Dynamic Interfacial Tension at the Oil/Surfactant−Water Interface

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We have used dynamic interfacial tension measurements to understand the structure of the ordered monolayer at the hexadecane/water interface induced by the presence of surfactant molecules. No abrupt changes in the interfacial tension (γ) are observed during the expansion and contraction cycle below the interfacial ordering temperature (T_i) as observed for alkanes in contact with air. The lack of an abrupt change in γ and the magnitude of this change during the expansion process indicate that the ordered phase may not be crystalline. The change in the interfacial tension is due to an increase in contact between water and hexadecane molecules and the disordering of the interfacial ordered layer. At low surfactant concentrations, the recovery of the interfacial tension is slower below T_i, suggesting that there is a critical surfactant concentration necessary to nucleate an ordered phase at the interface.

Introduction

The addition of a small quantity of surfactant in water to reduce the interfacial tension between the oil and water phases is well known and has important technological applications in emulsion stability, underground oil recovery, and detergency. Recently, it was reported that in addition to lowering the interfacial tension the surfactant molecules induce the ordering of alkane molecules at the alkane/water interface at temperatures above the bulk melting temperature of alkane (T_m).[1,2] This ordered phase is analogous to surface freezing, where a crystalline, hexagonal monolayer exists above T_m at the surface of liquid alkane or alkane analogs in contact with air.[3−7] Surface freezing has also been observed for mixed monolayers of surfactant with alkanes at the air/surfactant solution interface.[8,9] In contrast, no such ordered phase is observed at the alkane/water interface,[10] and in fact, most materials show the opposite behavior of surface melting, where the surfaces disorder much below the bulk T_m. Because of the lack of any direct structural measurements of interfacial structure for the alkane/surfactant−water system, it is difficult to establish whether the ordered phase is crystalline and similar to that observed for the alkane/air or air/solution interface.[4,9] Recently, we have demonstrated that dynamic surface tension measurements can distinguish the rupture of the crystalline ordered layer at the alkane/air surface,[11] and we used this approach to understand the structure of the ordered state at the alkane/surfactant−water interface.

The interfacial tension (γ) was measured by expanding and contracting an alkane bubble inside a surfactant solution in water. We find that the γ during the oscillation cycle is in phase with the interfacial area. The ordering below the interfacial ordering temperature (T_i) at the interface is disrupted continuously during the expansion cycle. In contrast, there is a discontinuous change in γ at the onset of the expansion and contraction cycle for the hexadecane/air system due to the rupture of the crystalline ordered monolayer below the surface freezing temperature (T_s). The changes in γ ($\Delta\gamma$) during the oscillation cycle and the lack of abrupt change in γ for the alkane/surfactant−water interface indicate that the ordered layer at the interface is not consistent with crystalline order and is different from that present at the hexadecane/air surface. The recovery of γ at the hexadecane/water interface after a step change in area requires the diffusion of surfactant molecules from the water phase to the interface. Below T_i, this recovery is slower than above T_i and cannot be explained by the diffusion process alone. Instead, we postulate that this difference is due to the critical concentration of surfactant molecules necessary to nucleate an ordered phase.

Hexadecane ($C_{16}H_{34}$, $T_s = 290.7$ K, $T_m = 289.5$ K, Alfa Aesar, 99% purity) was distilled twice using a reduced pressure method. The values of static γ, T_s, and the slope of γ above and below T_s agreed with those reported in the literature.[4] Stearyl trimethyl ammonium bromide (STAB) (TCI America, 99% purity) was recrystallized twice from 1:1 acetone/methanol before use. Ultrapure deionized water (resistivity ≥18 MΩ·cm) was used to prepare STAB solutions with varying concentrations (ϕ_b). The interfacial tension between hexadecane/water was 50−52 mN/m and was stable over time, confirming that no significant polar impurities were present in hexadecane or water. The STAB concentration where γ for the air/water surface becomes constant was found to be 0.2 mM at 293.2 K and was similar to 0.3 mM at 306.2 K reported in the literature.[12] The dynamic tension of air and aqueous interfaces of alkane was investigated using a commercial oscillating bubble rheometer (Thetadyne Corp., NC). The details of the experimental protocol are described elsewhere.[13] The hexadecane/air surface was created by injecting air of a predetermined volume inside liquid hexadecane placed in a quartz cuvette using an inverted needle. The needle was attached to a motorized syringe. The hexadecane/water interface was created by injecting hexadecane through an inverted needle inside STAB solution placed in the cuvette (shown as an inset in Figure 1b).

