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Ionic Janus Liquid Droplets Assembled and Propelled by Electric Field

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The traditional Janus particle approaches to produce active motion are based on using solid particles¹⁻⁹ so it is interesting to consider liquid droplets instead. This is especially relevant because, when one uses solid particles, the experimental self-assembly of synthetic active matter normally requires the moving objects to sit in a near-planar 2D (two-dimensional) geometry, and this is a significant limitation. Emulsions,^{10,11} cross-linked polymers,^{12,13} and porous materials¹⁴ have been proposed for 3D self-assembly but with limitations to propel them actively. There are two principal novel aspects of this study. First, it is demonstrated that, having resolved the density mismatch problem that results from the traditional approach of using silica-based and metal-capped Janus solid particles, Janus liquid droplets can be used as building block in an active propulsion system. Second, it is demonstrated that using an ionic liquid motif, the droplet system can be tuned from core-shell to Janus and multipatches, using facile surfactant-based methods. The experimental approach was stimulated by the success of electro-hydrodynamic (EHD) flow produced by alternative (AC) electric field to produce motion of colloidal particles,⁶⁻⁸ here its usefulness to also propel ionic liquids is demonstrated. In this paper we present this new experimental system and discuss the respects in which it resembles, and also differs, from the traditional solid particle approach.

The design requirement for a 3D active propulsion system is to have material with relatively high dielectric constant but low density. We achieve this in aqueous media by forming stable droplet suspensions of ionic liquids (IL) due to wide ranges of tunable properties¹⁵⁻¹⁸ including density, solubility, viscosity, and volatility. Depending on the mix-and-match of their cationic and anionic components, the density of IL is close to that of water. The many available varieties of IL cations with different long hydrophobic alkyl chains are also appealing when designing suspensions to avoid aggregation.¹⁹ In term of generating stable droplets over wide temperature ranges,²⁰ thermal stability of IL is well-known and its temperature related behavior is known in detail.^{21,22}

To produce phase-separated droplets with the tuned Janus asymmetry needed for EHD flow, we employed standard rapid microfluidic injection of ionic liquid and silicone oil into a

glycerol/water medium. As the minority component in the resulting droplets, silicone oil was selected because it possesses significantly lesser dielectric constant than IL as well as low-density. To begin, we screened several IL cations with bis(trifluoromethylsulfonyl)imide functional group as anion (Figure 1a) due to its excellent hydrophobicity in water. Selecting IL droplet with long alkyl chain for cations not only enhanced stability of these droplet dispersions but also avoided spontaneous cationic solvation, which we monitored through increase of solvent conductivity over time (Figure S1). For further study, we chose trihexyltetradecylphosphonium ([P₆₆₆₁₄][NTf₂]) cation as it is insoluble in water on the time scale of 24h. This choice eliminated the possibility of droplet motion due to cation discharging²³⁻²⁵ in subsequent experiments.

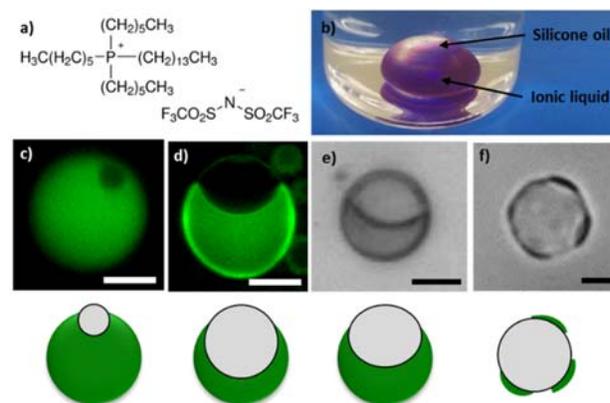


Figure 1. The concept of Janus liquid particle composed of two immiscible liquids, one an ionic liquid (IL) because of the advantages presented by this material. The second liquid in this study was silicon oil. (a) the [P₆₆₆₁₄][NTf₂] ionic liquid and (b) Image of a cm-size Janus droplet in an equilibrium state, showing the less-dense silicone oil at the top. (c, d) Fluorescence imaging of μm-size droplets (green) shows location of ionic liquid within the Janus droplet. (e, f) Bright field microscopy of μm-size droplets (the darker spaces are IL) gives equivalent information but with less contrast. Scale bar is 10 μm.

