The Crack Tip: A Nanolab for Studying Confined Liquids

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We study the equilibrium properties of a liquid phase condensed at the nanoscale between the surfaces of a sharp crack in fused silica in a moist controlled atmosphere. The extension of the condensed phase along the fracture is measured by *in situ* atomic force microscopy phase imaging and it is shown to be determined by a critical distance between the opposite crack surfaces, which is an increasing function of humidity. The present technique is very promising for measuring the properties of confined liquids at the nanoscale as well as for modeling the physics and chemistry of slow crack propagation in glasses.

The presence of a liquid condensed phase inside the nanometrically sharp cracks in glasses plays an important role in the physics and chemistry of crack propagation, as well as in many industrial problems related to the strength and lifetime of glass products. The slow crack propagation in glasses is commonly explained by the stress-corrosion theory [1]: water molecules that move in the crack cavity effectively reduce the bond strength at the strained crack tip and thus enhance the subcritical crack propagation velocity, which is ruled by the rate of a thermally activated chemical reaction. However, the details of the local environmental condition at the crack tip in moist air are very complex and still need careful investigation. Recent studies have shown the subtle role of nanoscale capillary interactions in determining the mechanical behavior of multiphase systems [2,3]. The difficulties in these studies lie in the complex structure of water in confined geometry that is still the subject of intense research, especially concerning water in nanoporous silica (cf. [4,5] and references therein).

In a previous work [6] we reported direct evidence of the presence of a submicrometric liquid condensate at the crack tip of a pure silica glass during very slow propagation. These observations were based on *in situ* atomic force microscopy (AFM) phase imaging techniques applied on double cleavage drilled compression (DCDC) glass specimens in controlled atmosphere. Several macroscopic measurements of anomalous crack propagation in glasses had hinted at the presence of such a condensate [7,8], yet the direct observation of this phenomenon was not possible until recently due to the difficulty of real-time measurements at such small scale.

We present here a different approach where the humidity is made stable over long periods of time and a series of measurements at different values of the stress intensity factor (SIF) K_I are obtained by changing the applied force (and thus the crack opening) with great care and measuring the direct changes in the condensate length L. This allows us to obtain a new twofold result: the possibility of concluding on the equilibrium condition of the condensate and

the possibility of measuring the critical condensation distance H_c as a function of relative humidity.

Experimental setup.—Fractures are initiated and propagated on a DCDC setup [9] at a constant temperature of $(22.0 \pm 0.5)\,°C$ in a leak-proof chamber under an atmosphere composed of pure nitrogen and water vapor at a given relative humidity level. The parallelepipedic DCDC samples ($4 \times 4 \times 40$ mm^3, with 10 μm tolerance) of pure fused silica glass (Suprasil 311, Heraeus, Germany), were polished to a rms roughness of 0.25 nm (for an area of 10×10 μm^2) and a hole of radius $R = (531 \pm 5)$ μm was drilled at their center to trigger the start of the two symmetric fractures of length c shown in Fig. 1. For an applied stress σ, the SIF is given by $K_I = \sigma R^{1/2}/(0.353 c/R + 2.125)$ [9]. By coupling optical and atomic force microscopy, the crack propagation velocity can be measured in a range from 10^{-5} m/s down to 10^{-12} m/s. The details of the technique can be found in [10].

Tracking of water by AFM phase imaging.—AFM observations are done in tapping mode on a D3100 from Veeco Metrology Inc., Santa Barbara, CA. In this mode, the tip is oscillated at constant frequency ω (close to the resonance frequency ω_0) and at an amplitude A kept constant to a set value thanks to a feedback loop controlling the distance between the tip and the surface. The phase
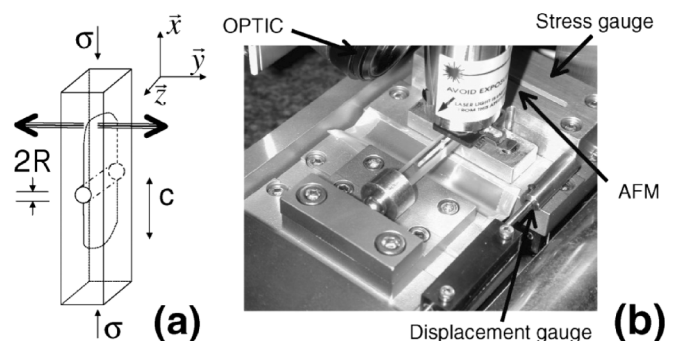

