \), with \( n(t) \) the number of clusters at time \( t \) and \( s_j \) the number of colloids inside cluster \( j \), and the fraction of particles inside clusters of increasing size. One readily distinguishes three regimes. At short time \( t < 2s \), isolated particles aggregate in small clusters of average size \( \langle s \rangle < 10 \) and maximal size \( s_{\text{max}} \approx 250 \) (regime I). The transition to the second regime is marked by the abrupt slowing down of the coarsening, when most of the individual particles have aggregated. \( \langle s(t) \rangle \) remains flat for another 2s before coarsening resumes via a complex fragmentation-aggregation dynamics (regime II). Finally, the phase separation is interrupted at long times \( t = 20s \), leading to a regime dominated by strong fluctuations of the average cluster size around \( \langle s \rangle = 30 \), with \( s_{\text{max}} \approx 2000 \) (regime III).

When the clusters form, they rapidly develop hexagonal order, and polar alignment of the particles. Fig 2-(c) reveals how structural and polar order develops. For each cluster of size \( s \), the structural order is characterized using the hexagonal, respectively hexatic, order parameter \( \psi_h(s) \), hexatic \( \psi_h(s) \), aligning \( \pi \), and polar \( \Pi \), order parameters (see text for definitions).

\[
\psi_h(s) = \frac{1}{s} \sum_{k=1}^s |\psi_h|, \quad \psi_h = \frac{1}{s} \sum_{k=1}^s \psi_6, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|, \quad \psi_6 = \frac{1}{2} \sum_{k=1}^s |\psi_6|. \]

The phase separation is interrupted at long times \( t = 20s \), leading to a regime dominated by strong fluctuations of the average cluster size around \( \langle s \rangle = 30 \), with \( s_{\text{max}} \approx 2000 \) (regime III).

When the clusters form, they rapidly develop hexagonal order, and polar alignment of the particles. For each cluster of size \( s \), the structural order is characterized using the hexagonal, respectively hexatic, order param-

---

**Regime I: Clustering** — The initial aggregation follows a standard route, akin to equilibrium aggrega-

---
Fig. 3. Regime I, Statistics of sizes: (a) Cumulative distribution of the cluster size, \( C_p(s, t) \), for increasing times \( t \in [0, 2] \) s every 0.2 s (from blue to red); inset: \( \langle s(t) \rangle \); the continuous blue line is an exponential fit \( e^{t/t_1} \), with \( t_1 = 25 s \); the continuous red line is a power law fit \( s^\gamma \), with \( \gamma = 2/3 \). (b) Cluster size histogram \( c_s(t) \) as a function of time, for \( s \in [1, 12] \); the continuous lines are fits of the form \( b(t) \propto (t/t_2)^{\gamma/s} \), with \( t_2 = 10 s \), \( p(s) = 0.6 (s-1) \) and \( q(s) = s-1 \) (see text for details).

tion: the cluster size distribution \( p(s, t) \) is exponential at very short times and progressively develops a power law regime. This is best illustrated by the cumulative distribution \( C_p(s, t) = \int_0^s \, d\rho(u, t) \) plotted at successive times on Fig. 3-(a), from which we infer that: \( p(s, t) \propto s^{-\alpha} \exp(-s/s'(t)) \), with \( \alpha \leq 4/3 \), smaller than the typical values \( \alpha \in [1, 7, 2] [6, 19, 27, 47] \), indicating a truly broad distribution of sizes. The crossover size \( s' \) sets the average cluster size \( \langle s \rangle \), the evolution of which is displayed in the inset. The initial exponential growth, expected for an aggregation instability, coincides with the formation of branched clusters (see Fig (1-b)). This initial regime is followed by a power law growth of the cluster size \( \langle s \rangle \sim s^{\gamma} \), with \( \gamma_1 \approx 2/3 \), during which the clusters rapidly become rather compact. The characteristic length \( L \) associated with the clusters growth thus follows \( L \sim s^{\gamma} \), as prescribed by the Cahn-Hilliard equation, which describes the simplest from of phase separation for a conserved field [48]. The short-time dynamics can be further characterized by the cluster size histogram \( c_s(t) = n_s(t)/M \), with \( n_s(t) \) the number of clusters of size \( s \), displayed in Fig (3-b). Assuming constant rate aggregation among clusters, one would show that, starting with an initial state only composed of individual particles, \( c_s(t) = \left( \frac{t/t_1} {1 + (s/t_1)^q} \right)^{-p} \), with \( p(s) = s-1 \) and \( q(s) = s-1 \) [49]. Here we find \( p(s) \approx 0.6 (s-1) \) and \( q(s) \approx s-1 \). The observed differences, especially the fact that for \( t \gg 1 \), \( c_s(t) \) decreases much slower than the prescribed \( 1/t^2 \), indicate that the constant rate aggregation hypothesis does not hold: aggregation process starts competing with evaporation and/or fragmentation events.

