Active Crystallization

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Motility-induced phase separation (MIPS), the phenomenon in which purely repulsive active particles undergo a liquid-gas phase separation, is among the simplest and most widely studied examples of a nonequilibrium phase transition. Here, we show that states of MIPS coexistence are in fact only metastable for three dimensional active Brownian particles over a very broad range of conditions, decaying at long times through an ordering transition we call active crystallization. At an activity just above the MIPS critical point, the liquid-gas binodal is superseded by the crystal-fluid coexistence curve, with solid, liquid, and gas all coexisting at the triple point where the two curves intersect. Nucleating an active crystal from a disordered fluid, however, requires a rare fluctuation that exhibits the nearly close-packed density of the solid phase. The corresponding barrier to crystallization is surmountable on a feasible time scale only at high activity, and only at fluid densities near maximal packing. The glassiness expected for such dense liquids at equilibrium is strongly mitigated by active forces, so that the lifetime of liquid-gas coexistence declines steadily with increasing activity, manifesting in computer simulations as a facile spontaneous crystallization at extremely high activity.

Introduction.– The equilibrium crystallization of hard spheres [1] is the canonical example of entropically driven ordering of particle configurations: For a range of volume fractions \( \phi \), a fluid of hard spheres in three dimensions (3D) undergoes a symmetry breaking transition into coexisting disordered (fluid) and ordered (solid) phases [2–4]. Boltzmann statistics provide an unambiguous physical interpretation of the driving force for this transition: the free volume generated by ordering permits a more diverse set of particle configurations, whose entropy is the sole contribution to the free energy of hard spheres. This order-disorder transition is entirely geometric in origin and is controlled solely by \( \phi \).

The influence of nonconservative dynamics on the melting transition of hard spheres is an open and important subject in nonequilibrium statistical mechanics: how do driven dynamics compete with entropic geometric forces to create or destroy order? To this end, active Brownian particles (ABPs) have emerged as a paradigmatic minimal model of driven systems and have aided in advancing our general understanding of nonequilibrium phase behavior [7–9]. In the athermal limit, the ABP model has only two distinct control parameters, both geometric in character. Simple dimensional analysis reveals one as \( \phi \) and the other as the ratio of the persistence (or “run”) length of a free particle’s trajectory \( \ell_0 \) to the particle size \( \sigma \). This run length provides a convenient and direct measure of the time-irreversible motion of active particles, allowing for a continuous departure from reversible dynamics (\( \ell_0/\sigma \to 0 \)) [10–12], where equilibrium hard-sphere physics should be precisely recovered.

Further motivating the study of active crystallization is the knowledge that for finite run lengths, ABPs exhibit a distinct geometric transition that has garnered considerable interest: the so-called motility-induced phase separation (MIPS) [7–13, 15]. This uniquely nonequilibrium phenomenon requires no interparticle attraction, yet appears to be a genuine liquid-gas transition, with no evidence of rotational symmetry breaking between the coexisting phases in 3D [16–18]. The apparent and conspicuous absence of an ordered phase for activities in the vicinity of the MIPS phase boundary raises the intriguing question: does the crystallization transition disappear as the system departs from equilibrium?

In this Letter we aim to clarify the relationship between MIPS and crystallization out of equilibrium. To this end, we present results of extensive computer simulations of active Brownian hard spheres, conducted over a broad range of conditions. The majority of computational work on ABPs has focused on repulsive disks in 2D [19–22], where the relationship between MIPS and crystallization is muddied by complications that long obscured the nature of freezing even for hard disks at equilibrium [23, 24]. We instead construct phase diagrams for active Brownian hard spheres in 3D, where the order-disorder transition is straightforward in the equilibrium limit. These results reveal that the crystallization coexistence region in fact expands with increasing activity, engulfing the MIPS phase boundary everywhere except for a narrow range of control parameters. Slightly above the critical activity, the solid-fluid phase boundary intersects the liquid-gas binodal, forming an active triple point where solid, liquid, and gas may coexist. The proximity of the triple and critical points renders nearly the entirety of the MIPS phase boundary metastable, with solid-fluid coexistence being the globally stable configuration. The frequent observation of liquid-gas coexistence (and its apparent stability) is due to the remarkably nar-
row region of the phase diagram where nucleation of an active crystal from a disordered fluid can be readily observed. By locating these regions, we are able to identify the rate-limiting features of the active crystal nucleation landscape.