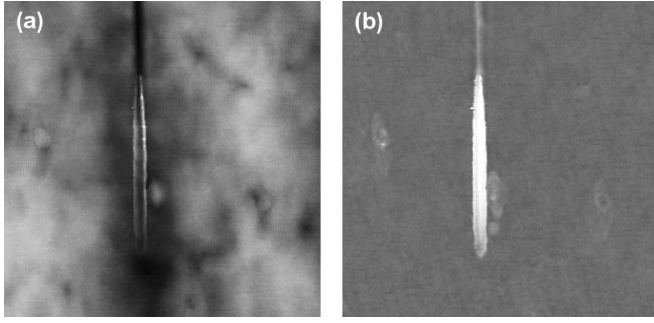FIG. 1. Experimental setup: (a) sketch of the DCDC geometry, (b) picture of the experiment.

FIG. 2. Typical AFM height (a) and phase (b) images of the crack tip for a fracture propagating from top to bottom of the image (1×1 μm). The linear gray scale range is, respectively, 10 nm and 10°.

FIG. 3 (color online). Plot of the condensation length L versus K_I for three different relative humidities (RH). Dashed curves represent equilibrium model. Continuous curves represent the constant volume model. The incertitudes on L and K_I values are, respectively, 20 nm and 0.008 MPa m$^{1/2}$. The inset contains the fitted values of the critical distance H_c for each relative humidity.

delay ($\vartheta \in [-\pi:0]$) between the stimulation and the oscillation of the tip can be related to the energy E_D dissipated per cycle by the tip-surface interactions [11]:

$$E_D = \frac{\pi k A^2}{Q}\left(-\frac{A}{A_0}\sin\vartheta - \frac{\omega}{\omega_0}\right), \qquad (1)$$

where k, Q, A_0 are, respectively, the stiffness of the AFM cantilever, the quality factor, and the free resonance amplitude.

Figure 2 shows typical height and phase images of the crack tip. The crack plane intersects perpendicularly the observed external surface of the sample. The region along the crack characterized by a strong phase contrast corresponds to the portion of the crack cavity which is filled by a condensed liquid phase. According to Eq. (1), the phase contrast on the condensate region corresponds to an increase in the energy dissipated by the tip-sample interaction [12]. Under humidity, the presence of thin water films on both the external sample surface and the AFM tip entails energy dissipation due to the combination of two phenomena: (i) the formation and rupture of a capillary bridge at each oscillation of the AFM tip [13] and (ii) the viscoelastic displacement in the thin films [14]. The dissipated energy is very weak when scanning the glass surface, but it is greatly enhanced when the AFM tip crosses a portion of the crack tip filled with liquid water [12]. The resolution of the AFM technique does not allow us to measure the opening of the crack accurately (a few nanometers here), but it allows us to measure the length L of the condensed region, ranging between 100 nm and 2 μm in our experiments, with an incertitude of the order of ± 20 nm. The measurement of the length was shown not to be dependent on the AFM working conditions, nor on the details of the AFM tip shape or chemical nature within the given incertitude.