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(1) Lei, Q.; Bain, C. D. *Phys. Rev. Lett.* **2004**, *92*, 176103/1−4.
(2) Sloutskin, E.; Bain, C. D.; Ocko, B. M.; Deutsch, M. *Faraday Discuss.* **2005**, *129*, 339−352.
(3) Wu, X. Z.; Ocko, B. M.; Sirota, E. B.; Sinha, S. K.; Deutsch, M.; Cao, B. H.; Kim, M. W. *Science* **1993**, *261*, 1018−21.
(4) Ocko, B. M.; Wu, X. Z.; Sirota, E. B.; Sinha, S. K.; Gang, O.; Deutsch, M. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1997**, *55*, 3164−3182.
(5) Gang, O.; Wu, X. Z.; Ocko, B. M.; Sirota, E. B.; Deutsch, M. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1998**, *58*, 6086−6100.
(6) Gautam, K. S.; Dhinojwala, A. *Phys. Rev. Lett.* **2002**, *88*, 145501/1−4.
(7) Gautam, K. S.; Kumar, S.; Wermeille, D.; Robinson, D.; Dhinojwala, A. *Phys. Rev. Lett.* **2003**, *90*, 215501/1−4.
(8) Wilkinson, K. M.; Qunfang, L.; Bain, C. D. *Soft Matter* **2006**, *2*, 66−76.
(9) Sloutskin, E.; Sapir, Z.; Tamam, L.; Ocko, B. M.; Bain, C. D.; Deutsch, M. *Thin Solid Films* **2007**, *515*, 5664−5668.
(10) Tikhonov, A. M.; Mitrinovic, D. M.; Li, M.; Huang, Z.; Schlossman, M. L. *J. Phys. Chem. B* **2000**, *104*, 6336−39.
(11) Prasad, S.; Dhinojwala, A. *Phys. Rev. Lett.* **2005**, *95*, 117801/1−4.
(12) Lu, J. R.; Simister, E. A.; Thomas, R. K.; Penfold, J. *J. Phys. Chem.* **1993**, *97*, 6024−6033.
(13) Rao, A.; Kim, J.; Thomas, R. R. *Langmuir* **2005**, *21*, 617−621.

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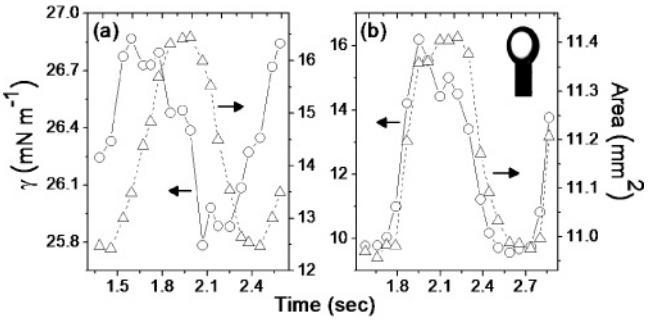

Figure 1. γ in an oscillation cycle with a period of 1 s along with the corresponding change in area for the hexadecane/air surface during the oscillation of a 5 μL air bubble with a 30% volume change at 289.9 K ($<T_s$) (a) and for the hexadecane/STAB−water ($\phi_b = 0.007$ mM) interface during the oscillation of a 4 μL hexadecane bubble with a 10% volume change at 293.5 K ($<T_i$) (b). The inset of b shows a picture of a hexadecane bubble in water attached to the tip of an inverted needle taken using a CCD camera.

The syringe and cuvette were thermally equilibrated using a circulating water bath (accuracy of 0.2 K). The images of the bubble formed at the needle tip were captured using a CCD camera and were subsequently digitized and analyzed by software using the Laplace equation. Dynamic measurements were performed by oscillating a bubble with a 10−30% volume change and by pulse experiments with a 10−40% change in bubble volume. The change in the Bond number for a 10% volume change is a factor of ≤ 2 during the oscillation cycle. The changes in $\Delta\gamma$ were similar for oscillation periods of 1−5 s, and we have reported data for an oscillation period of 1 s. For longer periods, the interfacial tension starts to recover by diffusion of the surfactant molecules.

