2D phase behaviors of colloidal ellipsoids and rods

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In recent years, the shape of particles has emerged as a key factor influencing their self-assembly and phase behaviors. Understanding the phase behaviors of systems containing shape anisotropic particles remains challenging. In this mini-review, we will summarize our recent experimental studies on the phase behaviors of colloidal systems in which all or part of particles have anisotropic shapes. We focus on two types of shape anisotropic particles, ellipsoids and rods. In particular, it was found that 1) in equilibrium, the anisotropic particles form a nematic phase in 2D, 2) when quenched, they can form a stable glassy state with a two-step glass transition, and 3) when they are dispersed as impurities in a 2D colloidal crystal of spheres, they can destroy the 2D crystal phase. We will discuss the current challenges in the field.
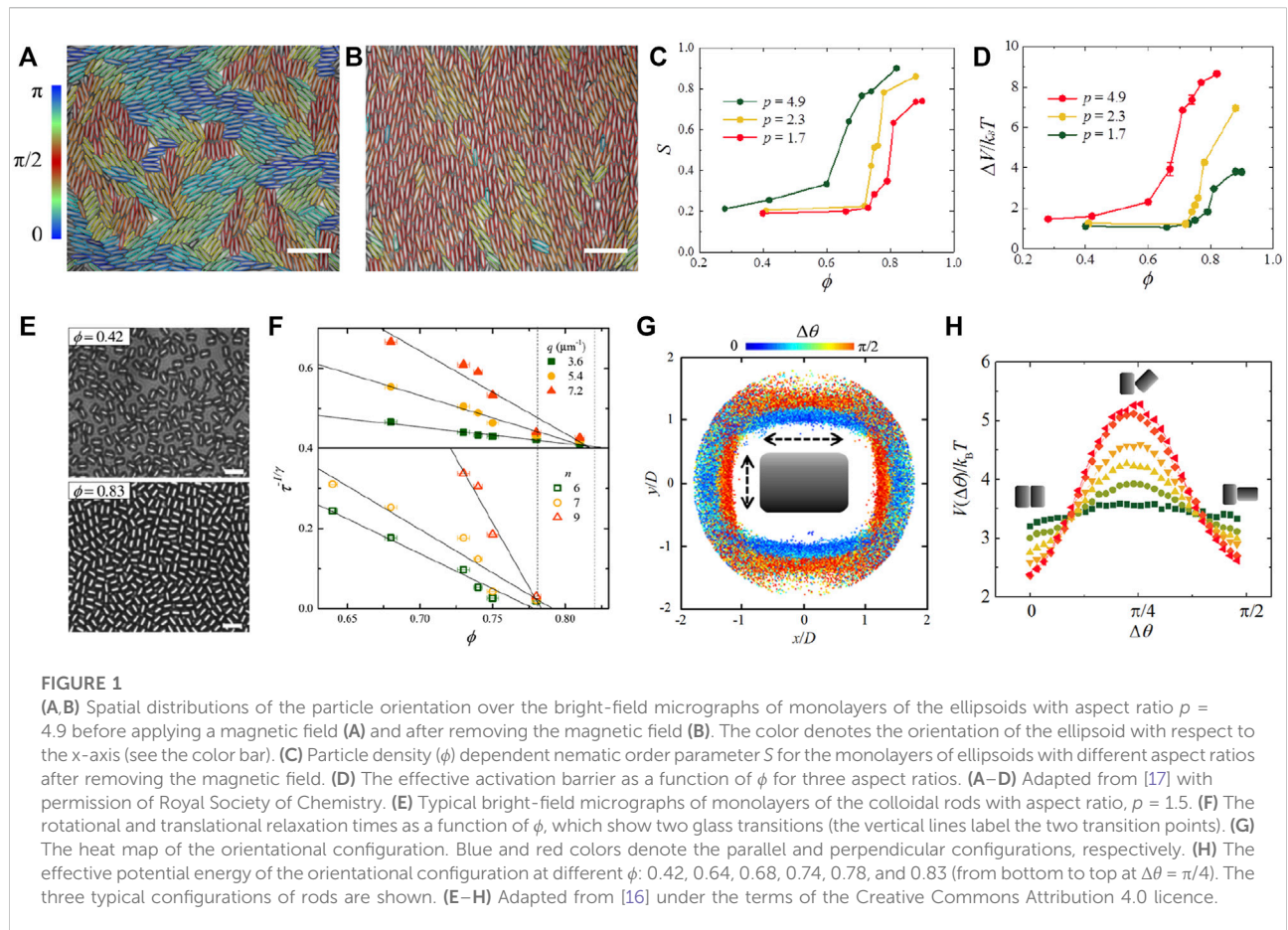
KEYWORDS

