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Shishir Prasad

Ali Dhinojwala
University of Akron Main Campus, ali4@uakron.edu

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Rupture of a Two-Dimensional Alkane Crystal

Shishir Prasad and Ali Dhinojwala*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA
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We have studied the breaking of a two-dimensional alkane crystal above the disordered melt using an oscillating bubble rheometer. Surface tension changes abruptly during the expansion and contraction cycle. We postulate that this is due to rupture of the 2D crystal at grain boundaries. The magnitude of the abrupt change in surface tension decreases with a decrease in the rate of change of bubble surface area with a power law exponent of 0.8. The interfacial area formed after rupture decreases with a decrease in rate. These results provide new insights in understanding defect-mediated rupture in confined geometry.

Surfaces of n-alkanes and alcohols freeze (at T_s) before the bulk crystallizes (T_m), and, as a consequence, a two-dimensional (2D) crystalline monolayer skin is formed on top of the disordered melt [1–3]. This phenomena is opposite of what is expected for most liquids [4] and the reasons are not yet clearly understood [5]. We have studied the rupture of this crystalline monolayer using an oscillating bubble rheometer. An air bubble is grown in the alkane melt and the expansion and contraction of this bubble is accompanied by a discrete change in surface tension ($\Delta\gamma$) (for $T_m < T < T_s$), indicating a rupture of this 2D surface crystal. The energy required to break this 2D crystal is many orders of magnitude less than that required for a single crystal and is determined by the presence of grain boundaries (grain size $\approx \mu$m). Surprisingly, $\Delta\gamma$ is a strong function of the rate of change of surface area [$d(\ln A)/dt$] and temperature. For long periods (≈ 1000 sec), the bubble oscillates without disrupting the crystal structure due to the fast recrystallization at the surface (≤ 1 sec). Although the modulus of 2D crystals has been studied in Langmuir monolayers [6,7], this is the first study of rupture of a surface frozen layer of alkane on top of its disordered melt. These results have important consequences in understanding defect-mediated properties in 2D crystals [8]. Current theoretical understanding does not explain the rate-dependent elastic rupture observed in these experiments.

Nonadecane ($C_{19}H_{40}$; T_m : 303.1 K; T_s : 305.5 K) was used as received (TCI America, purity >99%). Equilibrium and dynamic surface tension measurements were performed using a commercial oscillating bubble rheometer (ThetaDyne Corporation). Nonadecane was placed in a quartz cuvette. The alkane-air interface was created by injecting air (≈ 4 μl) through the inverted needle attached to a motorized syringe. Similar results were obtained for bubbles with sizes of 3–6 μl. The sample and the syringe were thermally equilibrated using a circulating water bath (with an accuracy of 0.2 K). The image of the drop formed at the needle tip was captured by a CCD camera and subsequently digitized and analyzed by the

software using the Laplace equation [9]. The density of air (0.001 16 g cm^{-3}) and alkane (0.776 g cm^{-3} [10]) were used for the calculation of γ. For dynamic measurements, the air bubble was oscillated with a 5%–35% volume change (for the square pulse experiments a volume change of 30% was used). The changes in surface area, γ and the images of the bubble during an oscillation cycle with a period 1 sec ($T < T_s$) are shown in Fig. 1. For the position marked (a), the surface area is minimum and γ is similar to the static γ. For position (b), γ has increased abruptly due to rupture of the 2D crystal. In the case of (c), γ has recovered to its equilibrium value, and in (d) the change in γ is due to rupture during the beginning of the contraction cycle.