— Regime II: Aggregation-Fragmentation — The onset of the second dynamical regime is initially marked by the slowing down of the aggregation process (Fig 2-a). For \( t > 2 s \), most of the particles are already trapped within clusters. They form domains of locally aligned particles ((\( \langle \pi \rangle \) is saturated). These domains point in random directions (Fig 1-c) and thereby prohibit large scale motion. Their size increases ((\( \langle \|\Pi\|\rangle \) slightly increases) until polar correlations reach the cluster size and, after another 2 s, new dynamics set in (Fig 4-c): structural order develops, as indicated by the increase of both the hexagonal \( \langle \psi_{\|}\rangle \) and hexatic \( \langle \psi_{\perp}\rangle \) order parameters, and the combination of local alignment and structural ordering leads to the emergence of rigid-body motion. The dynamics are heterogeneous – some clusters are static, other translate almost at the nominal speed of the individual colloids and others spin, like rigid bodies – and highly intermittent because collisions among the clusters redistribute the alignment of the colloids.

For a given cluster of size \( s \) at time \( t \), we measure the velocity of each colloid \( \bar{v}_k = (r_i(t + \Delta t) - r_i(t))/\Delta t \), with \( \Delta t = 0.02 s \), and subsequently extract the position \( \bar{r} = \frac{1}{s} \sum_{k=1}^s r_k \), velocity \( \bar{v} = \frac{1}{s} \sum_{k=1}^s v_k \) of the center of mass, the radius of gyration \( R_G = \left( \frac{1}{s} \sum_{k=1}^s |\bar{v}_k - \bar{v}|^2 \right)^{1/2} \) and the absolute angular rotation \( \omega = \left| \frac{1}{s} \sum_{k=1}^s (\bar{r}_k - \bar{r}) \times n_k \right| \). Here we assume each colloid exerts a force \( f_k n_k \) on the cluster it belongs to. Then the amplitude of the mean force exerted on a cluster of size \( s \) is simply \( f = f_0 \|\Pi\| \) and the amplitude of the mean torque is \( \tau = f_0 \left[ \frac{1}{s} \sum_{k=1}^s (\bar{r}_k - \bar{r}) \times n_k \right] \).
ure 4-(d), shows how the radius of gyration, the translational and angular velocity, the mean force and the mean torque scale with the cluster size: \( R_G \sim s^{0.5}, \  \langle v \rangle \sim s^{-0.25}, \ \omega \sim s^{0.0}, \ f \sim s^{-0.25} \) and \( \tau \sim s^{3.0} \). As a result, the translational drag coefficient \( \xi_t = \frac{f}{\omega} \sim s^{1.0} \) while the rotational drag \( \xi_r = \frac{\omega}{s} \sim s^{2.0} \). Both scalings contrast with the Stokes prediction for a disk, \( \langle \eta \rangle \sim s^0 + \log \text{corrections} \), prohibiting the description of the cluster as a simple solid disk. The obtained scalings are however in agreement with the cumulative drag model proposed to describe active clusters [27]. These scaling laws are of crucial importance since they set the collision frequency amongst clusters, and thereby the temporal scaling of the coarsening dynamics. Within the limited range of dynamics we have access to, we propose the following bounds for the growth of the average cluster size: \( \langle s \rangle \sim t^{3/2} \), with \( \gamma s \in \{2/3, 3/4\} \) (see Fig 2-a). On the theoretical side, there are very few cases where the master equation, governing the probability density of cluster sizes, can be solved exactly and one often restricts the description to the “monomer approximation” [27, 50]. It is however clear that the present dynamics, which mainly involve cluster-cluster processes, would not be captured within such an approximation. Furthermore, the long time scales dynamics never take place, as we shall now see that the phase separation is anyway interrupted.

— Regime III : Interrupted Phase Separation — At long times, one would expect that most colloids aggregate into a few very large clusters (\( s \approx 1000 \)), which eventually merge and form one dense droplet surrounded by a very dilute gas of individual colloids. Coarsening would then saturate because of the finite number \( M \) of colloids. The dynamics are actually far more complex, as evidenced by the large fluctuations observed in the temporal evolution of the mass-weighted average of the cluster size \( \langle m \rangle (t) = \sum_n \frac{n^2}{\sum n} \) (Fig. 5-(a)). Frequent very sharp breaking events take place, which, as we shall now argue, result from the imperfect aggregation of the clusters beyond a certain size.

