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Surface nano-crystallization of an Ionic Liquid

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Surface crystallization at the vapor/liquid interface of the ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) is observed in synchrotron X-ray diffraction studies. Sharp Bragg reflections emerge in grazing-angle X-ray diffraction patterns 37 °C above the bulk melting temperature indicating the presence of long-range ordered phase at the surface in coexistence with the bulk parent liquid. The unique structure of the vapor/liquid interface where butyl chains attached to the cations are expelled to the vapor side facilitates inter-ionic electrostatic interactions that lead to the crystallization. Our results demonstrate the complexity of ionic-liquids structure with their tendency to spontaneously phase separate into nano-domains with finite correlation lengths in coexistence with the liquid phase. By virtue of interfacial boundary conditions these nano-domains grow laterally to form quasi-two-dimensional crystals.

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Ionic liquids (ILs), the notable room-temperature liquid salts exhibit a wide range of scientifically intriguing and technologically appealing properties, and have been recently widely recognized as solvents and reaction media for ‘green’ chemistry [1–5]. Despite extensive studies in the last decade, their definitive molecular-length-scale structure continues to elude experimental and theoretical researchers. The complexity of their structures stems from the multiple competing nearest-neighbor couplings and long-range interactions including Coulombic, hydrogen-bonding, van-der-Waals interactions [6], and spatial steric constraints that lead to frustration and to the formation of a glassy state often observed upon cooling [7].

On the issue of low melting temperature of ionic liquids, previous studies assigned a major role to the alkyl chain attached to the cation in perturbing crystallization. Seddon and coworkers reported that the melting temperature (T_m) of 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_n\text{MIM}][\text{PF}_6]$, $n = 2 - 18$) changes sensitively with the length of the alkyl chain attached to the imidazolium ring of the cation [6]. This study points to the dual role the alkyl chain plays in controlling the melting temperature. By intervening between ions, the alkyl chain weakens Coulomb interactions thereby lowering T_m , and by interacting with its neighboring chains via van-der-Waals interactions it increases T_m , leading to the observed minimum in T_m . In view of this, one envisions that melting will also be affected by boundary conditions of the liquid such as those imposed by interfaces. Indeed, boundary conditions imposed at the vapor/liquid interface was considered as the main drive for smectic layering of nematic liquid crystals [8], and surface crystallization of normal alkanes [9, 10]. Similar phenomenon has also been observed in long-chain alcohols and polymer melts [11–15]. Apart from one unique phenomenon such as surface freezing of long chain alcohol monolayer on the sapphire surface [13], all the reported surface freezing temperatures (hereafter denoted by T_s) of pure liquid were very close to the bulk melting temperature, within $1 - 3^\circ\text{C}$ of T_m [9–11, 14, 15]. For all these systems, surface freezing was realized by in-plane ordering of alkyl chains or partial ordering of alkyl chains in polymer melts. Here, we report on the surface crystallization of the ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}][\text{PF}_6]$) by using synchrotron surface sensitive X-ray diffraction techniques. The observed surface freezing differs from previously studied systems in that T_s is much higher than T_m , and we propose it is not driven by chain-chain interactions but by cation-anion Coulomb interactions. Long-range crystalline order at the free IL surface clearly distinguishes itself from surface layering of ILs in contact with charged sapphire surface [16, 17] and at the free surface [18, 19].

PF_6 of 1-butyl-MIM ($[\text{BMIM}][\text{PF}_6]$, purity better than 99 wt %, water content < 100 ppm, chloride content < 10 ppm) was purchased from C-TRI in Korea. The X-ray diffraction (XRD) measurements were conducted on the Ames Laboratory Liquid Surface Diffractometer at the Advanced Photon Source (APS) in Argonne National Laboratory [20] (at 8 keV; $\lambda = 1.5498 \text{ \AA}$). Rod-scans, the intensity distribution of the 2D Bragg reflections normal to the surface, were measured with a position sensitive detector (PSD-50M-ASA, MBraun, Germany) situated behind a Soller collimator (0.1° divergence). The sample, (contained in a 10 cm diameter stainless steel trough, 0.3 mm deep) was encapsulated in an airtight enclosure, and was continuously purged with a dry helium gas during the course of the experiments. Prior to the X-ray experiments, the sample was heated to $\sim 80^\circ\text{C}$ under dry helium conditions. Heating and cooling rates during the experiment were $\sim 0.7 \text{ K/min}$ and $\sim 0.4 \text{ K/min}$, respectively. By changing the incident angle (α) with respect to the critical angle $\alpha_c = 0.172^\circ$ for total external reflection, either surface or bulk structure can be probed specifically. X-ray reflectivity study on this sample and other ionic liquids using similar conditions has been reported by us [21].

