Perspective/Overview (**PREPRINT**)

Physical discoveries enabled by ionic liquid droplets , A. Méndez-Vilas, Zenodo (2022),
https://doi.org/10.5281/zenodo.7317133

Physical discoveries enabled by ionic liquid droplets

A. Méndez-Vilas

Independent researcher and freelance science writer (currently), Badajoz, Spain*
*Correspondece: amendezvilas@gmail.com , Phone: +34 644389624
Personal website: https://scholar.google.es/citations?user=i4lMLrYAAAAJ&hl=es
Formerly at CIBER-BBN: the Biomedical Research Networking Center in Bioengineering, Biomaterials and Nanomedicine, Spanish Ministry of Health, and University of Seville (Department of Didactics of Mathematics), Seville, Spain.

1. Introduction

As a physical scientist, my interest in ionic liquids (ILs), which dates back to 2008, stems from the potential applications of their micro- and nano- droplets. At that time we published a review in *Small* on the production, imaging and wetting of ultrasmall droplets, which has been very successful, a success symptomatic of the enormous interest that these minute droplets are arousing.[1] In this current (narrative) overview, my interest is to provide an accessible and entertaining view, in particular of ionic liquid droplets (ILDs) and the new research niches they are finding in Physics, beyond sharing the findings of other research groups. Accordingly, the structure I am going to develop is intended for an easy reading, the reader be a physicist or a biologist, or even an undergraduate science student. If you are not familiar with ILs, what you should know on them for following this work is rather simple: these liquids are salts that are liquid at room temperature, highly polar, non-volatile, electrically conductive, of intermediate viscosity, and that comprise an organic cation and either an organic or inorganic anion. They are considered "designer solvents", because of the virtually inifnite number of them that can be produced, and also as "green" alternative to the volatile organic solvents.[2] As a curiosity, the first produced IL dates back 1914 (by Paul Walden), although no much attention was due to it at that time. ILs are widely used today in fundamental Chemistry and also in industry. To put it in context, the market size of ILs is predicted to reach USD 41.9 million by 2026, with annual growth rates of 11.6% between 2021 and 2026.[3] In Physics, the field is newer so it is especially apt to be developed from a what is usually known as exploratory, discovery or curiosity-driven perspective. The use of ILs is beginning to mature in Physics and there is enough work done for an overview paper to be of broad interest. In this paper, first we will sow curiosity about different aspects and potential discoveries that may arise enabled by ILDs, and then some references featuring particularly fascinating or unforeseen results or applications will be offered. As of the notation to be used, we will refer to macroscopic, microscopic and nanoscopic IL droplets as M,m,n(ILDs), respectively. This is is because in some specific fields the term "mini" is sometimes used to refer to small systems but that can be either macroscopic, microscopic or nanoscopic. For example, you can find that in the literature a "miniemulsion" refered to as an emulsion with nanometer-size droplets, or that a "minilense" can refer to a milimeter sized optical lense. Here we will adopt dimensional prefixes ("nanoemulsion" and" lense" would then be used here).

ILs are a substance usually thought of as a solvent in the chemical industry and also in fundamental chemistry. In our case, however, we will focus on ILs when they are in the form of droplets, i.e. compartmentalized and enveloped by a surface generated by surface tension. This is obviously a rather physical or engineering approach and accordingly the reader will find here and within the referenced works data, concepts and magnitudes such as droplet profile, velocity, contact angle, density, topography, spatial confinement, spatial patterns, surface and line tension, wetting, electric, magnetic and electromagnetic fields, light, mirrors, lenses, vacuum etc. rather than those usually found in chemical essays. In many cases we are going to see that the findings and the innovations that are being produced with the use of ILDs are conceptually very simple even though the techniques required for their realization are some of the most advanced we have today. This allows me to present this work in an informative manner. This is not at odds with their importance. Accordingly, we will find that many of these advances are being published in high impact journals such as *Science*, *Nature*,... where everyone knows that only research projects or results with a very broad and deep scope are published. We will not deal with the hard chemical or simulation advances, which the reader can access in the many available bibliography. [4 5 6 7]

2. Physical discoveries enabled by ionic liquid droplets

Entering into the subject at hand, M,m,n(ILDs) are offering an astonishinly broad field of new experiments with interesting applications and potential in basic science, too, due to their unique general physical properties and also to the ease of tuning them. Why do I say this? Consider how many useful discoveries we may be able to make with having the these particular liquids compartimentalized into droplets (that is, separated from the environment by the surface tension produced surface). Have you ever thought of using them as tiny containers to carry out chemical reactions by using minimal amounts of reagents (that can be very expensive or unavailable) or to precisely synthesize crystals of minute sizes in a controlled manner? Synthesizing single-crystals in such small chambers has advantages over larger vessels at hand in a laboratory because they are less interfering variables (spatial heterogeneities in temperature or composition, for example).[8 9 10] Also, if our ultrasmall chambers are perfectly spherical and smooth there are no corners or irregularities and there is thus less possibility for other crystals to nucleate there. Nature actually its own oily microdroplets that operate as highly refined microfactories, the bacteria, which have evolved to synthesize all kinds of chemicals and nanoparticles.[11 12] Could our droplets be used for delivering a certain substance to a targeted location within the human body? First, the toxicity of the ILDs must be asseded (as it was done with C nanotubes or with nanoparticles of all kinds a few years ago, or with graphene nowadays...).[13] Let's not forget that a nILD of a given composition need not always behave in the same way as a bulk liquid: a nanodroplet can use its surface tension to burst the cell membrane and kill a pathogen. This, in turn, is reminiscent of the behavior of nanoparticles: Au is inert for humans and and then used in medical implants as stents or teeth, but an Au nanoparticle can kill a cell just by contact! [14]