Fig. 5 displays the clusters colored with the three relevant local order parameters, namely the hexagonal one (Fig. 5-b), the hexatic one (Fig. 5-c) and the polar one (Fig. 5-d). The clusters are typically hexagonally ordered (high local hexagonal order parameter) but do not form a unique crystalline domain, namely a set of adjacent particles with the same value of the local hexatic order parameter. The interfaces separating the incoming clusters are thus populated with structural defects. The polar ordering is also not realized at the cluster scale and one clearly identifies separated sets of adjacent and aligned particles. Not only the recently formed aggregate is not polar ordered, also the incoming clusters are not and present a few domains of aligned particles. The misalignment within the clusters is responsible for relative and disordered motion of the particles, leading to effective diffusion or super-diffusion, which in turn contributes to the healing of the interfaces populated with defects. This process is rather slow as evidenced by the slow growth of the hexatic order parameter \( \langle \psi_6 \rangle \) (Fig. 2-c). It competes with the intense shear induced in the interfaces by the rotational and, to a lesser extent, translational motions of the incoming clusters. While the shear rate increases with the cluster size like \( R_G \omega \), we expect the healing rate to decrease with the interface size, hence the clusters size. A critical size, above which coarsening is interrupted, is thus always reached, irrespective of the details of the healing mechanism. Altogether the advection induced coalescence is frustrated by the rotational induced shear. Additionally, we also observe spontaneous break up of clusters. Both are promoted by the misbalanced of the aligned sub-domains.

In summary, the coarsening dynamics result from the competition of three types of dynamics, that of Motility Induced Phase Separation, that of structural ordering and that of polar alignment of the particles. The MIPS dynamics is initially the fastest one and rapidly leads to the formation of dense and compact clusters during the first regime. As long as the clusters are not too large, the structural ordering dynamics is fast enough compared to the aggregation rate and the newly formed clusters rapidly become structurally homogeneous. Simultaneously, slower polar ordering develops spatial correla-
tions at the cluster scale. These correlations are responsible for the presence of torques and forces, which in turn ensure the motility of the clusters and thereby set the aggregation rate during the second regime. In the last regime, the clusters have reached sizes such that the structural ordering now competes with the stresses inherited from the misalignment within the aggregating clusters. In this situation the long time state is very much reminiscent of the traffic jam and gliders reported in a simulations of active rods [5]. Depending on the relative growth rate of the three types of dynamics, one may expect different asymptotic states, leaving space for yet unexplored collective organizations. We therefore expect our work to motivate further numerical studies in the spirit of [30].

— Acknowledgments — We thank Chantal Valeriani and Julien Tailleur for inspiring discussions and Jeroen Rijks for his contribution to the initial research. MNvdL acknowledges support from H2020 Marie Sklodowska-Curie Individual Fellowship “TOPACT”.