**Model System.**—We consider the simplest active system that captures the equilibrium crystallization limit for vanishing activity: 3D active Brownian hard spheres. Each of the \( N \) particles experiences three forces: a drag force \(-\dot{\mathbf{x}}\) proportional to the particle velocity \( \dot{\mathbf{x}} \); a conservative (pairwise) interparticle force \( F^C[\mathbf{x}^N] \), where \( \mathbf{x}^N \) is the set of all particle positions; and an active self-propelling force \( F^A = \zeta U_0 \mathbf{q} \). The particle orientations \( \mathbf{q} \) independently obey diffusive 3D rotary dynamics \( \dot{\mathbf{q}} = \Omega \times \mathbf{q} \) where the stochastic angular velocity has mean 0 and variance \( \langle \Omega(t)\Omega(0) \rangle = 2/\tau_R \delta(t) \mathbf{I} \) and \( \tau_R \) is the characteristic reorientation time. We take the interparticle force \( F^C[\mathbf{x}^N; \varepsilon, \sigma] \) to result from a Weeks-Chandler-Anderson (WCA) potential \( 25 \) (characterized by a Lennard-Jones diameter \( \sigma \) and energy scale \( \varepsilon \)) and take \( \zeta U_0, \sigma \), and \( \tau_R \) to be the characteristic units of force, length and time, respectively. The overdamped Langevin equation for the dimensionless velocity \( \dot{x} \) naturally follows as:

\[
\dot{x} = \frac{\ell_0}{\sigma} \left( q + F^C[\mathbf{x}^N; S] \right),
\]

where \( \ell_0 = U_0 \tau_R \). The dimensionless force \( \dot{F}^C \) depends on the reduced positions \( \mathbf{x}^N \) and is fully characterized by the “stiffness” parameter \( S \propto \varepsilon/((U_0 \sigma)) \).

Despite our use of a continuous potential, the limit of hard sphere behavior is very closely approached in these simulations. Lacking translational Brownian motion, which simply attenuates the influence of activity on the phase behavior \( 26 \), these particles strictly exclude volume with a diameter \( d \) set by \( S \). Continuous repulsions act only at distances between \( d \) and \( 2^{1/6} \sigma \), a range that quickly becomes negligible as \( S \) increases. We use a stiffness \( S = 50 \) for which \( d/(2^{1/6} \sigma) = 0.9997 \), effectively achieving hard-sphere statistics. Holding \( S \) fixed to remain in this hard-sphere limit, the system state is independent of the active force magnitude and is fully described by two geometric parameters: the volume fraction \( \phi = N \pi (2^{1/6} \sigma)^3/6V \) and the dimensionless intrinsic run length \( \ell_0/\sigma \).

All simulations were conducted with a minimum of 54,000 particles using the GPU-enabled HOOMD-blue software package \( 27 \). Additional details can be found in the Supplemental Material \( 28 \).

**Phase Diagram.**—The full phase diagram for 3D active hard spheres is presented in Fig. \( 1 \). Initially homogeneous \( 23 \) systems of active hard spheres prepared within the liquid-gas binodal are often observed to spontaneously phase separate, the widely reported MIPS. For all activities within the 3D MIPS phase boundary, the coexisting phases only differ in density, appearing to share precisely the same symmetry. This can be visually appreciated in Fig. \( 1(b) \). More quantitatively, Figs. \( 1(c) \) and \( 1(d) \) show the probability distribution of local density to be bimodal, while \( q_{12} \) (the per-particle Steinhardt-Nelson order parameter \( 29 \) measuring twelve-fold rotational symmetry), is Gaussian distributed to a good approximation.

The critical point associated with this liquid-gas transition is found by assuming critical scaling of the order parameter, which we take to be the difference between liquid and gas phase densities \( \phi_l - \phi_g \). Defining the reduced activity as \( \tau = \ell_0/\sigma \), the order parameter is anticipated to scale as \( \phi_l - \phi_g \propto \tau^{\beta} \) \((\tau > 0)\). By fitting the coexisting densities nearest to the critical point (self-consistently ensuring \( \tau \ll 1 \) for all points used), we extract a critical activity \( \ell_0/\sigma \approx 18.8 \) and critical exponent
Importantly, solid-fluid coexistence was observed to be a stable configuration for a range of $\phi$ at all values of activity – including those in which MIPS is observed. At small activities ($\ell_0/\sigma = 0.05$), our simulations closely recapitulate the equilibrium crystallization transition of hard spheres, with coexisting fluid and solid densities of 0.52 and 0.58, respectively. With increasing activity, we observe a rapid departure [note the logarithmic scale in Fig. 1(a)] from this limit; coexisting densities of both the fluid and solid phases increase markedly. The solid packing fraction quickly approaches the close-packed volume fraction $\phi_{cp} \approx 0.74$ and remains near this value for all $\ell_0/\sigma \geq 5$.