To prepare the droplets, the parent ionic liquid was subjected to vigorous vortex in excess water. Glycerol and Tween surfactant were added to density match the system (Table S1) and improve the droplet stability. The resulting size distributions (Figure S2) and zeta potential (Table S2) were recorded over time to measure equilibrium states. When to produce Janus droplets of IL was the aim, silicone oil was added at the desired mass fraction before the emulsification step to produce phase-separated liquid droplets (Figure 1b). To offer the capability to visualize phase separation by fluorescence imaging, Nile Red dye was dissolved in the IL. Bright field microscopy also could be used to image the Janus geometry (IL with dye appears darker) but with less contrast. For the most viscous silicone oil (1000 cSt), the phase-separated morphology was Janus IL droplets with added mass fraction of silicon oil directly proportional to its area in the droplet (Figure 1c,d).²⁶ This morphological transition is a metastable state due to interfacial

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author.

tension balance between the two fluids which can be altered by changing the surfactant.^{13,27} Intriguingly, patchy IL droplets (Figure 1e,f), probably the outcome of balance between line tension around the IL domains and electrostatic repulsion between these patches,²⁸ were obtained by using small amounts of silicone oil of lesser viscosity (100 cSt). Presently, the patch size, direction, and orientation are not controllable using our simple emulsification technique but it is not beyond logical extension to tailor high-order droplet generations by known microfluidic methods.²⁹⁻³² This method to produce multiple patches is simpler than those based on metal deposition^{6,9}, asymmetric synthesis or surface modification,^{26,33,34} and forming liquid shells around solid particles,^{7,35} though at the present state of development it is less well controlled.

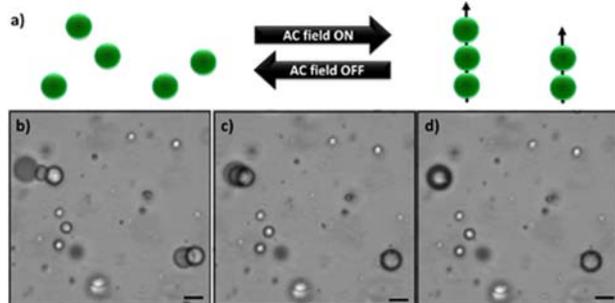


Figure 2. Illustration of reversible assembly of Janus IL droplets. (a) Schematic illustration of self-assembly under electric field owing to induced dipole-dipole attraction resulting in chains aligned in the z direction. The resulting self-assembly was imaged using bright field microscopy imaging after (b) 0s, (c) 6s, and (d) 16s. Scale bar 20 μm . In (b) and (c), note the chain formed by three droplets on the top left and two droplets on the bottom right. Density was matched to the surrounding aqueous medium by using water/glycerol mixtures. An electric field of 1 KHz was applied, 8.3 V/cm. Arrows in (a) call attention to direction of motion between successive frames in Movie S1.

The sample chamber consisted of two planar electrodes separated by a 120 μm spacer, specifically transparent indium tin oxide (ITO) connected to a function generator (1 KHz, 10 V). Thin films of silicon oxide (~ 21 nm) were coated onto the ITO electrodes to increase their hydrophilicity which was crucial to avoid droplet wetting and sticking to the surface. In addition, this thin film maintained the mean average surface roughness of the coated electrode to be around 10 nm (Figure S4). Electric fields were not observed to cause particle rearrangement with the surfactant concentrations that we employed.

