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ARTICLE

Observation of Isotropic-Isotropic Demixing in Colloidal Platelet-Sphere Mixtures

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Mixtures of colloids different in size and shape are ubiquitous occurring in nature and industry. The possible existence of isotropic-isotropic (I_1-I_2) demixing of platelets and spheres remains an open question. Here we present direct experimental evidence of I_1-I_2 demixing using platelets of very small thickness-to-diameter ratio mixing with silica spheres at size ratio $q = R_{sphere}/R_{disk} = 0.0901 \pm 0.0004$. The platelets make the isotropic-to-nematic phase transition at very low volume fraction because of their highly anisometric shape. The presence of silica spheres in the suspension accelerates the phase transition and packs the nematic phase more densely via the depletion interaction. Increasing sphere volume fraction to 0.0014, a tri-phase region emerges. This direct observation of I_1-I_2 demixing seems to validate the free-volume scaled particle theory and indicate the need for refinement of the fundamental measure density functional theory.

Introduction

Due to the ubiquitous occurrence of mixtures of colloidal particles in nature and industry, the understanding of the equilibrium properties and phase behaviours of colloidal systems with different sizes and shapes of particles is essential for creating new materials with desired properties and characters.[1] Colloids with a disk or plate shape are abundant in nature, including clay, red blood cells and blood platelets, and many other molecule assemblies. Through mixing, discotic materials can acquire exceptional thermal, electrical, and mechanical properties[2,3] for use in biotechnology[4,5] and nanotechnology.[6]

Since the isotropic-nematic (I-N) transition was attributed by Onsager in 1949 to a pure entropic origin,[7] a plethora of studies of this phase transition have been undertaken.[8-10] During the past few years, binary colloidal mixture systems have attracted much attention.[11-13] As the second component is incorporated, many new phenomena emerge, such as the dependence of demixing on size ratio,[14] the re-entrant phase boundaries,[15] and phase transitions due to the depletion interaction.[16,17]

However, many mixture systems are inclined to gelation,[16,18-20] presenting a challenge in the research of phase transitions in mixtures. Here, we found a platelet-sphere mixture. The zirconium phosphate (ZrP) monolayer suspensions make I-N transition at very low volume fractions due to their small aspect ratio, ξ, which is defined as thickness-to-diameter ratio, and experience no gelation when mixed with silica spheres. Since depletion interaction depends on size ratio $q = R_{sphere}/R_{disk}$, and relatively large and uniform silica spheres are easily obtained, we used relatively large diameter platelets in the experiments.

Still in question is the demixing between two isotropic fluids from the mixture of colloidal platelets and spheres. In previous studies, I-N demixing[13,16] was frequently observed, but isotropic-isotropic (I-I) demixing has seldom been observed. Several theoretical studies were carried out with the goal of better understanding of I-I demixing.[21-23] Here, we provide the direct experimental evidence.

Experimental

The α-zirconium phosphate we used in experiments was synthesized by the hydrothermal method.[24] To start, 6 g zirconium oxychloride ($ZrCl_2O \cdot 8H_2O$) was mixed with 60 ml of 15 M phosphoric acid. The mixture was fed into a 100-ml autoclave, and incubated at 200°C for 24 hours. The product was washed with deionized water by centrifugation for three times, and dried in the oven at 70°C. Tetra-n-butyl-ammonium hydroxide (TBAOH) was used to exfoliate the ZrP crystals. First, 1 g ZrP was dispersed in 10 ml DI water and then mixed with 2.2 ml of 1.5 M TBAOH solution (the molar ratio of ZrP and TBAOH was 1:1). After vortex mixing for 5 min, the mixture was ultrasonicated for 30 min and left for 3 days at room temperature. Centrifugation was used to remove the unexfoliated ZrP crystals. By this process, the monolayers of ZrP were obtained. The silica spheres were synthesized by the

Stöber method.[25] The SEM micrograph of ZrP crystals and TEM micrographs of ZrP monolayers and silica are presented in Fig. 1. Dynamic light scattering (DLS, Beckman Coulter, USA) measured the diameter of ZrP as 1277±160 nm,[26] and the diameter of silica spheres as 115±20 nm.