Figure 1a,b shows the changes in the area of the bubble and γ during one oscillation period for the hexadecane/air (below T_s) and hexadecane/STAB−water system (below T_i), respectively. For the hexadecane/air system, we observe an abrupt increase in γ at the start of the expansion and contraction cycle and the γ recovers back to the equilibrium value rapidly during the cycle. This is a signature of the rupture of the surface frozen layer and has been discussed in a previous publication.[11] The response of γ is in phase with the change in interfacial area for the hexadecane/surfactant−water system.

The changes in γ during an oscillation cycle increases significantly below T_i for the hexadecane/STAB−water system as shown in Figure 2. We have shown five oscillation cycles at various temperatures for different surfactant concentrations in Figure 2b−d. The transition temperature (T_i), where the slope of the static interfacial tension changes, is indicated by an arrow in the Figures. As a control, we have also plotted the data for the hexadecane/water system in the absence of surfactant (Figure 2a). In this case, no change in the slope of static γ is observed with the decrease in temperature down to the hexadecane T_m. The changes observed during oscillation are not correlated with the change in area and are within the error bars of the static measurements for the hexadecane/water system. It is expected that there will be an increase in interfacial tension during the expansion cycle at the hexadecane/surfactant−water interface due to a decrease in surfactant concentration at the interface. However, the new results are that the changes in γ are much larger below T_i and that they are in phase with the changes in the interfacial area for the hexadecane/STAB−water system. This response to the change in area is very different from that at the hexadecane/air surface.

The $\Delta\gamma$ values during the oscillation cycle are plotted as a function of ($T - T_i$) in Figure 3 for $\phi_b = 0.007$, 0.01, and 0.02 mM. The data for all three surfactant concentrations collapse on a single curve, and $\Delta\gamma$ is almost temperature-independent above T_i and increases rapidly as we cool below T_i. Even though the static interfacial tension is a strong function of surfactant concentration, $\Delta\gamma$ depends only on ($T - T_i$). The $\Delta\gamma$ above T_i is due to the increase in interfacial area that leads to an increase in the interaction of alkane molecules with water at the interface. To explain the data below T_i, we consider two possibilities. The first possibility is that the expansion process involves the breaking of the crystalline solid in a manner similar to that observed for the hexadecane/air surface. In this case, one can imagine a situation

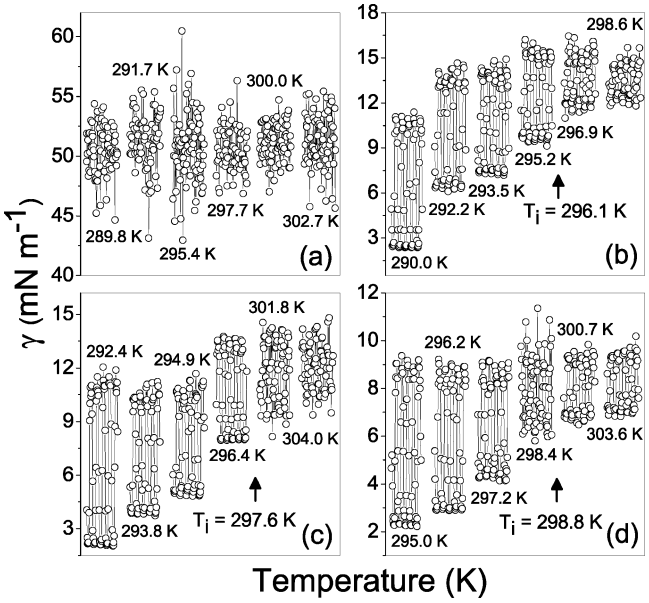

Figure 2. Plots of γ during the oscillation of a 4 μL hexadecane bubble with a 10% volume change and a period of 1 s as a function of temperature inside pure water (a) and aqueous STAB solutions with $\phi_b = 0.007$ (b), 0.01 (c), and 0.02 mM (d). The arrows indicate the interfacial ordering temperature, T_i.