First, we demonstrated reversible chain formation of homogeneous IL droplets in density-matched solvent. The images in Figures 2b to 2d, obtained from time-lapse bright field microscopy, show motion of these droplets when AC electric field was applied in the out-of-plane direction. Dielectric constant mismatch with the solvent caused the IL droplets to align their dipole parallel to the electric field direction, with rapid assembly of 1D chains, analogous to the chaining behavior of solid particles induced by dipolar interactions.³⁶⁻³⁸ When electric field was switched off, these chains reversibly disassembled due to thermal motion and long-range electrostatic repulsion between them. Control experiments showed that homogeneous silicone oil droplets exhibited no such responses (not assembly, deformation, or aggregation)³⁹⁻⁴¹ under these electric field conditions. Movie S1 illustrates chaining.

To achieve clearer imaging, in some experiments we mismatched the density and applied the setup to Janus IL droplets sedimented onto the bottom electrode such that the less dense silicone oil side pointed upwards. Upon applying an AC electric field out-of-plane, the initial response was that they rotated their denser IL side to align the dipole moment parallel to the external field (Figures 3b-c). Droplet propulsion resulted (Movies S2 and S3). The direction of motion was perpendicular to the external field with IL at the tail end owing to stronger induced charge and flow imbalance. These droplets were stable and continuously swam in linear directions provided that the droplet concentration remained low. Occasional collisions produced change of direction but without coalescence at this average speed (2.8 $\mu\text{m/s}$).

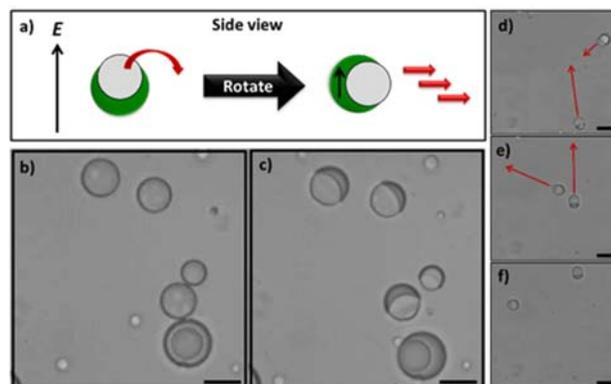


Figure 3. Illustration of internal rearrangement within a moving self-assembled liquid object. (a) Schematic illustration of a Janus droplet whose dipole moment is aligned parallel to the electric field before it translates, with ionic liquid patch at the backside in response to EHD. (b-c) Janus droplets rotate their mutual positions to align with the direction of electric field so that they present a clear divide between silicone oil and ionic liquid (darker region); then (d to f) they translate in space with linear trajectories whose direction in the xy plane is random. The electric field is 1 KHz, 8.3 V/cm out-of-plane. Scale bar 20 μm . In (d) and (e), arrows call attention to direction of motion between successive frames in Movies S2 and S3.

Both patch size and orientation mattered. For example, Figure 4 and Movie S4 show an IL droplet with 2 patches of equal size at the angle, 165° with respect to the center of mass of the bottom patch. EHD theory predicts the direction of motion (Figure 4a). Because in this example the projected 2D area of the bottom patch is $\sim 20\%$ larger than that of the top patch, motion of this droplet motion agrees qualitatively with what one expects owing to the dielectric mismatch. Notably, patchy IL droplets of this composition showed no rotational motion when electric field was applied, retaining their translational direction regardless of their droplet center of mass. The sum of parallel dipoles from IL patches dictated the initial droplet orientation under the action of AC electric field and this direction did not change with time elapsed.

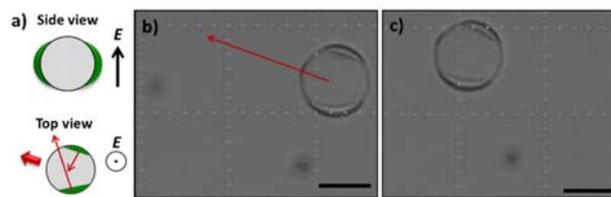


Figure 4. Within liquid Janus particles, velocity vectors perpendicular to each ionic liquid patch determine overall translational direction of the droplet. (a) Schematic illustration. (b, c) Bright field images of active motion for patchy droplet

in 1 KHz (8.3 V/cm, out-of-plane) when electric field is started and after few seconds, respectively. Scale bar 20 μm . Arrows call attention to direction of motion between successive frames in Movie S4.