Changing the subject. Everyone remembers from physics classes that a drop of water works like a lens. So, if we have unaltered mILD on either a solid or another liquid, it is quite tempting to assume that, given that you can vary the liquid and thus the refractive index of the medium, and that the walls are perfectly smooth, we can use our ILDs to make microlenses. They are intrinsically smooth without polishing and their 3D shape is easier to tune than if it were a solid.[15] [16] [17] Wondering how could we change their shape? The electrowetting phenomenon can be used for this: since ILDs are conductive, a potential difference can be established between it and a conductive substrate and the contact angle (that is, the degree of flattening) and thus the focal length of the lens, will change. In this way we can build variable focus lenses, the kind used by the cameras of our modern smartphones.[18] [19] What if we coat the ILDs with a reflective substance to manufacture micro mirrors or micro- light concentrators for optical applications or energy harvesting applications? Believe me or not, a *Science* paper reported some years ago a method for constructing a lunar telescope mirror by coating an IL surface with reflective Ag. And, by the way, yes, space technologist are also pointing to ILs for obvious reasons (non-volatility and wide liquid temperature range)![20] Further, considering how light bounces inside a spherical droplet, perhaps we can concentrate the light to generate a laser! I remember how fascinating resulted to me reading some years how microcavities like those we were developing using ILDs were being tested by optics experts as "whispering gallery mode" cavities for constructing microlasers![21] [22] Let's carry on.

Lets now think that way: if ILs are conductive and non-volatile, we might be tempted to place ILDs in a Scanning Electron Microscope (SEM) or Environmental Scanning Electron Microscope (ESEM) to observe them. Weird, isn't it? One is not accustomed to imagine a liquid in an SEM chamber because everyone knows that it evaporates instantaneously there. With this possibility of imaging ILDs, specially micro/nanodroplets, we could retrive 1D physical profiles of the droplets (this allowing us to extract relevant geometrical parameters like height, radius, contact angle, deviations from a spherical geometry...)![1] [23] [24] [25] Now let's think about the 2D surface of those droplets and how to map its topography quantitatively. We could use the tip of an atomic force microscope (AFM) to do a scan, either in air or in a lidquid and obtain nanometer resolution images, with confidence that it will remain unchanged during experiments! Very good. (A liquid surface might be considered as smooth as other standards like mica or silicon).[26] [27] With this cability of the AFM we could explore process tracking right at the surface of the liquid, thus opening the door observe the formation, for example, of organic monolayers or self-assembled systems directly on the liquid surface, without the need to be transferred to a solid support to be observed by AFM. And why not with any type of electron microscopy?[28] We could even change the polarity, the surface tension or any other parameter of the liquid to our liking (depending on the study). Appealing! So far we have dealt with isolated droplets and as you can see a myriad of potential applications come to mind, conceptually simple. Moreover, if we could have them patterned on a surface could, we could turn into more advanced optical applications: we could replicate a system of lenses, an array (like a compound eye of a fly), if we have a way to deposit ILs in an orderly fashion on a surface.[29] Fortunately we all are familiar with inkjet printers, whose basic technology can be used for depositing droplets in an automatized way. Here we have another field that opens up before our eyes. And giving another twist, we could take advantage of the fact that we have liquid spherical topographies on a surface to transfer this topography to a solid. How? There are commercially available a series of plastics that are liquid but that solidify after heating. In other words, we could put these liquid plastics in contact with the mILDs arrays, heat and remove the solidified plastic, and magics!, we this obtain a solid with those microdroplets replicated without the need to use expensive lithography or laser systems to etch the surface. This is commonly refered to as soft lithography. There are countless current fields of science that are advancing thanks to the modification of the topographies of materials at increasingly minute scales, from implants, to antibacterial or super-repellent surfaces, to solar cells. These fields are continuously demanding new forms of topographies. And it all starts with liquid, not solid, molds! A few years ago, in the midst of international ecstasy about the promises of ILs (something similar is happening today with graphene, for example), it was discovered that ILs can also be distilled.[30] Hadn't we agreed that they are not volatile? Well, yes, but with vacuum and enough time we can make the molecules leave the liquid. Perfect. This gives us the option of creating droplets in another way: making them nucleate on a surface by condensation from the vapour phase. We may even previously modify the surface with chemical patches to attract the IL molecules to them! The longer the time vacuum is applied, the more volume the droplets will have! Easy. It is something similar to the formation of droplets on a mirror when we take a shower or the formation of bubbles of a soft drink on the irregularities of a glass. We would thus have two different solutions for depositing ILDs on a substrate; and they need not be equivalent: put a rough surface in water saturated atmosphere and let droplets nucleate and growth onto a hydrophobic surface; you shall see that display different shape, contact angle, than those formed if you deposit them on it using, for exmaple, a syringe. This is so because deposited droplets sometimes remain on the surface on a higher-energy state that nucleated ones (they are not completely "at rest" energetically speaking: only by giving them energy, for exmaple making them vibrate, they will evolve to their minimum energy state).[31] Of course, droplets must be of clean water and small enough (radius $\lessapprox$ 2.7 mm, the capillary lenght of water at common conditions) so as not to flatten the drop. Better, then. More diversity of methods within our reach. And already in a twist to the previous twists, the droplets of cylindrical geometry or more complex do not have to resist us. In other words, we can "write" (print) on a surface microscopic shapes other than spherical cap geometry droplets: lines, line intersections, circles-toroids,... Almost any kind of design made with liquid writing will certainly find a potential application. Do you feel constructing liquid cables is feasible, for example? Writing a nanoliquid line would allow scientists to precisely study them using