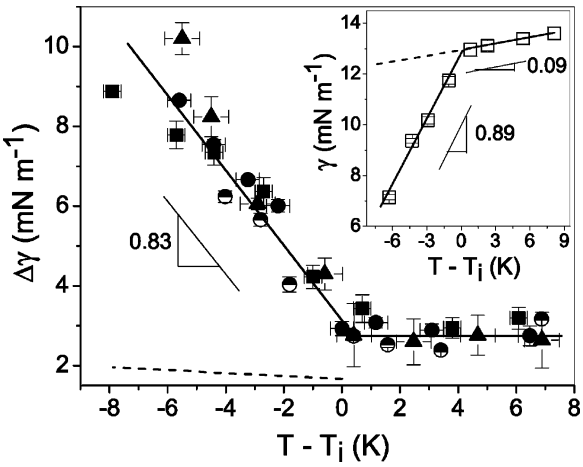

Figure 3. $\Delta\gamma$ as a function of temperature normalized by the corresponding T_i. The experiments were performed by sinusoidal oscillations (filled symbols) of a 4 μL hexadecane bubble with a 10% volume change and a period of 1 s inside aqueous solutions of STAB with $\phi_b = 0.007$ (■), 0.01 (▲), and 0.02 mM (◓). Shown also are the $\Delta\gamma$ values obtained from the pulse experiments with a 10% volume change (half-filled symbols). The solid line is a guide to the eye. The dashed line is $\Delta\gamma$ calculated using the heterogeneous model described in the text. The inset shows the static γ for 0.007 mM STAB concentration as a function of temperature normalized by T_i. Solid lines are fit to the data, and the dotted line is the extension of the fit above T_i to temperatures of the interfacial ordered phase.

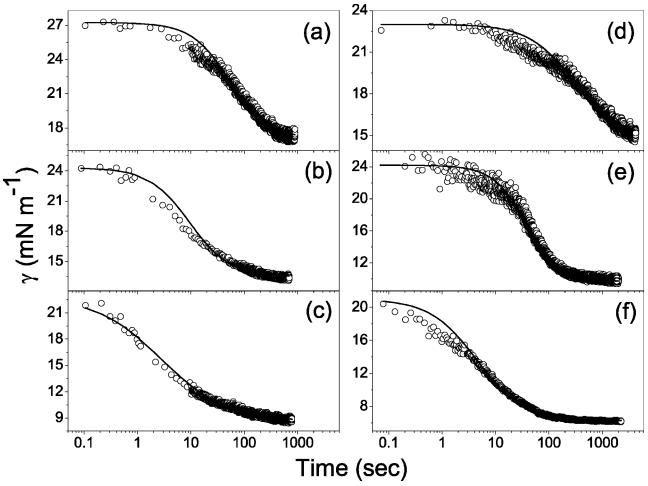

Figure 4. γ as a function of time after the rapid expansion of a 4 μL hexadecane bubble with 40% amplitude inside aqueous solutions of STAB with $\phi_b = 0.002$ mM (296.9 K (a), 291.2 K (d)), 0.007 mM (298.7 K (b), 293.5 K (e)), and 0.02 mM (303.5 K (c), 296.2 K (f)). The plots in the left panel are for $T > T_i$, and the right panel represents the corresponding plots for $T < T_i$. Solid lines are fits to the relaxation curves as described in the text.

similar to that of an ice slab floating on water. Upon expansion, the crystalline slab will break, and upon further expansion these broken slabs (without changing the area occupied by the crystalline layer) will drift apart and increase the surface area of liquid water in contact with air. If we use this heterogeneous model to predict $\Delta\gamma$, then we find that the model underestimates the values of $\Delta\gamma$ (shown as dashed line in Figure 3).[14] Therefore, both the lack of abrupt changes in γ during the expansion cycle and the change in $\Delta\gamma$ are inconsistent with that involved in breaking the crystalline order at the interface.

To explain the $\Delta\gamma$ below T_i, we explore the second possibility that involves the disordering of the ordered layer upon expansion. To determine $\Delta\gamma$, we use the static interfacial tension data shown as an inset in Figure 3. The γ changes slope at T_i and the dashed line in the inset shows the γ values expected if there was no ordering or phase transition at T_i. The differences in γ between the ordered and disordered interfacial layer below T_i ($\Delta\gamma_{order-disorder}$) increase with the decrease in temperature. This difference in γ along with the contribution from the increase in interfacial area agrees very well with $\Delta\gamma$ measured in the expansion cycle shown in Figure 3 ($\Delta\gamma \approx \Delta\gamma_{order-disorder} + \Delta\gamma_{T>T_i}$). This indicates that there is disordering of the chains at the interface during the expansion cycle.