Samples were prepared by adding appropriate amounts of silica spheres into ZrP monolayer suspensions, which were diluted by DI water to different concentrations, then transferred into 1-ml glass vial. For visual observation of the birefringence, the samples were placed between two cross-polarized polymer films, and images were taken at various times using a Canon 700D digital camera.

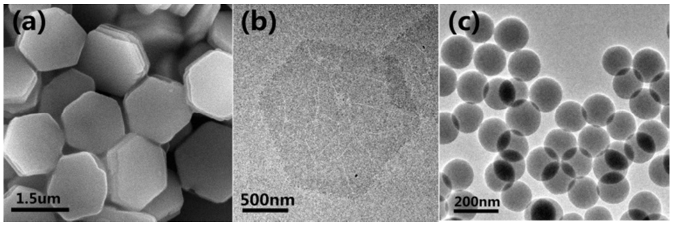

Fig. 1 (a) SEM micrograph of ZrP crystals. (b) TEM micrograph of ZrP monolayers. (c) TEM micrographs of silica spheres.

Results and discussion

A series of samples were made in which the volume fraction of the platelets ranged from 0.06% to 4%, and that of silica spheres ranged from 0 to 0.68%. About seven days after preparation, a clear boundary between I-N bi-phase emerged, the higher the spheres concentration, the faster the boundary arouse. It indicated that the addition of silica spheres accelerates the phase transition of ZrP platelets due to the depletion attraction induced by the spheres. With a low concentration of added spheres, the ZrP platelets exhibited I-N coexistence. Increasing concentration of added spheres, as discussed in detail below, I-I demixing emerged, and a tri-phase coexistence was observed.

As show in Fig. 2, a phase diagram of I-N transition of ZrP suspensions with different amounts of silica spheres was obtained. The equilibrium nematic fractions in the sample were plotted against platelet volume fractions of the samples. Curves were fitted to data using the logistic function, $H = a(1-[1+((\phi/\phi_c)^P])^{-1}$, where H is the nematic fraction; *a*, the upper asymptote; ϕ_c, the volume fraction of ZrP at the maximum rate of the logistic function; and P is defined by $(\phi_c/5)^P = (P-1)(P+1)$. To obtain the nematic fraction, the height of nematic phase is normalized by the sample heights. Since the nematic phase would be compressed by the gravity, a function of nematic fraction as a function of time based on a series of crossed-polarized photographs was constructed (see Ref. [27] for detail) and equilibrium nematic volume was obtained by extrapolating nematic fraction to time zero after sample preparation.

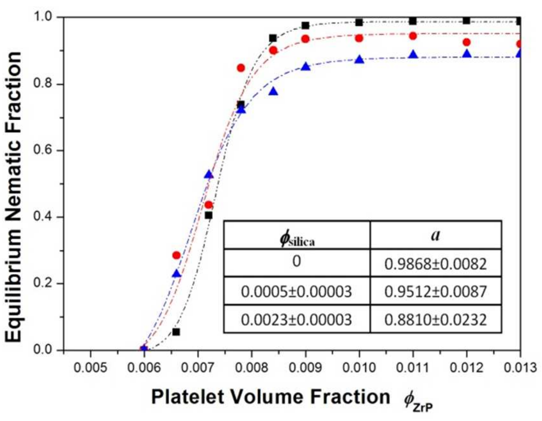

Fig. 2 (color online) The I-N transition phase diagram of ZrP suspension with different amounts of silica. Lines are fit to the data using nonlinear function. From top down, the volume fraction of silica are 0, 0.0005, and 0.0023, which have an error of ±0.00003

The upper asymptote value of N phase decreased as the silica spheres concentration increased due to the significant broadening of the I-N transition, as indicated in Fig. 3 and Fig. 4. The depletion attraction raised from the addition of spheres compresses the ZrP platelets, causing the nematic phase to be packed more closely, resulting in the higher volume fraction ϕ_N of the cloud nematic phase. Looking along ϕ_{ZrP} ~ 0.009 upwards in Fig. 4, the nematic fraction decreased as sphere concentration increased, hence *a* in Fig. 2 decreased. This is because on the tie-line of the coexisting I and N phase, ϕ_N became higher while ϕ_I remained the same, and more N phase was yielded. When the fraction of silica is 0.0023, a tiny amount of isotropic-2 (I_2) exists (with a fraction of 0.03 ± 0.005). We disregard it here for the discussion here of the I-N transition.