AFM without the burden that of to what degree it might be evaporating during, as it happens with conventional solvents. Or we could construct standard systems (nanolines, for example) to be used for Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) imaging. [32]

Anyone who has worked with ILs knows how quickly they become contaminated. Water vapor from the atmosphere is immediately incorporated into the IL and can change its properties (surface tension, for example) depending on the amount of water vapor absorbed. I myself have seen SEM images ILDs covered with changing patterns, probably of nanometer thickness, reminiscent of the surface of a soap bubble or of the shapes left by traces of gasoline on the surface of puddles of water and most likely due to contamination of the surface of the IL by water vapor or other organic gases. Incidentally, we were fortunate to discover that we could observe with SEM dynamic processes occurring at the liquid surface! (a beatiful example of opportunistic discovery, by the way).[33] Has it ever occurred to you that a small drop, appart from having a small volume, do also display large surface-to-volume ratio, and that given the high gas solubility characteristics of ILs, could be explored for build gas sensors? What about CO_2 sensors, now that greenhouse gas capture technologies are on the agenda? Whatever the gas, they could improve the performance of classical sensors that suffer from the evaporation of the solvent where the gas difuses. [34]

Emulsions (either macro/micro/nano) are where you commonly encounter macroscopic, microscopic and nanoscopic droplets immersed in another liquid, respectively. A lot of energy must normally be applied to the system to form really small droplets, whereas conventional mechanical agitation is sufficient to form macroscopic droplets (think of water-milk emulsion). These systems can also be examined by microscopy techniques. The smaller the droplets, the more the need to stabilize the emulsion, because the smaller droplets will tend to coalesce quickly to generate large ones (the Ostwald ripening phenomenon), leading to demulsification. In order to stabilize them, often surface active macromolecules are used. There are other highly advanced technologies, such as flow focusing, which allows the generation of liquid droplets of astonishing uniformity within another fluid, currently into the market and used for the production of encapsulators or solid microspheres.[35] A special class of emulsions that is receiving considerable attention today are the so-called Pickering emulsions, which are nothing more than emulsions where the stabilizers are not chemical substances but solid particles and which have been shown to be at times more effective than surfactants in protecting against coalescence and within which substances of interest can be encapsulated (e.g. for release into the human body if both the particles and the IL are biocompatible).[36] As a curiosity and not to tire with so many discoveries and so many brilliant ideas, it should be noted that the first publication on them dates from the early 1900s, and that two scientists, Walter Ramsden and Spencer Pickering, described them independently.[37] [38] Given the "green" character of ILs, they are being explored for the development of Pickering emulsions. When a liquid droplet completely resorbed from solid particles rests on a surface in air, then it is called a liquid marble.[39] Microfluidic and lab-on-a-chip applications may benefit from these systems. Due to the stability of ILDs, they are finding applications for the study of liquid marbles.[40]

Another way to "play" with the surface of these droplets in solution is to use ILs that are themselves surface-active (surfactants), that is they lower the interfacial tension. In some examples, like and oil and water, this could ease for example the oil recovery process in an oil reservoir.[41] And one last note about emulsion droplets. There is an interesting phenomenon that is attracting attention in recent years, called solvent exchange, discovered in 2000. An example: if we exchange the ethanol in an aqueous ethanol solution for oil and thus create an oil-saturated aqueous solution, and then map the surface with AFM, we will see that it is covered by oil nanodroplets over large areas! (try to figure out if we had to deposit them one by one!). In general, we have to substitute a good solvent of the desired droplet component with a poor one, both being miscible. It is therefore a method that does not require energy input to generate small droplets on a surface. Given the very wide range of solvent characteristics of ILs, they are perfect candidates to generate m,n(ILDs) in this very simple way.[42]