In contrast to the solid density, the activity dependence of the fluid’s coexistence density is nonmonotonic and defines some of the central features of the phase diagram. As the activity is increased from zero, the fluid density rapidly increases to a volume fraction of $\approx 0.59$ (at $\ell_0/\sigma = 5$), then decreases upon reaching the critical activity for MIPS. The fluid density continues to decrease with activity until intersecting the liquid side of the MIPS binodal at an activity ($\ell_0/\sigma = 21.25$) slightly above the critical point. The intersection of these coexistence curves results in an active triple point [40] where gas, liquid, and solid phases can coexist at the densities marked in Fig. 1(a).

For activities above the triple point, the fluid that coexists with the solid phase has a density that is strictly less than the MIPS gas-phase density. As a result, above the three-phase coexistence line, the liquid-gas binodal is entirely engulfed by the solid-fluid coexistence boundary [see Fig. 1(a)]. Systems above the triple point and within the MIPS binodal are observed to be stable for long times in either solid-fluid or liquid-gas coexistence. Establishing the globally stable form of coexistence in the region in question is all that remains to complete our characterization of the phase diagram.

Homogeneous Nucleation and Stability.—In equilibrium, importance sampling of the distribution of an appropriate order parameter would provide an unambiguous resolution to the question of whether solid-fluid or liquid-gas coexistence is globally stable. Despite recent significant progress in the development of importance sampling techniques for nonequilibrium systems [41–49], the ability to comprehensively survey the phase behavior of many-particle active systems [50,52] remains limited. In the absence of these tools, we make a simple appeal to two-state rate theory to identify the relative sta-

\[ \beta = 0.33. \] The latter value agrees suggestively (and perhaps fortuitously) with the 3D Ising universality class. A full critical scaling analysis [30–34] (such as those recently performed on 2D active systems [35–39]) will be required to confirm the robustness of this apparent agreement. The critical density is found to be $\phi_c \approx 0.483$.

The order-disorder transition, by contrast, is notably absent from the literature on 3D ABPs, a direct consequence of formidable nucleation barriers that will be described below [see Fig. 2]. To access this transition, we devise a simulation protocol [28] that biases the system to form FCC crystals, later established as the stable ordered phase for this system. In a nutshell, we initialize the particles in a perfect FCC configuration at $\phi = 0.7$ and perform a uniaxial extension to sweep through $\phi$ and identify regions of solid-fluid coexistence. Long simulations (of duration $2.5 \times 10^4 \sigma/U_0$) are then run to verify the stability of the observed coexistence.

![FIG. 2. Crystal nucleation from metastable active fluids with $\ell_0/\sigma = 50$. (a) Time evolution of $Q_{12}$ and accompanying simulation snapshots (right). (b) Dynamic structure factor $F(k,t)$ evaluated at the wavevector $|k| = k^*$ corresponding to the first peak of $F(k,0)$ [28]. Probe volume occupation probability $P_r(N)$ plotted as a function of $N$ in (c) for $\phi = 0.62$ at various probe diameters $D_p$, and in (d) for $D_p = 6.0\sigma$ at various densities. Lines are Gaussian distributions with the same mean and variance as simulation data.](image)

In equilib-
bility of the two coexistence scenarios. Observing one form of coexistence (e.g., liquid-gas) spontaneously transition to the other (e.g., fluid-solid), and failing to observe the reverse transition, would provide compelling evidence for the global stability of the latter coexistence scenario (and, naturally, the metastability of the former). However, long simulations at many such state points reveal no transitions. As one example, Fig. 1(e) shows the time evolution of the global order parameter $Q_{12} = \langle q_{12} \rangle$ (the particle-averaged $q_{12}$) at $(\ell_0/\sigma = 50, \phi = 0.5)$.

The lack of observation of a spontaneous transition from liquid-gas to solid-fluid coexistence further points to the looming larger question: can we observed the unbiased nucleation of an active crystal from a disordered fluid? We therefore turn to understanding the general forces that sculpt the crystal nucleation landscape and their dependencies on the state parameters $(\ell_0/\sigma, \phi)$.

Figure 2 surveys the nucleation landscape of active crystals from disordered fluids at dense packing fractions outside of the liquid-gas binodal ($\phi > 0.61$ for $\ell_0/\sigma = 50$). In this region of the phase diagram, solid-fluid coexistence is the unambiguously stable system state. We prepare these metastable high-density fluids by the isotropic compression of less-dense fluids [28]. A disordered fluid at $\phi = 0.635$ is observed to remain a liquid on all accessible time scales. Fluids at $\phi \geq 0.64$, by contrast, readily nucleate a tightly packed active crystal (FCC), which grows into a single ordered domain that coexists with a fluid (gas) bubble [see Fig. 2(a)]. The crystal symmetry and coexisting densities are consistent with those obtained from our crystal seeding procedure. Crystal nucleation remains facile up to $\phi = 0.65$ (near the maximal random packing [53]), the limiting density at which a hard-sphere fluid can still relax.