Figure 2 shows γ as a function of temperature using an oscillation period of 1 sec. Interestingly, large oscillations in γ are observed only below T_s. A discrete change in the slope of the static γ is also observed at T_s as shown in the
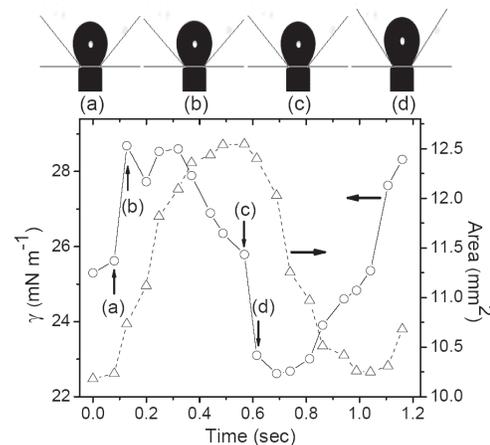
FIG. 1. Pictures of air bubble during the expansion and contraction cycle with a 20% volume change at 303.8 K ($<T_s$). The curvature of the bubble is controlled by γ. This makes (b) look more circular than (a) and (d) more oval than (c) (bubble volume is approximately the same at the two instants compared). The shape of the bubble recovers to its original shape at the beginning of each oscillation cycle.
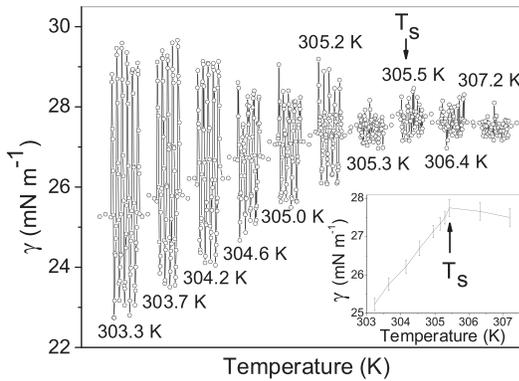
FIG. 2. Plot of γ during oscillations of 20% amplitude with a period of 1 sec as a function of temperature. These measurements were done during the heating cycle. A fresh air bubble was opened at each temperature. The inset shows the static γ as a function of temperature. These measurements are consistent with γ of nonadecane measured using Wilhelmy balance [1]. The arrows indicate the surface transition temperature, T_s.

inset of Fig. 2. The magnitude of these oscillations decreases as one approaches T_s. Since there is no abrupt change in bulk viscosity or density of nonadecane at T_s, the changes in γ are due to the crystalline surface phase on top of disordered melt. We have plotted the change in bubble area and the corresponding changes in γ for periods of 1, 10, 100, and 1000 sec in Figs. 3(a)–3(d). The crystalline structure is recovered when the bubble oscillation reverses direction, indicating that the crystal structure recovers rapidly. Since the feedback of the motorized syringe is not perfect, there is a small correction in volume at the end of each cycle. During this change in volume, discrete spikes in γ are observed, again indicating that the crystal-

line structure is recovered at the end of the oscillation cycle. For periods ≈ 100 sec, the changes in γ are small, and there is no clear abrupt discontinuity in γ. In this transition window, the response is out of phase with respect to the surface area. With an increase in the period (1000 sec), the response in γ becomes in phase with the change in area. This indicates that the bubble is expanding and contracting without any observable rupture of the crystalline surface layer.
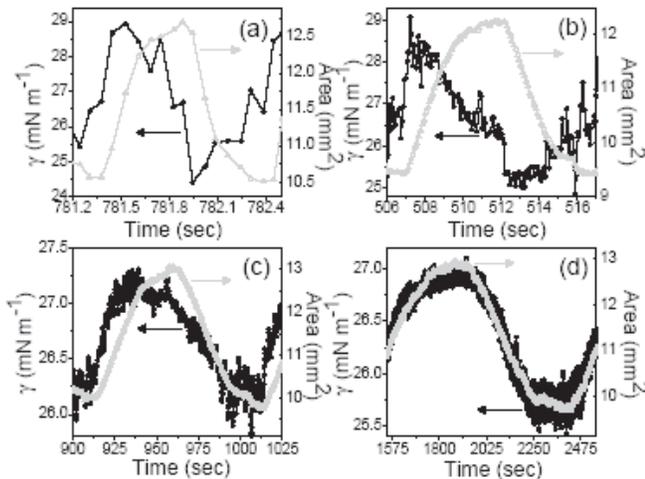
We have defined the abrupt change in γ ($\Delta\gamma$) as the difference in surface tension between points (a) and (b) in Fig. 1. The values of $\Delta\gamma$ during the expansion cycle as a function of $d(\ln A)/dt$ at various temperatures are shown in Fig. 4. We have also included in the graph the measurements using a 1 sec period and changing the amplitude of oscillation from 5%–35%. The similarity in the variable amplitude and variable period data indicates that $d(\ln A)/dt$ is an important parameter determining $\Delta\gamma$. For $T = 303.3$ K and at high rates the values of $\Delta\gamma$ are constant. Below this critical rate, the amplitude decreases with a decrease in rate (power law exponent of 0.8). With an increase in temperature, $\Delta\gamma$ drops sharply as we approach T_s. Because of the limited dynamic frequency range, we could not determine whether the critical crossover frequency has shifted to higher rates with an increase in temperature.