To move m,n(ILDs) in a controlled way on either a solid or a liquid may advance microrobotics or nanorobotics (soft robotics), a very lively subfield of micro/nanotechnology. In nature, there are examples of them, as swimming bacteria, which exhibit active systems of motion, called pili. Today, engineers are hunger for replicating them to construct microrobots.[43] [44] Physically, liquid microdroplets are actually very similar to bacteria (which are still water droplets surrounded by an oily coating!). Is it realistic to think we could move an ILD? Given their ionic (charged) nature, the first solution that can come to mind obviously involves the use of an external electric field (we may call it "eletrotactics").[45] Great then. Another wonderful synergy between chemistry and physics. But bacteria can move by themselves. Being ILs non-living matter, it is only logical to think it is impossible for ILDs to move on their own. Big mistake. As we can read elsewhere, imagination along with talent has given rise to self-propulsion, by using spatial gradients in for example wettability, surface tension or ionic content to move them. Something like chemotaxis in nature.[46] Isn't it cool to be able to move our ILs droplets on a surface without forcing them through pre formed channels, as is done in microfluidics? As a final point, for now: a charged object like an ILD moving across a surface has also the potential of generating electricity![47] [48] Exotic, certainly. And natural, at the same time: nature once again provides us with similes, the power generating bacteria![49] [50] Now let's switch to magnetism. As discussed earlier, the array of available ILs is quite wide and yes, we have a lot which have magnetic properties. Magnetic properties arise from themselves, with no need to add magnetic particles.[51] Once again, it is easy to intuit that a magnetic field can be used for making an ILD to move as it is also done with electric fields.[52]And once again, with the (magnetotactic) bacteria as a natural simile: they align themselves and migrate along Earth's magnetic field lines (this called magnetotaxis).[53] How advanced! And not just that: the energy stored in the magnetic field could also potentially be used to partition a droplet, thus yielding even smaller droplets.[54] More Teslas, smaller droplets. This is quite similar to the electrospray method of splitting one big droplet into many smaller droplets by using electric fields.[55] There, the motto might be "more V/m, smaller droplets". By the way, a final point: one could even use these electric, magnetic and electromagnetic fields to move the ILDs not only on a surface, but literally upwards. Yes, we can levitate ILs droplets, and, for example, making them to coalesce (react) with each other in a non-liquid environment! (containerless or touchless reactors).[56 57]

Let's consider now ILs droplets from another genuinely physical perspective: An ILD does not volatilize once produced, so its mass remains constant and can easily be calculated from a microscopy image (density is usually known or can be determined). Therefore, we can use the ILD as a mass standard to build a mass sensor (using, for example, an AFM cantilever, whose change in its vibrating behaviour can be precisely measured and correlated with its mass).[58] Isn't that cool?

We may think not only of *practical* applications, but also of another: progress in *basic* physics (pun intended, obviously). For example, there is a whole body of theoreticians advancing year by year towards understanding of the wetting behavior of droplets of any size. Data on micro/nano droplets will never hurt, as they are trickier to fabricate, control and characterise than the milimeter-sized. The fact ILDs follow the laws of wetting[59] means that, for example, we could use in their micro/nano form to advance into the solution of current scientific controversies such as whether or not the so-called line tension actually exists.[60 61] Line tension is analogous to the surface tension, but acts on the perimeter of the base of the droplet rather than on the entire surface, and scientists expect that if real, it could change the contact angle of nanodroplets with respect to macroscopic droplets (reported values are of the order of just 10^{-11} J/m). To give another example, ILs now also allow us to study the elusive so-called "precursor film", a film of nanometer thickness that any droplet display emanating from the three-phase contact line, by using SEM/ESEM (in vacuum) or AFM (in air).[62 63 64] For sure, wetting theoreticians are on the lookout for new experimental data obtained with ILDs. [65 66]

No matter what application we work on (Fig. 1), utilizing ILs will definitely make us more environmentally friendly ("greener") while doing science. In closing, as has been shown, for each of the ideas there is a practical realization published, a beautiful demonstration of the power of well-informed curiosity and hard work, especially needed in exploratory and emerging fields.

References

[1] A. Méndez-Vilas, A.B. Jódar-Reyes, M.L. González-Martín, Ultrasmall liquid droplets on solid surfaces: production, imaging, and relevance for current wetting research, Small . 2009 Jun;5(12):1366-90, https://doi.org/10.1002/smll.200800819

[2] Greer, A. J., Jacquemin, J., & Hardacre, C. (2020). Industrial applications of ionic liquids. Molecules, 25(21), 5207. https://doi.org/10.3390/molecules25215207

[3] Ionic Liquids Market By Application (Solvents & Catalysts, Process & Operating Fluids, Plastics, Batteries & Electrochemistry, Bio-Refineries) and By Region (North America,

Europe, Asia-Pacific and Rest of World) - Global Size, Share, Trends & Growth & Forecast to 2027 https://www.marketdataforecast.com/market-reports/ionic-liquids-market

[4] Zhigang Lei, Biaohua Chen, Yoon-Mo Koo, and Douglas R. MacFarlane, Introduction: Ionic Liquids, Chem. Rev. 2017, 117, 10, 6633–6635