Figure 1 shows two dimensional (Q_{xy}, k_z) maps ($k_z = k_0 \sin \beta$; β is the angle of the reflected beam) from the surface ($\alpha = 0.14^\circ < \alpha_c = 0.172^\circ$; (a) and (b)) and from the bulk ($\alpha = 0.6^\circ > \alpha_c$; (c) and (d)) at various temperatures. At high temperatures, the surface sensitive GIXD pattern is almost featureless (Fig. 1(a)), however as the sample is cooled down, two prominent rod-like Bragg reflections emerge at $Q_{xy} \sim 1.52$ and $\sim 1.68 \text{ \AA}^{-1}$ below $T_s \sim 47^\circ\text{C}$. These diffraction peaks vary in intensity and position with temperature, and disappear upon heating above T_s (see Fig. 2(a)). Such rod-like reflections, with strong enhancement at the outgoing critical angle $\beta_c = 0.172^\circ$; ($k_z = k_c = 0.122 \text{ \AA}^{-1}$, see Fig. 2(b)), indicate surface crystallization of $[\text{BMIM}][\text{PF}_6]$ while the bulk is in the liquid phase. The XRD patterns from the bulk are hardly changed in the corresponding temperature range, as shown in Figs. 1(c) and (d) (see more details in the Electronic Auxiliary Materials(EAM)). Similar diffraction patterns from the bulk have been observed for this system in small- and wide angle X-ray scattering studies [7, 16], confirming that the sample is in the liquid phase in the temperature range of $12 - 80^\circ\text{C}$. This demonstrates that surface crystallization for this system occurs at temperatures that are much higher than $T_m \sim 10^\circ\text{C}$ [2, 6, 22], compared to previous observations of free liquid surface freezing [9–11, 14, 15]. Intentionally exposing the ordered $[\text{BMIM}][\text{PF}_6]$ to humidity, by purging the sample’s enclosure with water-saturated helium, modified the diffraction pattern by broadening the peaks in the Q_{xy} direction, while the peak positions remained intact. We remark that as-poured, untreated samples do not exhibit surface crystallization until they are preheated to 80°C under dry helium environment. $[\text{BMIM}][\text{BF}_4]$ ($T_m = -83^\circ\text{C}$) did not show any surface freezing in the same temperature range investigated.

Based on the diffraction pattern and the anion/cation dimensions, we propose to refine a simple model consisting

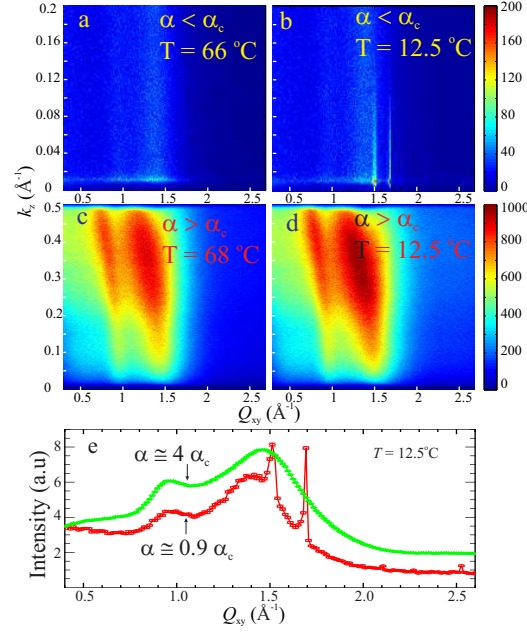


FIG. 1. (color online) 2D GIXD maps (Q_{xy}, k_z) surface surface ($\alpha < \alpha_c$) (a) at 66 °C, (b) 12.5 °C, and for bulk ($\alpha > \alpha_c$) (c) at 68 °C, and (d) at 12.5 °C, where $Q_{xy} \approx 2k_0 \sin(\phi/2)$ and $k_z = k_0 \sin \beta$ with incident beam k_0 , azimuthal in-plane angle ϕ , and out-of-plane angle β . (e) Q_{xy} cuts from the surface and from the bulk showing the bulk is in the liquid phase whereas the surface consists of crystalline and liquid phases in coexistence.