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Introduction

Understanding the phase behaviors in condensed matter physics remains a great challenge because many factors including the physical properties of the constituent particles and external environments can influence the phase behaviors. In recent years, colloidal systems have been proposed as excellent model systems to study the self-assembly and phase behaviors because their structures and dynamics can be measured on a single particle scale through video microscopy, which brings great benefits to understanding the mechanism of phase transitions [1, 2]. Due to the development of the synthesis of anisotropic colloidal particles [3–5], new possibilities open up for the studies of the phase behaviors of non-spherical particles in experiments and it is found that the particle shape plays a key role in controlling the self-assembly and phase behaviors [4].

Among various non-spherical colloids, ellipsoids and rods are two typical anisotropic particles. Their phase behaviors have been extensively investigated by simulation and theoretical studies [6–10], which demonstrate that their thermodynamic ground state at high density is a liquid crystal phase even in two dimensions (2D). However, the increase in the density of ellipsoids or rods creates frustration, thus forcing them into a metastable glassy state rather than the equilibrium liquid crystal phase. Therefore, convincing experiments to verify the numerical and theoretical results are urgently needed. On the other hand, previous experimental studies confirm that the ellipsoids are excellent

FIGURE 1
(A,B) Spatial distributions of the particle orientation over the bright-field micrographs of monolayers of the ellipsoids with aspect ratio p = 4.9 before applying a magnetic field **(A)** and after removing the magnetic field **(B)**. The color denotes the orientation of the ellipsoid with respect to the x-axis (see the color bar). **(C)** Particle density (ϕ) dependent nematic order parameter S for the monolayers of ellipsoids with different aspect ratios after removing the magnetic field. **(D)** The effective activation barrier as a function of ϕ for three aspect ratios. **(A–D)** Adapted from [17] with permission of Royal Society of Chemistry. **(E)** Typical bright-field micrographs of monolayers of the colloidal rods with aspect ratio, p = 1.5. **(F)** The rotational and translational relaxation times as a function of ϕ, which show two glass transitions (the vertical lines label the two transition points). **(G)** The heat map of the orientational configuration. Blue and red colors denote the parallel and perpendicular configurations, respectively. **(H)** The effective potential energy of the orientational configuration at different ϕ: 0.42, 0.64, 0.68, 0.74, 0.78, and 0.83 (from bottom to top at $\Delta\theta = \pi/4$). The three typical configurations of rods are shown. **(E–H)** Adapted from [16] under the terms of the Creative Commons Attribution 4.0 licence.

glass-formers [11–13], and their glass transition exhibits a unique feature compared with that of spherical colloids; they experience a two-step glass transition corresponding to the asynchronous freezing of rotational and translational degrees of freedom with increasing particle density. However, the underlying mechanism of the two-step glass transition remains elusive.

The frustration effects due to the shape-anisotropic particles also manifest when a small amount of them are dispersed as impurities in a system of spheres. For example, it is well known that the monodisperse spherical colloids will form a crystal phase at high densities. Once the anisotropic particles are introduced into the system, they serve as impurities. It was found that they have devastating effects on the topological order of the 2D colloidal crystal. Many interesting questions arise as to the physical mechanisms of the impurities effects caused by the anisotropic particles.