Finally, we investigated self-assembly of Janus IL droplets in 3D, using density-matched solvent. On the one hand, the droplets tended to assemble parallel to the electric field just as for homogeneous IL droplets, but on the other hand, droplets experienced self-propulsion in random directions within the plane normal to the electric field. The most stable situation resulted from jointly minimizing both dipole mismatch between adjacent patches and flow imbalance between neighboring droplets. Accordingly, we compared dimer assembly between a Janus IL (Figure 5b, top) and a patchy IL droplet (Figure 5b, bottom). In the early stage after electric field was applied, these two droplets swam in different directions; for the Janus particle the IL moiety was on the backside, while for the patchy droplet the larger patch was at the backside (Movie S5). After they collided, the Janus droplet aligned its IL side with the larger patch in the direction expected for a 1D chain architecture, which is the outcome expected if only energy minimization mattered. Subsequently the two droplets traveled as a pair.

It is non-trivial that within this traveling dimer, there ensued secondary adjustment of the orientation as the small patch responded not to the external field but also, interestingly, to the dipole induced on the adjacent Janus droplet. This produced rotation within the traveling chain. As a result, the chain displayed internal twisting motion even though overall it moved in a single direction as concerns its center of mass.

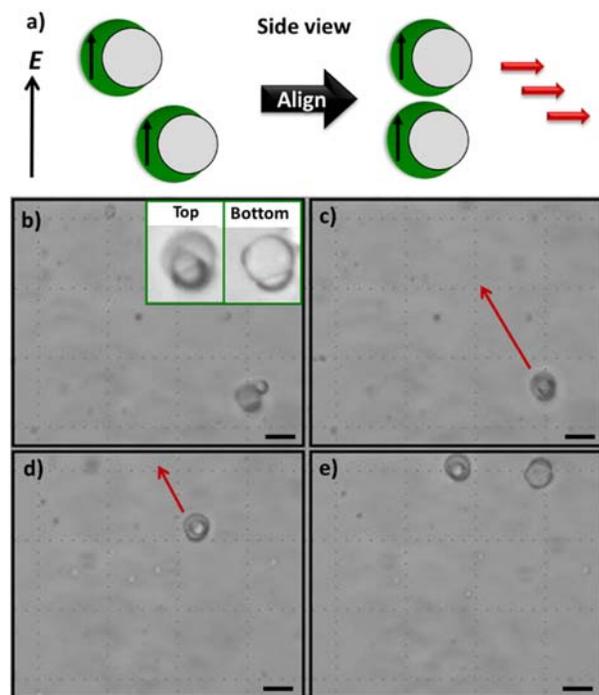


Figure 5. Patch reorientation within traveling Janus droplets of composition described in the text. (a) Schematic illustration of Janus IL droplets after density match with the surrounding aqueous liquid, with electric field applied in the z direction. Chains of droplets form spontaneously. (b) Phase contrast image of 1D chains; the Inset compares the configurations of top and bottom droplets. (c-d) Images of translation in space and center-of-mass balancing inside of a single chain. (e) Electrostatic repulsion between an assembled chain and a multipatch droplet. The incoming droplet is at a slightly higher plane of focus than the top

droplet and is not incorporated into the chain. All interaction is in response to 1 KHz AC field (8.33 V/m, out-of-plane). Scale bar 20 μm . Arrows call attention to direction of motion in successive frames in Movie S5.