of a set of stacked quasi-2D rectangular lattice with one molecule per single-layer unit cell, as illustrated in Fig. 3(a). The layers are stacked in a checker-board-like anion-cation (cation-anion) arrangement by gliding each successive plane by $(a/2, b/2, jc)$ ($j = 0, 1, 2, \dots, N$; c is the layer thickness). The details of the intensity calculations based on the structure factor of this model are provided in the EAM. The sharp diffraction peaks are superimposed on two broad peaks at $Q_{xy} \sim 1.0$ and 1.45 \AA^{-1} that are similar in shape and position to the diffraction pattern from the bulk. These two liquid-like peaks are included in the model as a sum of two gaussians with a constant and a linear background terms. Using this model self consistently to fit the GIXD and the rod scans (solid lines in Figs. 3 and 2(b)) yields $a = 4.99 \pm 0.02$ and $b = 7.47 \pm 0.02 \text{ \AA}$ with four stacked layers each of thickness $c = 9 \pm 1 \text{ \AA}$ (at $T = 12.5 \text{ }^\circ\text{C}$). The increased separation between the stacked layers compared to the in-plane separations may be attributed to the packing of the butyl tails. In this model, the two prominent reflections at 1.52 and 1.68 \AA^{-1} correspond to the (11) and (02) Bragg reflections with $d_1 = 4.13$ and $d_2 = 3.74 \text{ \AA}$ d -spacings, respectively as indicated in the Fig. 3(a). This structure is also akin to the triclinic structure found for the 3D crystal structure of [BMIM][PF₆] [22, 23]. Based on these unit cell dimensions, we rationalize the orientation of the imidazolium cores as shown in Fig. 3(a). In this model, the butyl chains (not shown) protrude into the vapor phase, or into interstitial positions in the stacked-layers. This is consistent with recent X-ray reflectivity and surface sum-frequency generation spectroscopy

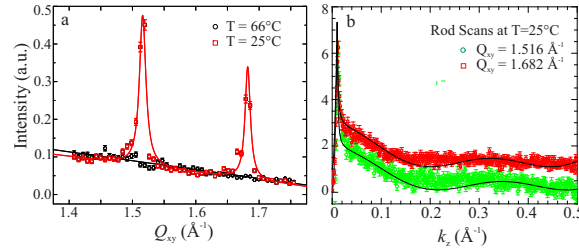


FIG. 2. (color online) (a) GIXD from [BMIM][PF₆] at two temperatures. The solid line lines is a fit using Lorentzian peaks. (b) Intensity vs. k_z rod-scans at the 2D Bragg reflections as indicated. Solid lines are obtained from a fit to the data using the model structure described in the text and in the EAM.

studies that found that loosely packed alkyl chains occupy the topmost layer of [BMIM][PF₆] at the vapor/liquid interface [21]. We therefore propose that surface crystallization, in this system, is not driven by the ordering of the topmost butyl chains, but by virtue of the fact that at the surface these chains are less likely to intervene between ions, enabling more tight anion-cation packing, i. e., stronger Coulomb interactions at the surface. However, as the layers are stacked the butyl chains gradually interfere with the ions more, and limit the stacking to a finite number of layers. Temperature dependence of the d -spacings shown in Fig. 4(a) is also consistent with the proposed structure. By increasing the temperature, one can envision that the rocking motion of the imidazolium core with respect to the surface normal is the easiest degree of freedom to excite, consistent with the thermal expansion coefficients (slopes in Fig. 4(a)) of d_2 ($3.4 \times 10^{-4} \text{K}^{-1}$) which is considerably larger than that for d_1 ($0.92 \times 10^{-4} \text{K}^{-1}$). Extrapolation of the d -spacings to high temperatures would eventually lead to $d_1 = d_2$, but the 2D crystal would melt before reaching that temperature. We also note that the average thermal expansion coefficient of the 2D lattice ($2.1 \times 10^{-4} \text{K}^{-1}$) is a just slightly smaller than that of the 3D lattice ($3 \sim 6 \times 10^{-4} \text{K}^{-1}$) [16, 24].

Integrated intensities of the diffraction peaks, as shown Fig. 2(a), as a function of temperature are shown in Fig. 4(b). Finite intensity is detected at approximately 47 °C, and it keeps increasing with the lowering of temperature but, it does not reach saturation to the lowest temperature measured [25]. This indicates that the crystallization is incomplete, namely, the surface is inhomogeneous with partial coverage of crystalline domains surrounded by moats in the liquid phase. This is corroborated with the observation of the superposition of strong sharp 2D Bragg reflections on the broad liquid like structure factor (Fig. 3(b)). Also, X-ray reflectivity measurements at the same temperatures although showing the interface is layered (within the first 8 Å)[19, 21], hardly show any features from the surface crystallization (~ 36 Å layer). XR data from the same samples was used to estimate the surface coverage of the crystalline domains. By assuming incoherent scattering from the liquid surface and the crystalline domains we find that the coverage of the crystalline domains is in the 5 -15% range (See EAM for details).