In this mini-review, our recent experimental studies on the phase behaviors of colloidal systems containing ellipsoids or rods are summarized. We found that in equilibrium, they form a nematic phase in 2D. When they are quenched, they form a stable 2D colloidal glass. When they are introduced into a system of colloidal spheres as impurities,

they cause a crystal-to-glass transition. The current challenges in the field will be discussed.

Formation of nematic phase in 2D

Although colloids provide excellent experimental systems to investigate phase transitions, such as crystallization and glass transition [14, 15], utilizing the colloidal systems for the study of liquid crystal transition, especially in 2D, remains challenging. The main difficulty is that the systems usually fall into the metastable glassy phase hindering the approaching of the equilibrium liquid crystal phase.

In recent work [15], we used a monolayer of superparamagnetic ellipsoid colloidal particles to study for the liquid crystal transition. We found that the free energy barrier between the metastable glassy phase and the equilibrium liquid crystal phase can be overcome by applying an external magnetic field. Before applying the magnetic field, the system holds an isotropic phase at different particle densities, indicating the spontaneous formation of the glass phase at high density (Figure 1A). When applying the magnetic field, the particles

align along the field direction resulting in the field-induced nematic phase which is independent of the particle density. After removing the magnetic field, the system of low density relaxes back to an isotropic phase while the system of high density remains in the nematic phase (Figure 1B). This demonstrates an isotropic-to- nematic transition with increasing the particle