By varying the oscillation period from 1 to 100 s, we find that γ relaxes during the expansion process toward the equilibrium values. This relaxation process was different above and below T_i. If the mechanism of recovery was only the diffusion of surfactant molecules to the interface, then there should be no difference in the recovery above and below T_i. (The diffusion constants of surfactants do not change significantly in this temperature window in water). To understand the recovery process, we expand the bubble area rapidly and measure the recovery of γ as a function of time. Parts a−c ($T > T_i$) and d−f ($T < T_i$) of Figure 4 show the recovery of γ as a function of time after the sudden expansion of an alkane bubble in aqueous STAB solutions with $\phi_b = 0.002$, 0.007, and 0.02 mM. The data are shown for 40% amplitude, and the trend is similar for lower amplitudes. One could visually observe that the relaxation below T_i slows down considerably for $\phi_b = 0.002$ mM compared to the recovery above T_i.

Table 1. Values of t^* and n above and below T_i for ϕ_b of 0.002, 0.007, and 0.02 mM Obtained from the Fits to the Recovery Process in Figure 4[a]

	$T > T_i$		$T < T_i$		
ϕ_b (mM)	t^* (s)	n	t^* (s)	n	$(t^*_{T<T_i}/t^*_{T>T_i})$
0.002	53	1.2	300	1.0	6.0
0.007	10	1.1	40	1.4	4.0
0.02	3	0.7	5	1.0	1.7

[a] Given also is the ratio of t^* below and above T_i.

We have used the following empirical equation to model the recovery of γ with time:[15]

$$\frac{\gamma_o - \gamma(t)}{\gamma(t) - \gamma_{eq}} = \left(\frac{t}{t^*}\right)^n \tag{1}$$

γ_o, $\gamma(t)$, and γ_{eq} are the interfacial tension just after the expansion cycle, at time t, and after the bubble reaches the equilibrium state, respectively. This model is described by two fitting parameters, t^* and n. It has been shown that this empirical equation models the dynamic surface tension for many surfactant systems and parameters t^* and n can be related to the nature of the diffusion process. We have also used the diffusion model developed by Ward and Tordai[16] and the diffusion-kinetics model.[17] Here, the purpose was to compare the difference in the recovery of γ above and below T_i, and the conclusions reached using both of these mathematical approaches were similar. The solid lines in Figure 4a−f are fits to the data using eqs 1 for $\phi_b = 0.002$, 0.007, and 0.02 mM. Parameters t^* and n obtained from the fits above and below T_i are shown in Table 1. The t^* values are much larger below T_i in comparison to those above T_i for the same values of ϕ_b. No clear trend in n was observed above and below T_i. Because we expect the surface coverage and diffusion constant for a given ϕ_b to be similar above and below T_i, the longer t^* values below T_i indicate that the ordering of the interfacial layer slows down the recovery of γ. The ratio $t^*_{T<T_i}/t^*_{T>Ti}$ is higher for lower ϕ_b (Table 1). The slow recovery of γ in comparison to the diffusion model at the air/surfactant−water surface has been attributed to the penetration and reorientation of surfactants in the surface layer.[18] At low ϕ_b, diffusion should be the rate-controlling effect, and the change in t^* upon interfacial ordering should be smaller. However, we observe the opposite trend.

We propose a simple qualitative model shown in Figure 5 to explain the results. For $T > T_i$, the expansion process disrupts the STAB concentration at the interfacial layer. The interfacial concentration of STAB recovers to its equilibrium value by diffusion of the STAB molecules to the interface. Below T_i, the recovery of γ involves two processes: diffusion of STAB and the ordering of the interfacial layer. We suggest that the ordering process requires a certain critical concentration, and this is easily achieved at high STAB concentrations. This is the reason that the recovery of γ above and below T_i is similar at $\phi_b = 0.02$ mM. At lower ϕ_b, the interfacial ordering slows down the recovery of the equilibrium γ.