This study has the following chief conclusions. First, ionic liquids (and their assembly into Janus particles with polysiloxane liquids) present an interesting platform from which to assemble multi-particle structures especially in 3D such that one can with facility circumvent density mismatch that promotes traditional solid Janus particles to sediment. Second, we have demonstrated that Janus liquid droplets display EHD flow and, more interestingly, internal flows within traveling chains. Lastly, we succeed in generating behavior that was known for solid Janus particles (chaining, swimming and swarming; Figures 2 and 3) while the non-uniform droplets' size (synchronized chain swimming; Figure 5) and patches (directional swimming; Figure 4) generate unexpected behavior that although not yet modelled quantitatively, is presented in this paper for what is considered to be the first time.

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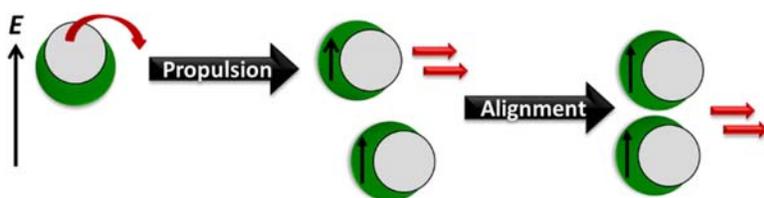
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- (1) Sengupta, S.; Ibele, M. E.; Sen, A. *Angewandte Chemie International Edition* **2012**, *51*, 8434.
- (2) Palacci, J.; Sacanna, S.; Steinberg, A. P.; Pine, D. J.; Chaikin, P. M. *Science* **2013**, *339*, 936.
- (3) Ma, F.; Wang, S.; Wu, D. T.; Wu, N. *Proceedings of the National Academy of Sciences* **2015**.
- (4) Yang, X.; Wu, N. *Langmuir* **2018**, *34*, 952.
- (5) Sacanna, S.; Rossi, L.; Pine, D. J. *J Am Chem Soc* **2012**, *134*, 6112.
- (6) Archer, R. J.; Campbell, A. I.; Ebbens, S. J. *Soft Matter* **2015**, *11*, 6872.
- (7) Zhang, J.; Grzybowski, B. A.; Granick, S. *Langmuir* **2017**, *33*, 6964.
- (8) Li, B.; Zhang, C.; Jiang, B.; Han, W.; Lin, Z. *Flow-Enabled Self-Assembly of Large-Scale Aligned Nanowires*, 2015; Vol. 54.
- (9) Zhang, J.; Luijten, E.; Granick, S. *Annual Review of Physical Chemistry* **2015**, *66*, 581.
- (10) Francis, W.; Fay, C.; Florea, L.; Diamond, D. *Chem Commun* **2015**, *51*, 2342.
- (11) Tsuchitani, S.; Takagi, N.; Kikuchi, K.; Miki, H. *Langmuir* **2013**, *29*, 2799.
- (12) Gong, J. P.; Matsumoto, S.; Uchida, M.; Isogai, N.; Osada, Y. *J Phys Chem-U S* **1996**, *100*, 11092.
- (13) Jeong, J.; Gross, A.; Wei, W. S.; Tu, F. Q.; Lee, D.; Collings, P. J.; Yodh, A. G. *Soft Matter* **2015**, *11*, 6747.
- (14) Ikezoe, Y.; Washino, G.; Uemura, T.; Kitagawa, S.; Matsui, H. *Nat Mater* **2012**, *11*, 1081.
- (15) Greaves, T. L.; Drummond, C. J. *Chem Rev* **2008**, *108*, 206.
- (16) Huang, M. M.; Jiang, Y. P.; Sasisanker, P.; Driver, G. W.; Weingartner, H. *J Chem Eng Data* **2011**, *56*, 1494.
- (17) Lee, D. W.; Im, D. J.; Kang, I. S. *J Phys Chem C* **2013**, *117*, 3426.