density, experimentally verifying the formation of the nematic phase in 2D. This equilibrium transition is clarified by calculating the nematic order parameter [7] S $(= 1/N \sum_i^N (\cos(2\theta_i))$, where θ_i is the angle between the particle i and the nematic direction) at different particle densities after removing the magnetic field. S increases for the systems composed of ellipsoids with different aspect ratios (Figure 1C), demonstrating the formation of the nematic phase for all aspect ratio at high particle density, which is consistent with the simulation results [7]. The mechanism of the transition is understood by a local kinetic model in which the effective potential energy (V) in the configuration space is determined [16]. The configuration represents the relative orientation between the nearest neighboring particles. The results demonstrate that the parallel configuration is thermodynamically favorable while the perpendicular configuration is unfavorable at high particle density. This leads to an effective activation barrier, $\Delta V = V_{//} - V_\perp$, where $V_{//}$ and $V_\perp$ represent the potential energies for the parallel and perpendicular configurations, respectively. Such effective activation barrier exhibits an increase with increasing particle density (Figure 1D), which freezes the motion in the orientational degrees of freedom at high particle density. Consequently, the ellipsoids remain at the energy favorable configuration, representing a nematic phase at high particle density. Furthermore, the long ellipsoids corresponding to the large barrier (Figure 1D) facilitate the formation of the nematic phase, which reveals the critical role of the shape anisotropy in the isotropic–nematic phase transition.
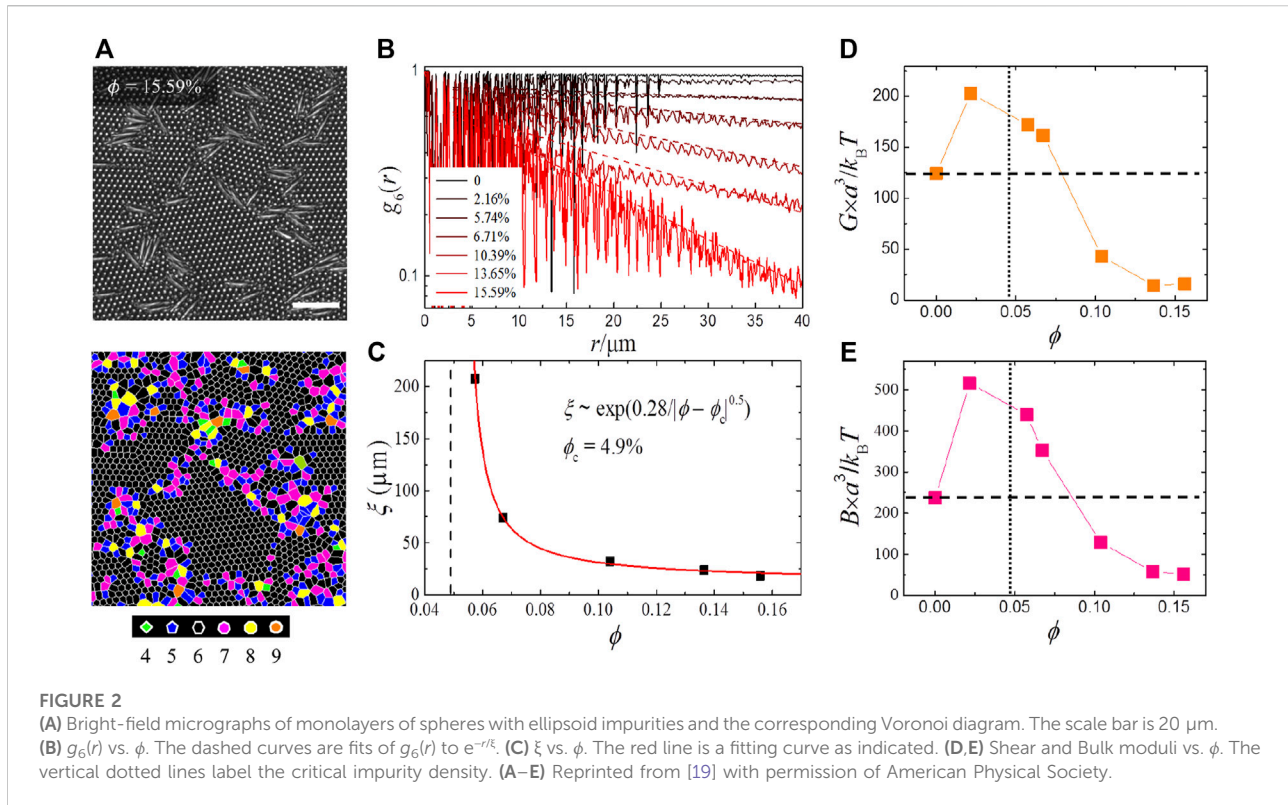
Two-step glass transition