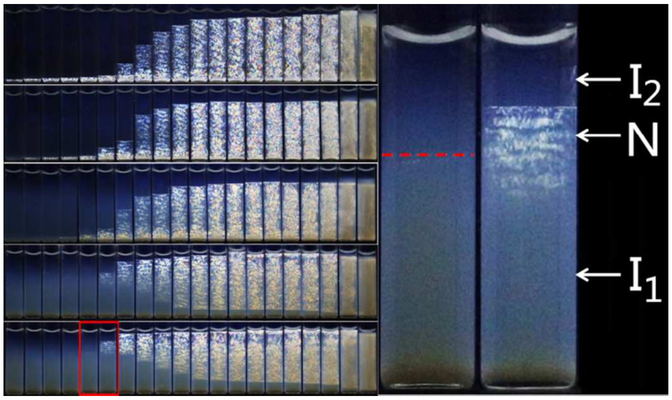

Fig. 3 (Color online) (a) Images of plate-sphere mixtures observed between crossed polarizers 30 days after preparation. From top to bottom, volume fraction of added silica spheres in percentage is 0, 0.05, 0.23, 0.45, and 0.68, the error bar of which is ±0.003. From left to right, volume fraction of ZrP in percentage is 0.36, 0.42, 0.48, 0.54, 0.6, 0.66, 0.72, 0.78, 0.84, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.7, 2, and 3, 4; the error bar is ±0.011. (b) Detail of the two samples boxed in (a), showing I-I demixing and tri-phase coexistence.

Fig. 3(a) shows the appearance of the samples after 30 days. Isotropic-isotropic demixing and isotropic-nematic inversion were observed here when the concentration of spheres was over 0.0014. Normally, the nematic phase is denser than isotropic phase, and appears below the isotropic phase inside the sample holder. An isotropic-nematic phase inversion in a binary mixture of thin and thick hard platelets was observed, and the significant size fractionation in thickness was confirmed by calculation using Onsager's theory. [28] Here, silica spheres and ZrP plates form a denser isotropic phase than the nematic phase with lesser silica sphere fractions. The density of silica, ρ_{silica} = 2.2, is higher than that of ZrP monolayers, ρ_{ZrP} = 1.6. Fig. 3(b) shows detail of the two samples boxed in red in Fig. 3(a), in which the I-I demixing is clearly seen. The left sample had a boundary between I_1 and I_2 phases, as indicated by a red dashed line segment. The right sample demonstrated the existence of the I_1-N-I_2 tri-phase. The isotropic and nematic phase were characterized by SEM separately, as shown in the supplementary information, Fig. S1. The results showed I_2 phase with fewer silica spheres than either the N phase or I_1 phase. The I_1 phase showed the most silica spheres.

The existence of polydispersity may also play a significant role in the phase diagram of sphere-platelet mixture. For our samples, the polydispersity of ZrP platelets is 0.13 and the silica spheres is 0.17, respectively. Fig S2 (supplementary information) compares the influence of platelet's polydispersity on the I-N transition between theory and experiments in a pure platelet system, which indicates that polydispersity would broaden the I-N transition region. Note that for the pure ZrP platelets used here with a 0.13 polydispersity, the I-N coexistence region in volume fraction is 0.0061 - 0.0088, which is consistence with the previous ZrP results.[8] However, for the platelet-sphere mixtures, neither theory nor systematic experimental study of the polydispersity influence is available yet. It waits for future experiments and theoretical calculations.