In general, systems undergoing surface freezing exhibit a change in the slope of their surface tension vs. temperature

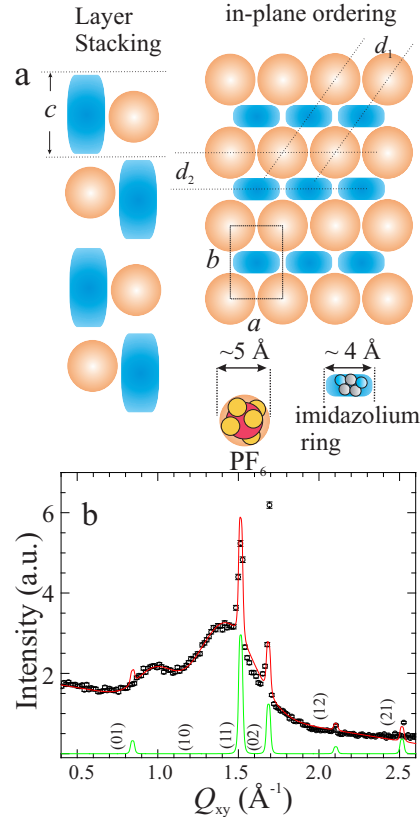


FIG. 3. (color online) (a) Proposed rectangular surface-crystalline structure of a layer, and its stacking for [BMIM][PF₆] viewed from ab -diagonal plane. Sphere and rectangle represent PF₆⁻ anion and imidazolium core of the cation, respectively. (b) In-plane surface GIXD from [BMIM][PF₆] at $T = 12.5$ °C, solid line is the best fit calculated intensity with above proposed crystal structure, and two broad gaussian like reflections due to the liquid-like structure at centered at ~ 1.0 and ~ 1.46 Å⁻¹ (See EAM)).

at T_s [9, 10, 15]. By contrast, our surface tension measurements of [BMIM][PF₆] show little change in the slope as a function of temperature, similar to previous reports [26–28]. We rationalize that the relatively low crystalline-surface coverage is the reason for the lack of strong anomalies in the the surface tension. Recent reports, based on X-ray diffraction and calorimetric studies, indicate that ILs display structural heterogeneity, and tend to form nanometer size aggregates on various length scales up to a few nanometers [29, 30]. Our extended analysis of the GIXD to the low- Q region are consistent with the presence of such nano-crystals in the bulk (see EAM). Such clusters at the vapor liquid interface can serve as nucleation centers to the lateral growth of the quasi-2D long-range-ordered domains we observe. The surface readily induces the lateral growth of the clusters, while the growth in the depth direction is restricted to the average size of nanoscale structures in the bulk [29]. The limited depth growth of the 2D crystals (four layers) is considered to be constrained by the inability to accommodate the butyl chains into the stacked layers in a regular arrangement. For normal alkanes [9, 10] and alcohols [11] in which surface freezing was reported, the temperature difference ΔT ($= T_s - T_m$) between the bulk (T_m) and surface (T_s) freezing is very small (1–3 °C). Dhinojwala and coworkers observed in polymer melts a pre-layering transition at roughly 10 °C above T_m [14, 15]. In that system, however, *in-plane* ordering was seen only 1–3 °C higher than T_m , similar to the case of normal alkanes. Large differences between surface and bulk freezing temperatures have been reported recently in liquid/liquid interface [31], and for alkanol-sapphire interfaces (liquid/solid interface) [13]. Thus, the ΔT (~ 37) °C, at the free liquid-vapor surface of [BMIM][PF₆] clearly distinguishes this from other systems. This behavior supports our proposed structure in which cation-anion Coulomb interaction is stronger at the surface without the intervening butyl chains [21]. It is also consistent with the trend in T_m for homolog series of $[C_n\text{MIM}][\text{PF}_6]$; when $n < 6$ [6], shortening of the alkyl chain works to increase the Coulomb interaction and increases the bulk melting temperature.

To summarize, surface crystallization in [BMIM][PF₆] at almost ~ 40 °C above the bulk melting temperature is observed in synchrotron X-ray measurements. We propose that the long-range crystalline order is dominated by the interaction between the imidazolium rings and accompanying anions. The characteristics observed near T_s including GIXD pattern, X-ray reflectivity, and surface tension indicate inhomogeneous nature of the ionic liquid surface with crystalline domains in coexistence with a liquid-surface phase. The unique feature of the surface layer in which all the butyl chains of the cations are forced out to the vapor side promotes the crystallization at the surface. Our present and previous x-ray reflectivity studies [21], although focused on interfacial properties of ionic liquids, have interesting implications on bulk properties of ionic liquids as well.