The remarkably narrow window of density ($0.64 \leq \phi \leq 0.65$) where active crystal growth can be observed in simulation makes evident why the 3D active order-disorder transition has, to our knowledge, previously eluded observation. That this nucleation window occurs near maximal packing can be understood from general ideas of classical nucleation theory, which has successfully described the nucleation of 2D active liquids [54, 55]. In this framework, the characteristic crystal nucleation rate should be governed by the product of the inverse fluid relaxation time $\tau_f^{-1}$ and the probability $P_{CN}$ of forming the critical nucleus in the course of spontaneous fluctuations [56].

Based on this perspective, high densities are generally considered inhospitable for nucleation, since fluids typically vitrify near maximal packing, i.e., $\tau_f$ diverges. Highly active fluids, however, exhibit no sign of glassy dynamics up to a density of (at least 57) $\phi = 0.635$, as evidenced by the self component of the dynamic structure factor plotted in Fig. 2(b). Significant arrest only occurs upon reaching the geometrically-frustrated maximal random limit, consistent with the findings in the emerging active glass literature [53, 64].

In the absence of vitrification, near maximally-packed fluids can be favorable for nucleation, since they promote fluctuations that feature solid-like local density. We quantify this enhancement of $P_{CN}$ by calculating the probability $P_{CN}(N)$ to observe $N$ particles in a spherical probe volume $v$ of diameter $D_p$. Much like hard spheres [65] at equilibrium, the distribution is Gaussian for many standard deviations, even for large densities and relatively small probe diameters [see Fig. 2(c)]. For a probe volume comparable in size to a plausible critical nucleus ($D_p = 6\sigma$), solid-like local densities are highly atypical at $\ell_0/\sigma = 50$ for fluids at all densities we have studied, as shown in Figure 2(d). For $\phi \leq 0.635$ such extreme local density fluctuations are so unlikely as to be unobserved in our long simulations. Near $\phi = 0.65$, they become discernible (while still rare), consistent with our observations of successful crystal nucleation.

Discussion and Conclusions.—The near close-packed density of active crystals restricts the region of the phase diagram where nucleation can be observed to near
maximally-packed fluids, where local close-packed fluctuations are accessible. This restriction makes clear why a transition from liquid-gas to solid-fluid coexistence was not observed in the trajectory of Fig. 1(e)] with liquid density $\phi \approx 0.61$: at low activities, the MIPS liquid-phase density is insufficient to nucleate an active crystal. With increasing activity, as the liquid-phase density approaches maximal packing, we indeed observe nucleation above the triple point activity. Consequently, liquid-gas coexistence is only the globally stable state in the narrow interval between the critical and triple points [see Fig. 1(a) inset]. We emphasize that in the athermal hard-sphere limit, no adjustable parameters are available to tune the relative location of the critical and triple points – the close proximity of these points (and the resulting stability implications) is an intrinsic property of the system.

The full phase diagram presented in this work bears a striking resemblance to the phase diagram of traditional equilibrium molecular or colloidal systems with short-ranged attractions. We therefore anticipate that 3D active hard spheres will serve as an important system to generalize the equilibrium arguments used in the construction of solid-fluid phase boundaries (and triple points) to nonequilibrium systems. Finally, we hope that the phase diagram and physical picture of the nucleation landscape provided in this study will aid in guiding ongoing experimental efforts to realize and characterize active crystals.

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[26] Thermal energy adds an additional dimension to the phase diagram that measures its strength relative to activity, \( T = k_B T/(\xi \mu_0 \sigma) \). In the limit that \( T \to \infty \), thermal effects dominate, and active phase behavior vanishes for all \( \ell_0/\sigma \). Our study aims to establish the active (i.e. athermal \( T = 0 \)) limit.
[28] See Supplemental Material at [URL] for additional simulation and calculation details, details and supporting information for constructing the phase diagram and videos of the nucleation process.
Note that three-phase coexistence occurs at a single point in the pressure-activity plane but for a continuous range of $\phi$ in the density-activity plane.

In equilibrium, this probability follows from the critical nucleus free energy barrier height (along the appropriate reaction coordinate) e.g., $P_{CN} \sim \exp[-\Delta G^*/k_BT]$.

We cannot characterize the dynamics the active fluids at $\phi = 0.640$ and 0.645 as the nucleation time is comparable to the fluid relaxation time. The short lifetime of these fluids also precludes the inclusion of these densities in the structural analysis presented in Figs. 2(b) and (c).

In the phase diagrams of the $(\phi, \sigma)$ plane, the coexistence region is found at $\phi = 0.640$ and 0.645, with the critical nucleus free energy barrier height along the appropriate reaction coordinate e.g., $P_{CN} \sim \exp[-\Delta G^*/k_BT]$.