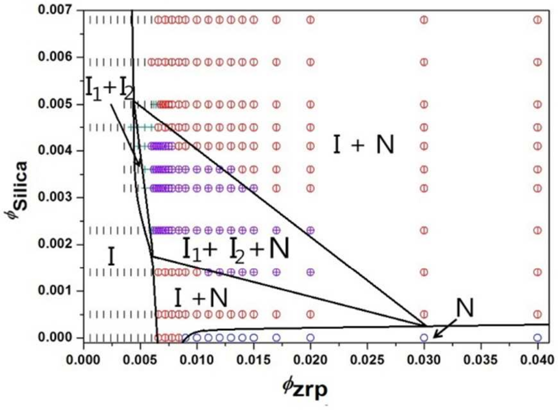

Fig. 4 (color online) Phase diagram as a function of ZrP plate and silica sphere concentrations. Phases observed were isotropic-1 (I_1, —), isotropic and isotropic-2 (I, I_2, │), nematic (N, ○). All data were extrapolated to equilibrium by taking care of sedimentation effect.

A phase diagram (Fig. 4) was constructed based on these experimental observations. The salient features of the phase diagram were the tri-phase (I_1-N-$I_{2)}$ coexisting regions and an isotropic-isotropic (I_1-I_2) coexisting region. The area of the I_1-I_2 coexisting region was quite small because upper limit of the concentration of ZrP platelets in the stable isotropic phase (I) was almost independent of silica sphere concentration. It is necessary to note in Fig. 3a that there was not an apparent sharp boundary between I_1 and I_2 in many samples which contain only I_1 and I_2 phases. As discussed above, below the tri-phase region, the I-N bi-phase gap significant broadened as silica sphere concentration increased.

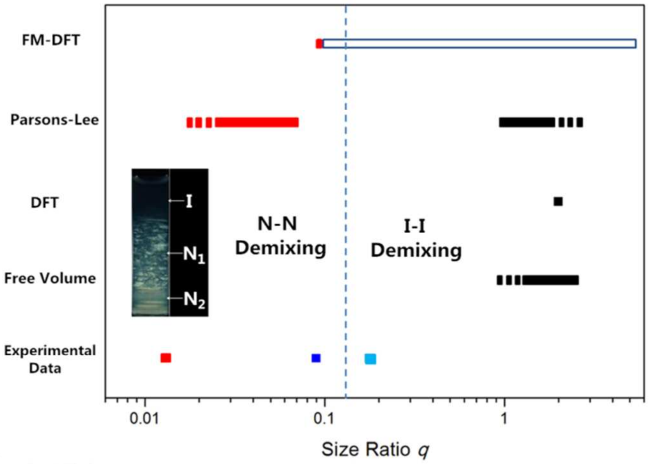

Fig. 5 (color online) The distribution of I-I and N-N demixing with the size ratio, q, in experiments and different theories. Symbol ■ gives the bare size ratio in experiment and ■gives the effect size ratio accounting for ion clouds. The long empty rectangle box▭ stands for neither I-I nor the N-N demixing, while the solid red rectangle ▬ stands for N-N demixing, and the solid black rectangle ▬ stands for the I-I demixing. Dashed rectangles indicate that the limit valve has yet to be determined. The graphic inset shows the experimental observation of N-N demixing at q ~ 0.013(symbol ■). The vertical dotted line indicates the possible boundary between I-I and N-N demixing.

Theoretically, the existence of I-I demixing is still an open question. To study this, different theories, summarized in Fig. 5, have been suggested. Oversteegen et al.[21] predicted an isotropic-isotropic phase separation in mixtures of spheres and platelets using free volume theory, where the I-I demixing took place at the size ratio q < 2.44. Coincidentally, the calculation of Harnau et al.[22] showed an I-I demixing at q = 2, where they extended the geometry-based density functional theory (DFT) for the binary mixture of hard spheres and thin rods to mixtures of hard spheres and thin hard platelets. However, both calculations above neglected excluded-volume interaction among platelets, hence, the obtained results were applicable only in mixtures with low concentration of platelets. According to the Parson-Lee theory, which took two-body interaction into consideration, I-I demixing emerged at size ratio q > 1 [23]. The I-I demixing, therefore, might occur in a relative large size ratio, q, according to the above-mentioned theories, and the value of q in I-I demixing would need to be adjusted when comparing to experimental results due to the intricacies of phase transition dynamics. It is important to note that, as indicated in Fig. 5, our experimental value of q, where the I-I demixing was observed, was significantly less than the current theoretical predictions. It might happen to be at the boundary of the N-N demixing and I-I demixing, because the observed I-I coexistence region was quite small, as shown clearly in Fig. 4.