As mentioned above, the ellipsoids tend to fall into a metastable glass state, which is quite stable in laboratory time scales, at high particle densities. More interestingly, their glass transition shows a two-step process; the increase of the particle density leads to the freezing of rotational motions first and then the freezing of translational motions. Despite the extensive study of the ellipsoidal two-step glass transition by colloidal experiments [11–13], the underlying mechanism is still lacking. Previous studies report that at small aspect ratios (<2.5) of the ellipsoids the local nematic domains disappear and the system transforms from the two-step glass transition to a one-step glass transition [12]. Once attractions are introduced between the ellipsoids with small aspect ratios, the local nematic domains appear and the system experiences the two-step glass

transition [13], similar to that of ellipsoids with large aspect ratios (>2.5) [11, 12]. These suggest that the local nematic domains may be the structural origin of the two-step glass transition. However, a recent experimental study of the glass transition of short rods (Figure 1E) reveals that they undergo the two-step glass transition (Figure 1F) with no appearance of the local nematic domains [16]. This calls for a new mechanism for the two-step glass transition. To this end, we proposed [16] the local kinetic model associated with the effective free energy in the configuration space mentioned above to understand the two-step glass transition [16]. By analyzing the heat map of the local configurations (Figure 1G) and their probability distribution, the effective free energy in the orientational configuration space is evaluated. The result demonstrates two energy favorable configurations, parallel and perpendicular configurations, and a significant energy barrier between them at high particle density (Figure 1H). Such energy barrier thus forbids the rotational motions of the particles, but does not affect the translational motions [the particles can move along the axis of the neighboring particles as indicated by the arrows in the heat map (Figure 1F)]. As a result, the rotational and translational motions are decoupled which thus gives rise to the two-step glass transition. Therefore, the energy barrier in the local kinetic model is suggested for the mechanism of the two-step glass transition of the rods, which can apply to the glass transition of ellipsoids. For the ellipsoidal system, the parallel configuration is energy favorable corresponding to the microstructures of local nematic domains and the perpendicular configuration is unfavorable, hence an energy barrier appears which induces the two-step glass transition. When the aspect ratio of the ellipsoids decreases below 2.5, the local nematic domains disappear associated with the negligible energy barrier thus leading the system to a one-step glass transition. In addition, it is worth to note that the two-step glass transition is found independent of the dimension. For 3D ellipsoid systems, it also has been experimentally revealed a liquid glass (orientational glass) phase whose orientational degrees of freedom are frozen but translation is free. This demonstrates the system undergoes the orientational glass transition before the translational glass transition, confirming a two-step glass transition in 3D [18].

2D crystal-to-glass transition due to ellipsoid impurities

Because of the shape mismatch between spheres and anisotropic particles, the anisotropic particles become impurities when their density is low among a system of spheres. We found [19] that the anisotropic impurities can destroy the host crystal phase composed of spheres. This is surprising since they can be viewed as floating disorder. At low density, they are expected to be less destructive than quenched disorder, or random pinning centers. 2D melting

FIGURE 2
(A) Bright-field micrographs of monolayers of spheres with ellipsoid impurities and the corresponding Voronoi diagram. The scale bar is 20 μm.
(B) $g_6(r)$ vs. ϕ. The dashed curves are fits of $g_6(r)$ to $e^{-r/\xi}$. **(C)** ξ vs. ϕ. The red line is a fitting curve as indicated. **(D,E)** Shear and Bulk moduli vs. ϕ. The vertical dotted lines label the critical impurity density. **(A–E)** Reprinted from [19] with permission of American Physical Society.

transition has been studied using numerical simulations and experimental studies [20–23]. The KTHNY theory [24–26] has been validated. Our observation [19] of the destruction of the 2D crystal phase caused by anisotropic impurities raises new and interesting questions.

In this study [19], a 2D colloidal crystal-to-glass transition due to ellipsoid impurities is investigated experimentally through video microscopy. With increasing the density of the ellipsoid impurity (ϕ), the 2D colloidal lattice is destroyed. This is characterized by Voronoi diagrams (Figure 2A, bottom panel), in which the color represents the number of the nearest neighbors (n_i). At high density, it is clearly observed that the number of particles with $n_i \neq 6$ characterizing the defects increases around the ellipsoid impurities, which demonstrates the breakdown of the lattice. To quantify the transition induced by the ellipsoid impurities, the orientational correlation function $g_6(r)$ is calculated (Figure 2B). At low ϕ, $g_6(r)$ displays algebraic decay, indicating that the system holds the quasi-long range orientational order and the ellipsoids act as floating disorder. However, at high ϕ the decay of $g_6(r)$ changes to be exponential. This demonstrates the loss of the quasi-long range orientational order, indicating that the ellipsoid impurity disrupts the host lattice. To illuminate the nature of such transition, the impurity density-dependent correlation length (ξ) of $g_6(r)$ is obtained, which shows an essential singularity $\xi \sim \exp(b/|\phi - \phi_c|^{0.5})$ with a critical impurity density $\phi_c = 0.049$ (Figure 2C), in accordance