[1] F. Peruani, A. Deutsch, and M. Bär, Phys. Rev. E 74, 030904 (2006).
[2] F. Peruani, L. Schimansky-Geier, and M. Bär, The European Physical Journal-Special Topics 191, 173 (2010).
[3] J. Deseigne, O. Dauchot, and H. Chaté, PRL 105, 098001 (2010).
[4] M. E. Cates, D. Marenduzzo, I. Pagonabarraga, and J. Tailleur, Proceedings of the National Academy of Sciences 107, 11715 (2010).
[5] F. Peruani, T. Klaus, A. Deutsch, and A. Voss-Boehme, Phys. Rev. Lett. 106, 128101 (2011).
[6] F. Peruani, J. Starruß, V. Jakovljevic, L. Søgaard-Andersen, A. Deutsch, and M. Bär, Phys. Rev. Lett. 108, 098102 (2012).
[7] J. Schwarz-Linek, C. Valeriani, A. Cacciuto, M. E. Cates, D. Marenduzzo, A. N. Morozov, and W. C. K. Poon, Proceedings of the National Academy of Sciences of the United States of America 109, 4052 (2012).
[8] I. Theurkauff, C. Cottin-Bizonne, J. Palacci, C. Ybert, and L. Bocquet, PRL 108, 268303 (2012).
[9] F. Fily and M. C. Marchetti, Phys. Rev. Lett. 108, 235702 (2012).
[10] F. D. C. Farrell, M. C. Marchetti, D. Marenduzzo, and J. Tailleur, PRL 108, 248102 (2012).
[11] S. M. Fielding, arXiv (2012), 1210.5464v1.
[12] J. Palacci, S. Sacanna, A. P. Steinberg, D. J. Pine, and P. Chaikin, Science 339, 936 (2013).
[13] I. Buttinoni, J. Bialké, F. Kümmel, H. Löwen, C. Bechinger, and T. Speck, PRL 110, 238301 (2013).
[14] M. E. Cates and J. Tailleur, EPL (Europhysics Letters) 101, 20010 (2013).
[15] G. S. Redner, M. F. Hagan, and A. Baskaran, PRL 110, 055701 (2013).
[16] J. Stenhammar, A. Tiribocchi, R. J. Allen, D. Marenduzzo, and M. E. Cates, PRL 111, 145702 (2013).
[17] B. M. Mogenthaler, A. Šarić, S. Angioletti-Uberti, A. Cacciuto, C. Valeriani, and D. Frenkel, PRL 111, 245702 (2013).
[18] Y. Fily, S. Henkes, and M. C. Marchetti, Soft Matter 10, 2132 (2014).
[19] D. Levis and L. Berthier, Phys. Rev. E 89, 062301 (2014).
[20] J. Stenhammar, D. Marenduzzo, R. J. Allen, and M. E. Cates, Soft Matter 10, 1489 (2014).
[21] S. Weitz, A. Deutsch, and F. Peruani, Phys. Rev. E 92, 012322 (2015).
[22] E. Mani and H. Löwen, Phys. Rev. E 92, 032301 (2015).
[23] C. Tung, J. Harder, C. Valeriani, and A. Cacciuto, Soft Matter 12, 555 (2015).
[24] G. Liu, A. Patch, F. Bahar, D. Yllanes, R. D. Welch, M. C. Marchetti, S. Thutupalli, and J. W. Shaeveitz, arXiv (2017), 1709.06012v1.
[25] A. Patch, D. Yllanes, and M. C. Marchetti, Phys. Rev. E 95, 012601 (2017).
[26] F. Alarcón, C. Valeriani, and I. Pagonabarraga, Soft Matter 13, 814 (2017).
[27] F. Ginot, I. Theurkauff, F. Detcheverry, C. Ybert, and C. Cottin-Bizonne, Nature Communications, 1 (2018).
[28] A. Martin-Gómez, D. Levis, A. Díaz-Guilera, and I. Pagonabarraga, Soft Matter 14, 2610 (2018).
[29] E. Sese-Sansa, I. Pagonabarraga, and D. Levis, arXiv (2018), 1807.07497v1.
[30] X.-q. Shi and H. Chaté, arXiv (2018), 1807.02949v2.
[31] T. Vicsék, A. Czirók, E. Ben-Jacob, I. Cohen, and O. Shochet, Phys. Rev. Lett. 75, 1226 (1995).
[32] H. Chaté, F. Ginelli, and R. Montagne, PRL 96, 170 (2006).
[33] H. Chaté, F. Ginelli, G. Grégoire, and F. Raynaud, Phys. Rev. E 77, 046113 (2008).
[34] A. P. Solon, H. Chaté, and J. Tailleur, Phys. Rev. Lett. 114, 068101(2015).
[35] J. Toner and Y. Tu, Phys. Rev. E 58, 4828 (1998).
[36] A. Peshkov, E. M. Bertin, F. Ginelli, and H. Chaté, The European Physical Journal-Special Topics 223, 1315 (2014).
[37] M. E. Cates and J. Tailleur, Annual Review of Condensed Matter Physics 6, 219 (2015).
[38] P. Ball, Physics 6, 134 (2013).
[39] E. Ben-Jacob, I. Cohen, and H. Levine, Advances in Physics 49, 395 (2000).
[40] D. Kaiser, Nature Reviews Microbiology 1, 45 (2003).
[41] C. Dombrowski, L. Cisneros, S. Chatkaew, R. E. Goldstein, and J. O. Kessler, PRL 93, 193 (2004).
[42] Q.-X. Liu, A. Doelman, V. Rottschäfer, M. de Jager, P. M. J. van Hecke, and W. M. van der Aa, Proceedings of the National Academy of Sciences of the United States of America 110, 11905 (2013).
[43] D. Nishiguchi and M. Sano, Phys. Rev. E 92, 052309 (2015).
[44] J. Yan, M. Han, J. Zhang, C. Xu, E. Luijten, and S. Granick, Nature Materials 15, 1095 (2016).
[45] S. Gangwal, O. J. Cayre, M. Z. Bazant, and O. D. Velev, PRL 100, 341 (2008).
[46] The reproducibility of the experiments is discussed in the Supp. Mat.
[47] G. S. Redner, C. G. Wagner, A. Baskaran, and M. F. Hagan, PRL 117, 166 (2016).
[48] J. W. Cahn and J. E. Hilliard, The Journal of Chemical Physics 28, 258 (1958).
[49] P. L. Krapivsky, S. Redner, and E. Ben-Naim, A kinetic view of statistical physics (Cambridge Univ. Press, New York, NY, 2010).
[50] F. Peruani and M. Bär, New Journal of Physics 15, 065009 (2013).