The inset of Fig. 4 shows the ratio of γ at the peak, γ_m, and static values of γ, γ_s for 303.3, 304.9, and 307.2 K. At 307.2 K, above T_s, the ratios are close to 1.0 as expected. For $T = 303.3$ K, below T_s, the ratios are higher, but the

FIG. 3. γ and change in area during the oscillation period of 1 (a), 10 (b), 100 (c), and 1000 sec (d) at 304.2 K. The oscillation amplitude was 20%. For periods <100 sec the change in γ is abrupt just after the reversal of the cycle. The surface tension is in phase with area for longer periods (1000 sec).
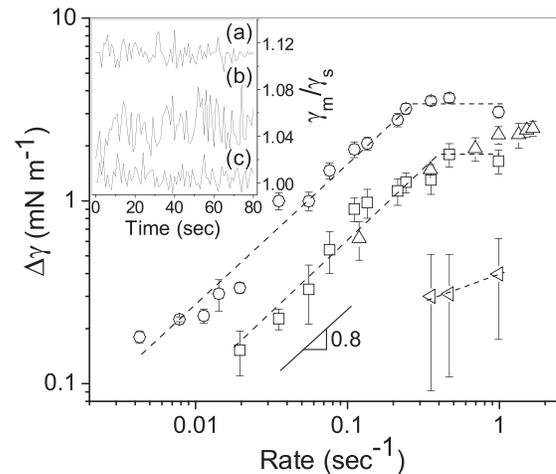
FIG. 4. $\Delta\gamma$ during the expansion cycle is plotted as a function of rate, $d(\ln A)/dt$ at 303.3 K (○), 304.9 K (□), and 305.2 K (◁). Rates were determined during the initial period of oscillation for the data shown in Fig. 3. The dashed lines are a linear fit to the data points below the critical crossover rate. Also plotted are $\Delta\gamma$ for a constant period of 1 sec with amplitude of 5%–35% at 304.5 K (△). The inset shows the ratio of the peak value of γ (γ_m) and static γ (γ_s) at 303.3 K (a), 304.9 K (b), and 307.2 K (c). These measurements were done using a period of 1 sec.

standard deviation in the fluctuations is similar to those above T_s. However, at $T = 304.9$ K, very close to T_s, the ratio of γ_m/γ_s shows much higher fluctuations between different oscillation cycles. The elastic response of this bubble (below T_s) is fluctuating with time. This is consistent with the expectation that the fluctuations should increase as the system approaches a first-order transition temperature. These fluctuations are also reminiscent of fluctuations observed during stick-slip transitions in confined fluids [11].

We propose a simple model to explain the magnitude of $\Delta\gamma$. The work done during the expansion of the bubble is $PdV + VdP$. Since $P = 2\gamma/R$, we determine $PdV \approx$ work done in increasing the surface area (γdA). The second term, VdP, is equal to $2A_f\Delta\gamma/3$, where A_f is the final area. We postulate that this is the work done in breaking the 2D crystal structure. For a grain size of radius R, the rupture involves the creation of an interface between the crystal and disordered melt as shown in Fig. 5. The additional energy for creating this interface is $2\pi RL(\gamma_{ls} - \gamma_g/2)$, where L is the length of nonadecane, γ_g is the interfacial energy of a grain boundary [12], and γ_{ls} is the interfacial energy of the crystal-melt interface. For a bubble of area, A_f, the additional energy is $2LA_f(\gamma_{ls} - \gamma_g/2)/R$. Equating this to VdP, we obtain a simple relationship between R and $\Delta\gamma$, $R = 3L(\gamma_{ls} - \gamma_g/2)/\Delta\gamma$. The value of $(\gamma_{ls} - \gamma_g/2)$ is not known. However, we can estimate the range of values it can take as 0–30 mJ/m^2 [13]. For example, the lower limit of zero will be for temperatures close to T_s. Using the values of $\Delta\gamma$ in Fig. 4 where $\Delta\gamma$ is independent of the rate and $L = 3$ nm, we obtain $R_{\max} \approx 0.1$ μm. The small energy to break the 2D crystal layer of nonadecane ($2/3\Delta\gamma$ compared to the energy of crystallization ≈ 400 mJ/m^2 [2,14]) during bubble expansion and contraction is analogous to the low shear modulus observed for Langmuir monolayers [15]. In those cases also the low modulus was attributed to the presence of grain boundaries. The microscopic modulus of 2D single crystals is many orders of magnitude larger [6], in agreement with theoretical predictions [16].
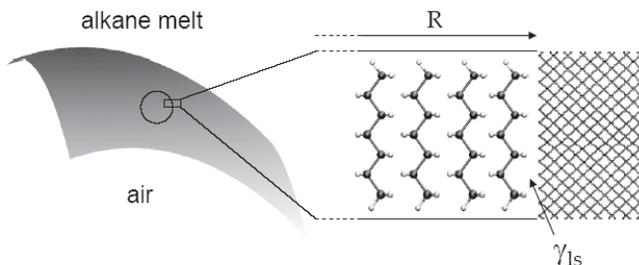
FIG. 5.   Sketch of the grain boundary just after rupture of the 2D-surface crystal. The cross-sectional plane is perpendicular to the bubble surface.