with the KTHNY theory [24–26]. Such essential singularity is observed in many other experimental studies of 2D melting [20, 27, 28], demonstrating its universality belongs to the KTHNY paradigm of phase transitions. Interestingly, although the defects become pronounced with increasing the impurity density, the elastic moduli characterizing the mechanical properties of the system change nonmonotonically (Figures 2D,E), which are measured from the dispersion relations calculated from displacement covariance matrices [29–31]. At low ϕ, an impurity strengthening behavior, reflected by the increased moduli, is observed, similar to that in metallurgy [32]. When the impurity density rises above ϕ_c, the elastic moduli decrease accompanied by the loss of the quasi-long range orientational order. As predicted by KTHNY theory, the shear modulus should drop to 0 at the critical point, ϕ_c. However, the observation in the experiment shows no sharp drop in shear modulus at ϕ_c. This is reasonable since the moduli are measured at finite time and length scales, and hence the system is considered a glass phase rather than a liquid phase. In addition, the experiments employ the colloidal samples with a constant large packing density, ~0.89, and varying impurity density [19]. This demonstrates that the system with disordered structures is a glass phase at high impurity density, further characterized by the obvious glassy dynamics [19]. Moreover, the measured elastic moduli show a correlation with the heterogeneous dynamics of the system induced by the increased disordered structures. At high

impurity densities beyond ϕ_c, the homogeneous dynamics of the system corresponds to high moduli, which are larger than those of the host crystal phase without impurities; the heterogeneous dynamics of the system corresponds to small moduli, which are lower than those of the host crystal phase.

Perspectives and challenges

Through the recent colloidal experiments, new insights of the phase behaviors for the system containing ellipsoids or rods are revealed. Nevertheless, there are still lots of challenges. For the nematic phase transition, it has been experimentally verified, while its nature, first-order vs. continuous, remains elusive. The present results suggest that the nature of the transition seems to depend on the anisotropy of the particles (aspect ratio for the ellipsoids). At small anisotropy, the nematic order parameter shows an abrupt increase with increasing the particle density indicating a first-order transition, while at large anisotropy the parameter exhibits a gradual increase suggesting a continuous transition. However, more solid evidences are needed to clarify the nature of the transition. Moreover, besides the nematic phase transition, ellipsoids or rods are predicted to form other interesting phases, such as the smectic phase, depending on their aspect ratio, which has been experimentally observed in suspensions of colloidal rods in 3D [33, 34]. This leaves open the issue whether the same transition will occur in 2D.

Though numerous studies have been paid to understand the nature of glasses, the origin of their apparent rigidity remains poorly understood since there is no long-range order to associate the glasses. For the anisotropic particles, their two-step glass transition is uncovered and the local configurations formed by the particles are found to play a key role in generating the two-step glass transition. It is expected that the local configurations may provide a structural clue to understand the rigidity of glasses. To clarify this, the correlation between the local structures and mechanical properties should be studied.

It is noted that the ellipsoids or rods with small aspect ratios will form a rotator phase, characterized by long-range positional order but short-range orientational order [12, 35]. Although such rotator phase has been experimentally verified in 3D, the corresponding phase behavior formed in 2D remains lacking of experimental evidence. This is an open question that may be studied by utilizing a shape-tunable colloidal system in which particle shapes can be continually switched from ellipsoidal to spherical [36].

The particle shape has been found to play a critical role in the assembly structures. For ellipsoids, they form local nematic domains [11, 12]. In contrast, for rods, the local structures are parallel or perpendicular arrangements [16]. For ellipsoids, the formation of the nematic domains of the ellipsoids depends on the particle aspect ratio [12, 37], but for rod, the aspect ratio seems not to change the local arrangements [16]. These observations suggest that a small difference in particle shape can strongly affect the assembled structures of the particles. Beyond the rod shape, there are lots of other superellipsoid shapes, which can lead to various complex structures and configurations. Therefore, it is envisioned that rich phases will be formed by the superellipsoids [38, 39], which deserve more future studies.

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Conflict of interest

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