[5] Computer Simulation of a "Green Chemistry" Room-Temperature Ionic Solvent, J. Phys. Chem. B 2002, 106, 46, 12017–12021, http://dx.doi.org/10.1021/jp021392u

[6] Molecular Modelling of Ionic Liquids: General Guidelines on Fixed-Charge Force Fields for Balanced Descriptions, Journal of Ionic Liquids, 2(2), 2022, Zhaoxi, Sun, Zhihao, Gong, Lei, Zheng, Payam , Kalhor, Zhe, Huai, Zhirong, Liu, https://doi.org/10.1016/j.jil.2022.100043

[7] Molecular Modeling of Ionic Liquids: Force-Field Validation and Thermodynamic Perspective from Large-Scale Fast-Growth Solvation Free Energy Calculations, Zhaoxi Sun,Mao Wang,Qiaole He,Zhirong Liu, Advanced Theory and Simulations, 5(9), 2022 2200274, https://doi.org/10.1002/adts.202200274

[8] Zhang M, Ettelaie R, Yan T, Zhang S, Cheng F, Binks BP, Yang H. Ionic Liquid Droplet Microreactor for Catalysis Reactions Not at Equilibrium. J Am Chem Soc. 2017 Dec 6;139(48):17387-17396. https://doi.org/10.1021/jacs.7b07731

[9] Dubois P, Marchand G, Fouillet Y, Berthier J, Douki T, Hassine F, Gmouh S, Vaultier M. Ionic liquid droplet as e-microreactor. Anal Chem. 2006 Jul 15;78(14):4909-17, https://doi.org/10.1021/ac060481q

[10] Keller D, Henninen TR, Erni R. Formation of gold nanoparticles in a free-standing ionic liquid triggered by heat and electron irradiation. Micron. 2019 Feb;117:16-21, https://doi.org/10.1016/j.micron.2018.10.008

[11] Du J, Shao Z, Zhao H. Engineering microbial factories for synthesis of value-added products. J Ind Microbiol Biotechnol. 2011 Aug;38(8):873-90, https://doi.org/10.1007%2Fs10295-011-0970-3

[12] Iravani S. Bacteria in Nanoparticle Synthesis: Current Status and Future Prospects. Int Sch Res Notices. 2014 Oct 29;2014:359316, https://doi.org/10.1155/2014/359316

[13] Flieger J, Flieger M. Ionic Liquids Toxicity-Benefits and Threats. Int J Mol Sci. 2020 Aug 29;21(17):6267. doi: 10.3390/ijms21176267, https://doi.org/10.3390%2Fijms21176267

[14] Umair M, Javed I, Rehman M, Madni A, Javeed A, Ghafoor A, Ashraf M. Nanotoxicity of Inert Materials: The Case of Gold, Silver and Iron. J Pharm Pharm Sci. 2016 Apr-Jun;19(2):161-80, https://doi.org/10.18433/j31021

[15] J. Perera-Núñez, A. Méndez-Vilas, L. Labajos-Broncano, and M. L. González-Martín, Ionic Liquid Microdroplets as Versatile Lithographic Molds for Sculpting Curved Topographies on Soft Materials Surfaces, Langmuir 2010, 26, 22, 17712–17719,

https://doi.org/10.1021/la102799x

[16] Cadarso, V., Perera-Nuñez, J., Mendez-Vilas, A., Labajos-Broncano, L., González-Martín, M., & Brugger, J. (2014). Microdrop generation and deposition of ionic liquids. Journal of Materials Research, 29(17), 2100-2107, https://doi.org/10.1557/jmr.2014.162

[17] Rola K, Zajac A, Czajkowski M, Cybinska J, Martynkien T, Smiglak M, Komorowska K. Ionic liquids-a novel material for planar photonics. Nanotechnology. 2018 Nov 23;29(47):475202, https://doi.org/10.1088/1361-6528/aae01e

[18] Sergio Calixto, Martha Rosete-Aguilar, Francisco J. Sanchez-Marin, Olga L. Torres-Rocha, E. Militza Martinez Prado, Margarita Calixto-Solano, Optofluidic Compound Lenses Made with Ionic Liquids, https://doi.org/10.5772/24197, in Applications of Ionic Liquids in Science and Technology, Scott Handy (Ed.), IntechOpen (2011)

[19] Xiaodong Hu,a Shiguo Zhang,b Chao Qu,a Qinghua Zhang,b Liujin Lu,b Xiangyuan Ma,b Xiaoping Zhang, and Youquan Deng, Soft Matter, 2011,7, 5941-5943, https://doi.org/10.1039/C1SM05585B

[20] Borra, E., Seddiki, O., Angel, R. et al. Deposition of metal films on an ionic liquid as a basis for a lunar telescope. Nature 447, 979–981 (2007). https://doi.org/10.1038/nature05909

[21] Valentin Barna and Luisa De Cola, "Mirrorless dye doped ionic liquid lasers," Opt. Express 23, 11936-11945 (2015), https://doi.org/10.1364/OE.23.011936