Finally, we reflect on the nature of the ordered layer below T_i. The difference in the slope of static γ above and below T_i is equal to the change in the entropy of the interfacial layer upon

(14) The changes in $\Delta\gamma$ predicted for this heterogeneous model are equal to $\Delta A(\gamma_{oil/water} - \gamma)/A_f$, where A_f is the final area, ΔA is the change in area during expansion, $\gamma_{oil/water}$ is 52 mN/m, and γ is the interfacial tension before expansion.

(15) Hua, X. Y.; Rosen, M. J. *J. Colloid Interface Sci.* **1988**, *124*, 652−9.
(16) Ward, A. F. H.; Tordai, L. *J. Chem. Phys.* **1946**, *14*, 453−61.
(17) Eastoe, J.; Dalton, J. S. *Adv. Colloid Interface Sci.* **2000**, *85*, 103−144.
(18) Alexander, A. E. *Trans. Faraday Soc.* **1941**, *37*, 15−25.

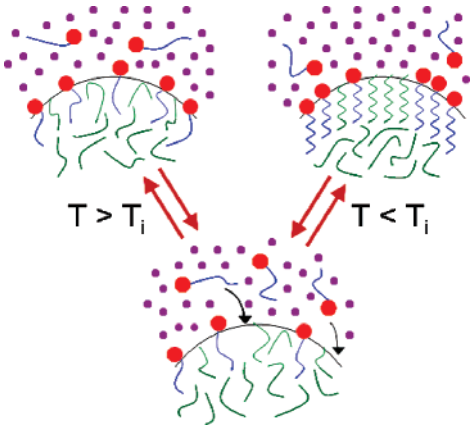

Figure 5. Sketch of the hexadecane/STAB−water interface before and after the sudden expansion of the hexadecane bubble at $T > T_i$ (left) and $T < T_i$ (right). The cross-sectional planes are perpendicular to the bubble surface. The top panel represents the interfaces at equilibrium, and the interface just after the expansion process is shown in the bottom panel. The re-equilibration process at $T < T_i$ involves both bulk diffusion and interfacial ordering.

ordering (ΔS).[3] The ΔS is 0.9 mJ·m^{-2}·K^{-1} for the hexadecane/air[4] and 0.8 mJ·m^{-2}·K^{-1} for the hexadecane/surfactant−water system. The interfacial concentration is needed to convert ΔS to the change in entropy per surface molecule upon ordering. For the hexadecane/air surface, the hexadecane monolayer forms a rotator phase below T_s (determined using grazing incidence X-ray diffraction (GIXD) and X-ray reflectivity measurements). No such direct structural information is available for the hexadecane/STAB−water system, and it is not possible to conclude whether this value of ΔS is due to a liquid-to-rotator transition. A partially fluorinated alkane with a longer hydrogenated part, an alkane/alcohol blend above a critical concentration, and comb polymer systems show large ΔS values and no X-ray diffraction peak in the GIXD measurements. In these cases, the surface ordered phase is associated with a rotator phase with a short correlation length (or a large density of defects)[19] or a smectic-like phase with short-range order in the surface plane.[7,20] The bubble expansion results for the hexadecane/surfactant−water interface are more consistent with the presence of an ordered interfacial layer rather than the rotator phase.

In summary, we have showed the structure of the interfacial ordered layer at the hexadecane/surfactant−water interface is disrupted continuously upon expansion of the bubble area. In contrast, the ordered layer at the hexadecane/air surface goes through a discontinuous change at the beginning of the expansion and contraction cycles. The recovery of this order is very rapid at the hexadecane/air surface but requires the diffusion of surfactants and ordering of the interfacial layer at the hexadecane/water interface. The slowing down of the interfacial ordering is more pronounced at low surfactant concentrations.

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(19) Ofer, E.; Sloutskin, E.; Tamam, L.; Ocko, B. M.; Deutsch, M. *Phys. Rev. E* **2006**, *74*, 021602/1−12.
(20) Gang, O.; Ellmann, J.; Moller, M.; Kraack, H.; Sirota, E. B.; Ocko, B. M.; Deutsch, M. *Europhys. Lett.* **2000**, *49*, 761−767.