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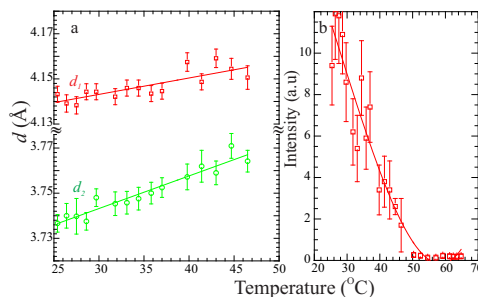


FIG. 4. (color online) (a) d-spacings extracted from the GIXD vs. temperature of the two prominent reflections from patterns as shown in Fig 3(b). (b) Integrated peak intensity of the (11) reflection vs. temperature (line is a guide to the eye).

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- [1] T. Welton, Chem. Rev. **99**, 2071 (1999).
- [2] J. G. Huddleston *et al.*, Green Chem. **3**, 156 (2001).
- [3] N. V. Plechkova, K. R. Seddon, Chem. Soc. Rev. **37**, 123 (2008).
- [4] P. Wasserscheid, Nature **439**, 797 (2006).
- [5] T. I. Morrow and E. J. Maginn, J. Phys. Chem. B **106**, 12807 (2002).
- [6] I. Lopez-Martin *et al.*, Chem. Phys. Chem. **8**, 690 (2007).
- [7] A. Triolo *et al.*, J. Phys. Chem. B **110**, 21357 (2006).
- [8] J. Als-Nielsen, F. Christensen, P. S. Pershan, Phys. Rev. Lett. **48**, 1107 (1982).
- [9] X. Z. Wu, E. B. Sirota, S. K. Sinha, B. M. Ocko, M. Deutsch, Phys. Rev. Lett. **70**, 958 (1993).
- [10] X. Z. Wu *et al.*, Science **261**, 1018 (1993).
- [11] O. Gang, B. M. Ocko, X. Z. Wu, E. B. Sirota, M. Deutsch, Phys. Rev. Lett. **80**, 1264 (1998).
- [12] E. Sloutskin, H. Kraack, O. Gang, B. M. Ocko, E. B. Sirota, M. Deutsch, J. Chem. Phys. **118**, 10729 (2003).
- [13] B. M. Ocko *et al.*, Phys. Rev. Lett. **106**, 137801 (2011).
- [14] K. S. Gautam *et al.*, Phys. Rev. Lett. **90**, 215501 (2003).
- [15] S. Prasad, Z. Jiang, S. K. Sinha, A. Dhinojwala, Phys. Rev. Lett. **101**, 065505 (2008).
- [16] M. Mezger *et al.*, Science **322**, 424 (2008).
- [17] M. Mezger *et al.*, J. Chem. Phys. **131**, 094701 (2009).
- [18] N. Nishi *et al.*, J. Chem. Phys. **132**, 164705 (2010).
- [19] E. Sloutskin *et al.*, J. Am. Chem. Soc. **127**, 7796 (2005).
- [20] D. Vaknin, *Characterization of Materials*, **2003** edited by E. N. Kaufmann, **2**, 1027-1047 (John Wiley & Sons, New York).
- [21] Y. Jeon *et al.*, J. Phys. Chem. C **112**, 19649 (2008).
- [22] A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, K. A. Johnson, J. Am. Chem. Soc. **127**, 16792 (2005).
- [23] S. M. Dibrov, J. K. Kochi, Acta Cryst C; Crys. Struc. Comm. **62**, o19 (2006).
- [24] R. G. de Azevedo *et al.*, J. Chem. Eng. Data. **50**, 997 (2005).
- [25] [BMIM][PF₆] supercools, and cannot be crystallized by cooling to 180 K. It can be crystallized in the heating process at around 226 K (see ref. 30).
- [26] G. Law, P. R. Watson, Langmuir **17**, 6138 (2001).
- [27] V. Halka, R. Tsekov, W. Freyland, Phys. Chem. Chem. Phys. **7**, 2038 (2005).
- [28] R. Osada, T. Hoshino, K. Okada, Y. Ohmasa, M. Yao, J. Chem. Phys. **130**, 184705 (2009).
- [29] A. Triolo *et al.*, Chem. Phys. Lett. **457**, 362 (2008).
- [30] T. Endo, T. Kato, K. Tozaki, K. Nishikawa, J. Phys. Chem. B **114**, 407 (2010).
- [31] L. Tamam *et al.*, Proc. Natl. Acad. Sci. **108**, 5522 (2011).