[22] H. Zhang, C. Zhang, S. Vaziri, F. Kenarangi and Y. Sun, "Microfluidic Ionic Liquid Dye Laser," in IEEE Photonics Journal, 13(1), pp. 1-8, 2021, https://doi.org/10.1109/JPHOT.2020.3044861

[23] Smith EF, Rutten FJ, Villar-Garcia IJ, Briggs D, Licence P. Ionic liquids in vacuo: analysis of liquid surfaces using ultra-high-vacuum techniques. Langmuir. 2006 Oct 24;22(22):9386-92. https://doi.org/10.1021/la061248q

[24] Kuwabata, S., Kongkanand, A., Oyamatsu, D. & Torimoto, T. Observation of Ionic Liquid by Scanning Electron Microscope. Chem. Lett. 35, 600–601 (2006), https://doi.org/10.1246/cl.2006.600

[25] Costa JC, Mendes A, Santos LM. Morphology of Imidazolium-Based Ionic Liquids as Deposited by Vapor Deposition: Micro-/Nanodroplets and Thin Films. Chemphyschem. 2016 Jul 18;17(14):2123-7, https://doi.org/10.1002/cphc.201600198

[26] Spreading of nanodroplets of ionic liquids on the mica surface. X Gong, B Wang, L Li. ACS omega 3 (12), 16398-16402, 2018, http://dx.doi.org/10.1021/acsomega.8b02423

[27] Yufei Mo, JibinPu, Fuchuan Huang, Dynamic forces of ionic liquid nano-droplets measured by atomic force microscope, Colloids and Surfaces A: Physicochemical and

Engineering Aspects, 429, 19-23 (2013), https://doi.org/10.1016/j.colsurfa.2013.03.050

[28] Wang, C. (2016). Imaging Liquid Processes Using Open Cells in the TEM, SEM, and Beyond. In F. Ross (Ed.), Liquid Cell Electron Microscopy (Advances in Microscopy and Microanalysis, pp. 56-77). Cambridge: Cambridge University Press. https://doi.org/10.1017/9781316337455.004

[29] Gunawan, C., Ge, M. & Zhao, C. Robust and versatile ionic liquid microarrays achieved by microcontact printing. Nat Commun 5, 3744 (2014). https://doi.org/10.1038/ncomms4744

[30] Earle, M., Esperança, J., Gilea, M. et al. The distillation and volatility of ionic liquids. Nature 439, 831–834 (2006). https://doi.org/10.1038/nature04451

[31] F.J. Montes Ruiz-Cabello, M.A. Rodríguez-Valverde, M.A .Cabrerizo-Vílchez, Equilibrium contact angle or the most-stable contact angle?, Advances in Colloid and Interface Science, 206, 320-327, 2014, https://doi.org/10.1016/j.cis.2013.09.003

[32] Senoner M, Maassdorf A, Rooch H, Österle W, Malcher M, Schmidt M, Kollmer F, Paul D, Hodoroaba VD, Rades S, Unger WE. Lateral resolution of nanoscaled images delivered by surface-analytical instruments: application of the BAM-L200 certified reference material and related ISO standards. Anal Bioanal Chem. 2015 Apr;407(11):3211-7, https://doi.org/10.1007/s00216-014-8135-7

[33] Personal communication (Prof. Luis Labajos Broncano, UNEX, Spain).

[34] Gas diffusion and evaporation control using EWOD actuation of ionic liquid microdroplets for gas sensing applications Sensors and Actuators B: Chemical , 2018, Federico Ribet, Luca De Pietro, Niclas Roxhed, Göran Stemme, http://doi.org/10.1016/j.snb.2018.04.076

[35] Wang WH, Zhang ZL, Xie YN, Wang L, Yi S, Liu K, Liu J, Pang DW, Zhao XZ. Flow-focusing generation of monodisperse water droplets wrapped by ionic liquid on microfluidic chips: from plug to sphere. Langmuir. 2007 Nov 6;23(23):11924-31, https://doi.org/10.1021/la701170s

[36] Luo Q, Wang Y, Yoo E, Wei P, Pentzer E. Ionic Liquid-Containing Pickering Emulsions Stabilized by Graphene Oxide-Based Surfactants. Langmuir. 2018 Aug 28;34(34):10114-10122, https://doi.org/10.1021/acs.langmuir.8b02011

[37] Pickering, Spencer Umfreville (1907). "Emulsions". Journal of the Chemical Society, Transactions. 91: 2001–2021, https://doi.org/10.1039%2FCT9079102001

[38] Ramsden, W (1903). "Separation of Solids in the Surface-layers of Solutions and 'Suspensions'". Proceedings of the Royal Society of London. 72 (477–486): 156–164, https://doi.org/10.1098%2Frspl.1903.0034

[39] L. Gao and T. J. McCarthy, Ionic liquid marbles, Langmuir, 2007, 23, 10445–10447, https://doi.org/10.1021/la701901b

[40] Liquid marbles as miniature reactors for chemical and biological applications, NK Nguyen, CH Ooi, P Singha, J Jin, KR Sreejith, HP Phan, NT Nguyen, Processes 8 (7), 793, https://doi.org/10.3390/pr8070793