The I-I demixing, however, might not exist at all, which makes our experimental observation a significant discovery. Heras et al.[23] calculated the phase diagram for mixture of thin circular platelets and spheres using a geometry-based fundamental measure density functional theory (FM-DFT). They did not find I-I demixing for q ranging from 0.1 to 5. In the same reference, they noted a demixing between two nematic phases with different compositions when the size ration q was 0.1, and according to the Parsons-Lee theory,[23] the N-N demixing occurred when $q < 0.067$. Experimentally, we observed here that I-I demixing took place when the bare size ratio of sphere over platelets was $q = 0.0901 \pm 0.0004$. Since the platelets and spheres are negative charged and the mixture with an salt concentration of 0.01 mmol, an effect size ratio $q_{eff} = 0.1779$ was obtained by taking Debye screening length (which was calculated to be about 52.6nm) into consideration.[29-31] Therefore, the I-I demixing prefer to occur at light blue square in Fig.5. We also observed the N-N demixing at $q \sim 0.013$,[32] as shown in the inset of Fig. 5 (for details in supplementary information Fig. S3 and Fig. S4). Our experimental results, therefore, were consistent with theoretical prediction that N-N demixing occurs at relatively small q and I-I demixing at relatively large q. The exact boundary between N-N and I-I demixing still awaits for further experimental and theoretical investigations.

Conclusions

In conclusion, we investigated phase behaviors of ZrP platelet mixtures with silica spheres. The I_1-I_2 demixing and I_1-N-I_2 tri-phase coexistence were discovered. The observation of I-I demixing provides direct experimental evidence to support the theory (for example, free volume [21]]) which predicted the existence of I-I demixing, and also calls for possible refinement of the fundamental measure density functional theory [23] that has not found I-I demixing. The small aspect ratio, ξ, of thickness to diameter of the ZrP monolayers would have played a role in the I-I demixing, which was also the approximation used in the calculations accomplished thus far. [21-23] Small ξ suggests the I-N transition took place at low platelet volume fractions, avoiding the gelation which frequently exists in clay suspensions. Our experimental results were in consistence with theoretical prediction that N-N demixing at relatively small q and I-I demixing at relatively large q. The exact boundary between N-N and I-I demixing still waits for further experimental and theoretical investigations.

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Notes and references

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Electronic supplementary information (ESI) available: SEM for observing the morphology of particles; the influence of platelet's polydispersity in the pure platelet system; and the observation of N-N (nematic-nematic) demixing. See DOI: 10.1039/b000000x/