- (18) Wakai, C.; Oleinikova, A.; Ott, M.; Weingartner, H. *J Phys Chem B* **2005**, *109*, 17028.
- (19) Gebbie, M. A.; Smith, A. M.; Dobbs, H. A.; Lee, A. A.; Warr, G. G.; Banquy, X.; Valtiner, M.; Rutland, M. W.; Israelachvili, J. N.; Perkin, S.; Atkin, R. *Chem Commun* **2017**, *53*, 1214.
- (20) Ivanov, A. O.; Kantorovich, S. S.; Zverev, V. S.; Elfimova, E. A.; Lebedev, A. V.; Pshenichnikov, A. F. *Physical Chemistry Chemical Physics* **2016**, *18*, 18342.
- (21) Hjalmarsson, N.; Atkin, R.; Rutland, M. W. *Chem Commun* **2017**, *53*, 647.
- (22) Qiao, Y.; Ma, W.; Theyssen, N.; Chen, C.; Hou, Z. *Chem Rev* **2017**, *117*, 6881.
- (23) Im, D. J.; Ahn, M. M.; Yoo, B. S.; Moon, D.; Lee, D. W.; Kang, I. S. *Langmuir* **2012**, *28*, 11656.
- (24) Im, D. J.; Noh, J.; Moon, D.; Kang, I. S. *Anal Chem* **2011**, *83*, 5168.
- (25) Ahn, M. M.; Im, D. J.; Kim, J. G.; Lee, D. W.; Kang, I. S. *J Phys Chem Lett* **2014**, *5*, 3021.
- (26) Zhang, Q. Q.; Xu, M.; Liu, X. J.; Zhao, W. F.; Zong, C. H.; Yu, Y.; Wang, Q.; Gai, H. W. *Chem Commun* **2016**, *52*, 5015.
- (27) Zarzar, L. D.; Sresht, V.; Sletten, E. M.; Kalow, J. A.; Blankschtein, D.; Swager, T. M. *Nature* **2015**, *518*, 520.
- (28) Pontani, L. L.; Haase, M. F.; Raczkowska, I.; Brujic, J. *Soft Matter* **2013**, *9*, 7150.
- (29) Guzowski, J.; Korczyk, P. M.; Jakiela, S.; Garstecki, P. *Soft Matter* **2012**, *8*, 7269.
- (30) Lone, S.; Cheong, I. W. *Rsc Adv* **2014**, *4*, 13322.
- (31) Haase, M. F.; Brujic, J. *Angew Chem Int Edit* **2014**, *53*, 11793.
- (32) Choi, C. H.; Weitz, D. A.; Lee, C. S. *Adv Mater* **2013**, *25*, 2536.
- (33) Bradley, L. C.; Stebe, K. J.; Lee, D. *J Am Chem Soc* **2016**, *138*, 11437.
- (34) Ge, L.; Cheng, J.; Wei, D.; Sun, Y.; Guo, R. *Langmuir* **2018**, *34*, 7386.
- (35) Walther, A.; Müller, A. H. E. *Chem Rev* **2013**, *113*, 5194.
- (36) Vutukuri, H. R.; Demirors, A. F.; Peng, B.; van Oostrum, P. D. J.; Imhof, A.; van Blaaderen, A. *Angew Chem Int Edit* **2012**, *51*, 11249.
- (37) Yanai, N.; Sindoro, M.; Yan, J.; Granick, S. *J Am Chem Soc* **2013**, *135*, 34.
- (38) Yethiraj, A.; van Blaaderen, A. *Nature* **2003**, *421*, 513.
- (39) Vigo, C. R.; Ristenpart, W. D. *Langmuir* **2010**, *26*, 10703.
- (40) Salipante, P. F.; Vlahovska, P. M. *Phys Rev E* **2013**, *88*.
- (41) Rozynek, Z.; Mikkelsen, A.; Dommersnes, P.; Fossum, J. O. *Nat Commun* **2014**, *5*.

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Text for Table of Contents

Melinda Sindoro and Steve Granick*

*Page No. – Page No.*Ionic Liquid Droplets Assembled and
Propelled by Electric Field