[41] Hanamertani, A.S., Pilus, R.M., Irawan, S. (2017). A Review on the Application of Ionic Liquids for Enhanced Oil Recovery. In: Awang, M., Negash, B., Md Akhir, N., Lubis, L., Md. Rafek, A. (eds) ICIPEG 2016. Springer, Singapore. https://doi.org/10.1007/978-981-10-3650-7_11

[42] Formation of Surface Protic Ionic Liquid Nanodroplets for Nanofabrication, H Yu, BP Dyett, SK Pathirannahalage, M Li, CJ Drummond, TL Greaves, Advanced Materials Interfaces 7 (4), 2020, https://doi.org/10.1002/admi.201901647

[43] Biological Soft Robotics, Annual Review of Biomedical Engineering, Vol. 17:243-265, 2015, https://doi.org/10.1146/annurev-bioeng-071114-040632

[44] Ali, J., Cheang, U.K., Martindale, J.D. et al. Bacteria-inspired nanorobots with flagellar polymorphic transformations and bundling. Sci Rep 7, 14098 (2017). https://doi.org/10.1038/s41598-017-14457-y

[45] Francis, Wayne, Wagner, Klaudia, Beirne, Stephen , Officer, David , Wallace, Gordon , Florea, Larisa and Diamond, Dermot (2016) Electrotactic ionic liquid droplets. Sensors and Actuators B: Chemical, 239 . pp. 1069-1075, http://dx.doi.org/10.1016/j.snb.2016.08.098

[46] Wayne Francis, Cormac Fay, Larisa Florea, Dermot Diamond, Self-propelled chemotactic ionic liquid droplet, Chemical Communications, 2015, № 12, p. 2342-2344s, https://doi.org/10.1039/c4cc09214g

[47] Yin J, Li X, Yu J, Zhang Z, Zhou J, Guo W. Generating electricity by moving a droplet of ionic liquid along graphene. Nat Nanotechnol. 2014 May;9(5):378-83, https://doi.org/10.1038/nnano.2014.56

[48] Shanshan Yang, Yudan Su, Ying Xu, Qiong Wu, Yuanbo Zhang, Markus B. Raschke, Mengxin Ren, Yan Chen, Jianlu Wang, Wanlin Guo, Y. Ron Shen, and Chuanshan Tian, Mechanism of Electric Power Generation from Ionic Droplet Motion on Polymer Supported Graphene, J. Am. Chem. Soc. 2018, 140, 42, 13746–13752, https://doi.org/10.1021/jacs.8b07778

[49] https://theconversation.com/this-is-how-microorganisms-can-produce-renewable-energy-for-us-149933

[50] Light, S.H., Su, L., Rivera-Lugo, R. et al. A flavin-based extracellular electron transfer mechanism in diverse Gram-positive bacteria. Nature 562, 140–144 (2018).

https://doi.org/10.1038/s41586-018-0498-z

[51] Magnetic Ionic Liquids: Synthesis, properties and applications, E. Santos, J. Albo and A. Irabien, RSC Adv. 2014;4:40008–40018, https://doi.org/10.1039/C4RA05156D

[52] Misuk, Viktor et al. “Micro magnetofluidics: droplet manipulation of double emulsions based on paramagnetic ionic liquids.” Lab on a chip 13 23 (2013): 4542-8, https://doi.org/10.1039/C3LC50897H

[53] Bazylinski, D., Frankel, R. Magnetosome formation in prokaryotes. Nat Rev Microbiol 2, 217–230 (2004). https://doi.org/10.1038/nrmicro842

[54] Zhu GP, Wang QY, Ma ZK, Wu SH, Guo YP. Droplet Manipulation under a Magnetic Field: A Review. Biosensors (Basel). 2022 Mar 2;12(3):156. https://doi.org/10.3390%2Fbios12030156

[55] Y.-H.Chiu, G.Gaeta, D.J.Levandier, A.Dressler, J.A.Boatz, Vacuum electrospray ionization study of the ionic liquid, [Emim][Im], https://doi.org/10.1016/j.ijms.2007.02.010

[56] Containerless reaction monitoring in ionic liquids by means of Raman microspectroscopy, Mercedes López-Pastor, Ana Domínguez-Vidal, María José Ayora-Cañada, Thomas Laurell, Miguel Valcárcel and Bernhard Lendl, Lab Chip, 2007,7, 126-132, 2006, https://doi.org/10.1039/B608618G

[57] Interaction of Levitated Ionic Liquid Droplets with Water, Jonas Schenk, Ulrich Panne, and Merwe Albrecht, J. Phys. Chem. B 2012, 116, 48, 14171–14177, https://doi.org/10.1021/jp309661p

[58] Microdrops on Atomic Force Microscope Cantilevers: Evaporation of Water and Spring Constant Calibration Elmar Bonaccurso and Hans-Jürgen Butt, https://doi.org/10.1021/jp0471406

[59] Gao LC, McCarthy TJ, Ionic liquids are useful contact angle probe fluids, Journal of the American Chemical Society, Vol.129, No.13, 3804-3804, 2007, https://doi.org/10.1021/ja070169d

[60] Measurement of Line Tension on Droplets in the Submicrometer Range, Lars-Oliver Heim and Elmar Bonaccurso, Langmuir 2013, 29, 46, 14147–14153

[61] Resolving the Apparent Line Tension of Sessile Droplets and Understanding its Sign Change at a Critical Wetting Angle, Binyu Zhao, Shuang Luo, Elmar Bonaccurso, Günter K. Auernhammer, Xu Deng, Zhigang Li, and Longquan Chen, Phys. Rev. Lett. 123, 2019, https://doi.org/10.1103/PhysRevLett.123.094501.