References

1. L. Bailey, H. N. W. Lekkerkerker and G. C. Maitland, *Soft matter*, 2015, **11**, 222-236.
2. E. Yasuda, T. Enami, N. Hoteida, L. J. Lanticse-Diaz, Y. Tanabe and T. Akatsu, *Mat. Sci. Eng. B*, 2008, **148**, 7-13.
3. R. Verdejo, F. Barroso-Bujans, M. A. Rodriguez-Perez, J. Antonio de Saja and M. A. Lopez-Manchado, *J. Mater. Chem.*, 2008, **18**, 2221-2226.
4. L. J. Bonderer, A. R. Studart and L. J. Gauckler, *Science*, 2008, **319**, 1069-1074.
5. C. Ortiz and M. C. Boyce, *Science*, 2008, **319**, 1053-1054.
6. H.-J. Sue, K. T. Gam, N. Bestaoui, N. Spurr and A. Clearfield, *Chem. Mater.*, 2004, **16**, 242-249.
7. L. Onsager, *Ann. Ny. Acad. Sci*, 1949, **51**, 627-659.
8. A. F. Mejia, Y.-W. Chang, R. Ng, M. Shuai, M. S. Mannan and Z. Cheng, *Phys. Rev. E*, 2012, **85**, 061708.
9. D. Sun, H.-J. Sue, Z. Cheng, Y. Martínez-Ratón and E. Velasco, *Phys. Rev. E*, 2009, **80**, 041704.
10. X. Wang, D. Zhao, A. Diaz, I. B. Nava Medina, H. Wang and Z. Cheng, *Soft matter*, 2014, **10**, 7692-7695.
11. S. Jungblut, R. Tuinier, K. Binder and T. Schilling, *J. Chem. Phys.* , 2007, **127**, 244909.
12. N. Doshi, G. Cinacchi, J. S. van Duijneveldt, T. Cosgrove, S. W. Prescott, I. Grillo, J. Phipps and D. I. Gittins, *J. Phys-Condens. Mat.*, 2011, **23**, 1-10.
13. G. Cinacchi, N. Doshi, S. W. Prescott, T. Cosgrove, I. Grillo, P. Lindner, J. S. Phipps, D. Gittins and J. S. van Duijneveldt, *J. Chem. Phys.*, 2012, **137**, 204909.
14. J. Phillips and M. Schmidt, *Phys. Rev. E*, 2010, **81**, 041401.
15. S. Varga, A. Galindo and G. Jackson, *Mol. Phys.*, 2003, **101**, 817-826.
16. J. Landman, E. Paineau, P. Davidson, I. Bihannic, L. J. Michot, A. M. Philippe, A. V. Petukhov and H. N. Lekkerkerker, *J. Phys. Chem. B*, 2014, **118**, 4913-4919.

17. D. de las Heras, N. Doshi, T. Cosgrove, J. Phipps, D. I. Gittins, J. S. van Duijneveldt and M. Schmidt, *Sci. Rep*., 2012, **2**, 1-5.
18. D. Kleshchanok, V. Meester, C. E. Pompe, J. Hilhorst and H. N. Lekkerkerker, *J. Phys. Chem. B*, 2012, **116**, 9532-9539.
19. Fabrice Cousin, Vale´rie Cabuil, Isabelle Grillo, and Pierre Levitz, *Langmuir*, 2008, **24**, 11422-11430.
20. D. Kleshchanok, J.-M. Meijer, A. V. Petukhov, G. Portale and H. N. W. Lekkerkerker, *Soft matter*, 2012, **8**, 191-197.
21. S. M. Oversteegen and H. N. Lekkerkerker, *J. Chem. Phys.*, 2004, **120**, 2470-2474.
22. L. Harnau and S. Dietrich, *Phys. Rev. E*, 2005, **71**, 011504.
23. D. de las Heras and M. Schmidt, Philosophical transactions. *A Math. Phys. Eng. Sci*., 2013, **371**, 1-16.
24. M. Shuai, A. F. Mejia, Y.-W. Chang and Z. Cheng, *Cryst. Eng. Comm.*, 2013, **15**, 1970-1977.
25. N. Plumere, A. Ruff, B. Speiser, V. Feldmann and H. A. Mayer, *J. Colloid Interf. Sci.*, 2012, **368**, 208-219.
26. P. He, A. F. Mejia, Z. Cheng, D. Sun, H.-J. Sue, D. S. Dinair and M. Marquez, *Phys. Rev E*, 2010, **81**, 026310.
27. H. Li, X. Wang, Y. Chen and Z. Cheng, *Phys. Rev. E*, 2014, **90**, 020504.
28. G. J. V. H. H. Wensink, and H. N. W. Lekkerkerker, *J. Phys. Chem. B*, 2001, **105**, 10610-10618.
29. J. K. G. Dhont, C. Smits and H. N. W. Lekkerkerker, J. *Colloid Interf. Sci.*, 1991, **152**, 386-401.
30. Y.-W. Chang, A. F. Mejia, Z. Cheng, X. Di and G. B. McKenna, *Phys. Rev. Lett.*, 2012, **108**, 247802.
31. Z. Cheng, Q. He. University of Science and Technology of China Press. 2009, 22-23
32. A. Mejia. Discotic Colloids. Doctor of Philosophy Dissertation, Texas A&M University. 2013(August), 200-204.