The measurements of grain size on planar substrates for a surface frozen layer of alkanes have been indirect. The grazing incident x-ray diffraction (GIXD) measurements on alkane surfaces by Ocko *et al.* [2] indicate that the grain size has to be >100 nm based on the width of the diffraction peak. Their upper estimate was $\approx$ mm based on the observation of periodicity of 60° upon rotation of the sample with respect to the x-ray beam. The estimate of the grain size in our dynamic experiments is many orders of magnitude smaller than those predicted from GIXD measurements on planar substrates. There are two possible explanations. First, the dynamic surface tension measurements were done on curved surfaces, and the number of defects per unit area for 2D crystals is expected to decrease as $1/R$ [17,18]. The second hypothesis is that the interfacial area generated during rupture is rate dependent. It is expected that deformation results in stress concentration at grain boundaries leading to failure. At low rates, this buildup is more distributed and the rupture takes place at the weakest links. However, for faster rates this process involves breaking at boundaries that are not necessarily the weakest links, leading to a larger interfacial area. An analogy of this would be sheets of ice floating on water; the size of these crystalline sheets after rupture will depend on $d(\ln A)/dt$. This mechanism is complicated further by the rapid recrystallization of alkanes and perhaps migration of defects during deformation [8]. If we take the lowest values of $\Delta\gamma$ measured in our experiments (0.1 mN/m), we obtain the maximum grain size ≈ 3 μm. The differences between the static and dynamic measurements may be due to the combination of curvature and the dependence of $\Delta\gamma$ on the rate of deformation.

The 2D crystals of alkanes are intriguing because the time constants for recovery of the crystalline structure or healing of defects is expected to be fast since it requires only ordering of the chains rather than diffusion of molecules to the surface. This is also observed experimentally after a step change in volume of the bubble, γ recovers in less than 1 sec [Fig. 6(a)]. In addition, the crystal structure recovers very rapidly when the bubble reverses direction. Interestingly, this recovery time is similar to the critical rate (0.1–1 sec^{-1}) above which $\Delta\gamma$ becomes independent of the rate. Finally, we comment on the drop in γ after the break during the expansion cycle [Fig. 6(b)]. For comparison the time is normalized by the period and γ by $\Delta\gamma$. The recovery of γ is rate independent when the area is increasing, indicating that the mechanism of recovery for a moving interface is different from that associated with a step change in surface area [Fig. 6(a)]. GIXD and infrared-visible sum frequency generation experiments on a Langmuir trough are in progress to elucidate the structure of these transient states.

In summary, we have for the first time studied the breakage of a 2D-crystalline layer of alkane on top of a disordered melt. Although dynamic measurements have been
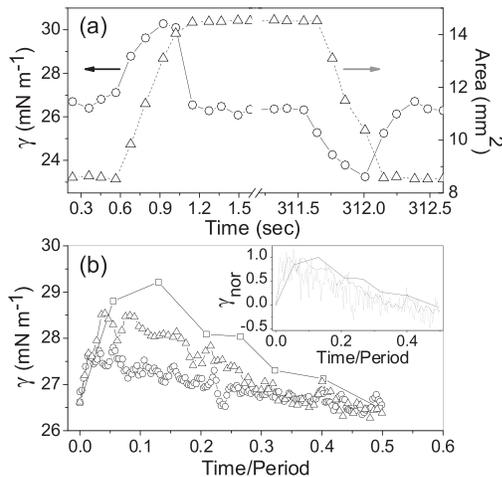
FIG. 6. (a) γ and change in area during the pulse experiment at 304.2 K. γ recovers to the equilibrium value after step change in ≤ 1 sec. (b) γ in the expansion cycle as a function of time normalized with the oscillation period [1 sec ($\square$), 10 sec ($\triangle$), and 30 sec ($\bigcirc$)]. The measurements were done at 304.2 K. γ recovers to equilibrium value at the cycle reversal. The inset shows the normalized surface tension, $\gamma_{nor} = (\gamma - \gamma_s)/(\gamma_m - \gamma_s)$ as a function of normalized time for the three measurements. All three curves merge, indicating time independent recovery.