[62] Xiao Gong, Bingchen Wang, and Lei Li, Spreading of Nanodroplets of Ionic Liquids on the Mica Surface, ACS Omega. 2018 Dec 31; 3(12): 16398–16402, https://doi.org/10.1021%2Facsomega.8b02423

[63] Spreading Dynamics of a Precursor Film of Ionic Liquid or Water on a Micropatterned Polyelectrolyte Brush Surface Shohei Shiomoto, Hayato Higuchi, Kazuo Yamaguchi, Hiromitsu Takaba, and Motoyasu Kobayashi* Cite this: Langmuir 2021, 37, 10, 3049–3056, https://doi.org/10.1021/acs.langmuir.0c03260.

[64] Molecularly-thin precursor films of imidazolium-based ionic liquids on mica, DA Beattie, RM Espinosa-Marzal, TTM Ho, MN Popescu, J Ralston, ..., The Journal of Physical Chemistry C 117 (45), 23676-23684

[65] Wettability by Ionic Liquids, Hongliang Liu,Lei Jiang, small 2016, 12, No. 1, 9–15, https://doi.org/10.1002/smll.201501526

[66] Contact Angles and Wettability of Ionic Liquids on Polar and Non-polar Surfaces, Advances in Colloid and Interface Science, 222, 162-171 (2015), http://dx.doi.org/10.1039/C5CP05873B

Figures

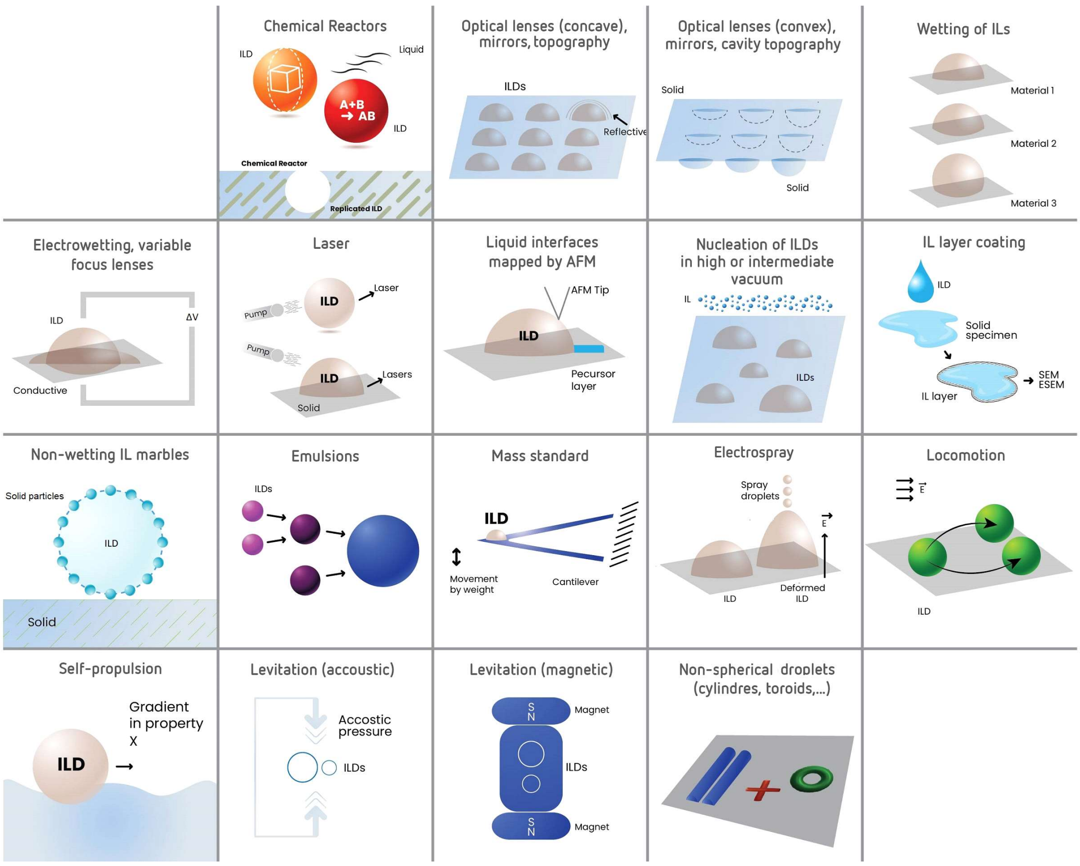

Fig. 1. A graphical summary of some of the most relevant applications in Physics requiring ILDs.