done on a frozen alkane monolayer to elucidate increased surface rigidity [19] and reduced surface mobility [20], these studies were unable to capture the monolayer rupture. Discrete changes in γ during the expansion and contraction cycle are attributed to the crystal fracture at grain boundaries. The magnitude of this discrete change in γ is found to decrease with a decrease in rate (with power law exponent of 0.8) and an increase in temperature. The resemblance of this power law exponent to the value of 1.0 observed for viscous modulus in viscoelastic materials [21] is intriguing. The mechanism here is clearly elastic rather than viscous, indicated by discontinuity in γ. Here, we have not emphasized the mechanism involved during contraction, even though the trend of $\Delta\gamma$ (power law exponent of ≈ 0.8) is similar to that in the expansion cycle. We expect a bucklinglike transition, and this will be the focus of our future work. These results have important consequences in understanding not only 2D crystals but also the role of grain boundaries in jammed systems such as colloids, glasses, granular materials [22,23], and mechanical response of fluids in confined geometry.

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*Electronic address: ali4@uakron.edu

[1] X. Z. Wu, B. M. Ocko, E. B. Sirota, S. K. Sinha, M. Deutsch, B. H. Cao, and M. W. Kim, Science **261**, 1018 (1993).

[2] B. M. Ocko, X. Z. Wu, E. B. Sirota, S. K. Sinha, O. Gang, and M. Deutsch, Phys. Rev. E **55**, 3164 (1997).

[3] O. Gang, X. Z. Wu, B. M. Ocko, E. B. Sirota, and M. Deutsch, Phys. Rev. E **58**, 6086 (1998).

[4] H. Dosch, *Critical Phenomena at Surfaces & Interfaces* (Springer-Verlag, Berlin, 1992), 1st ed.

[5] A. V. Tkachenko and Y. Rabin, Phys. Rev. Lett. **76**, 2527 (1996).

[6] H. Bercegol and J. Meunier, Nature (London) **356**, 226 (1992).

[7] L. Pauchard and J. Meunier, Phys. Rev. Lett. **70**, 3565 (1993).

[8] R. Bruinsma, B. I. Halperin, and A. Zippelius, Phys. Rev. B **25**, 579 (1982).

[9] A. W. Adamson, *Physical Chemistry of Surfaces* (John Wiley & Sons, Inc., New York, 1976), 3rd ed.

[10] L. T. Chu, C. Sindilariu, A. Freilich, and V. Fried, Can. J. Chem. **64**, 481 (1986).

[11] A. D. Levent and S. Granick, Phys. Rev. Lett. **77**, 4330 (1996).

[12] J. E. Hilliard and J. W. Cahn, Acta Metall. **6**, 772 (1958).

[13] D. Turnbull and R. L. Cormia, J. Chem. Phys. **34**, 820 (1961).

[14] S. Prasad, L. Hanne, and A. Dhinojwala, Macromolecules **38**, 2541 (2005).

[15] B. M. Abraham, K. Miyano, J. B. Ketterson, and S. Q. Xu, Phys. Rev. Lett. **51**, 1975 (1983).

[16] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[17] M. J. Bowick, D. R. Nelson, and A. Travesset, Phys. Rev. B **62**, 8738 (2000).

[18] A. R. Bausch, M. J. Bowick, A. Cacciuto, A. D. Dinsmore, M. F. Hsu, D. R. Nelson, M. G. Nikolaides, A. Travesset, and D. A. Weitz, Science **299**, 1716 (2003).

[19] N. Maeda and V. V. Yaminsky, Phys. Rev. Lett. **84**, 698 (2000).

[20] P. Huber, V. P. Soprunyuk, J. P. Embs, C. Wagner, M. Deutsch, and S. Kumar, Phys. Rev. Lett. **94**, 184504 (2005).

[21] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986), 5th ed.

[22] M. E. Cates, J. P. Wittmer, J.-P. Bouchaud, and P. Claudin, Phys. Rev. Lett. **81**, 1841 (1998).

[23] A. J. Liu and S. R. Nagel, Nature (London) **396**, 21 (1998).