Modeling the condensation length.—Figure 3 reports three data series taken at different relative humidity, concerning the measurement of the condensation length L as a function of K_I. The data points were taken by carefu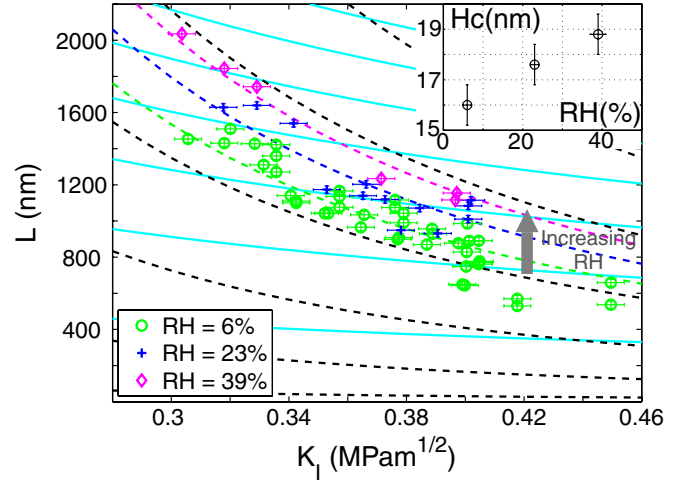lly changing the force applied to the sample every 20 min. For each data series, a clear inverse dependence of L on K_I can be observed, and the direct dependence of L on relative humidity can be observed through the shift between different series.

According to the theory of capillary condensation, the length L of the condensed region is expected to correspond to the portion of the crack where the separation between opposite crack surfaces is less than a critical distance H_c in the nanometer range [15] (Fig. 4). Since we cannot measure precisely the local crack opening on the AFM images, we need a model to relate the condensation length to the SIF. The crack opening profile $2u(X, K_I)$ in the neighborhood of a brittle crack tip is provided by the Irwin relation [8]:

$$2u(X, K_I) = \frac{2K_I}{E'}\left(\frac{8X}{\pi}\right)^{1/2}, \qquad (2)$$
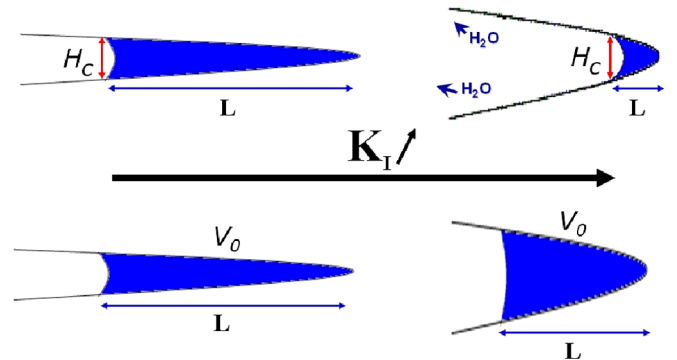

FIG. 4 (color online). Sketch of the variation of the condensation length after an increase of the SIF: (top) case of equilibrium, (bottom) constant volume. N.B.: exaggerated vertical scale.

where $E' = E/(1 - \nu^2)$, with E the Young modulus, ν the Poisson ratio, and $u(X, K_I)$ the elastic displacement perpendicular to the crack surfaces as a function of the distance X from the crack tip. By combining a finite element simulation and a measurement of the crack opening profile by reflection laser interferometry [16], it can be shown that in the DCDC geometry of our experiments the crack opening profile is in agreement with the Irwin relation when X is less than 30 μm, as it is comfortably the case in our measurements. The lower limit of validity of the Irwin relation is expected for X in the order of few nanometers in glass.

The equilibrium length L_{eq} of the condensed phase can then be related to the critical distance H_c and to K_I by imposing the condition $H_c = 2u(L_{eq}, K_I)$. We obtain the relation

$$L_{eq}(H_c, K_I) = \frac{\pi}{8}\left(\frac{E'H_c}{2K_I}\right)^2 \propto K_I^{-2} \qquad (3)$$

that is plotted in dashed lines in Fig. 3 for a series of values of H_c. These curves provide an excellent fit of the experimental data and thus suggest that the liquid condensation has reached equilibrium within the typical 20 min time between different measurements. This implies that evaporation and condensation processes are quite rapid.

This conclusion can be tested against the opposite assumption of very slow evaporation, i.e., for the case where the volume of the condensed phase remains constant during the changes of the applied stress (Fig. 4). The Irwin relation (2) is used to relate the volume V of the condensation to L and K_I. Then by inverting the relation $V(L_{vol}, K_I) = V_0$ we obtain the relation between L_{vol} and K_I at constant volume (h being the thickness of the specimen):

$$L_{vol}(V_0, K_I) = \left(\frac{3}{2}\frac{E'}{K_I}\sqrt{\frac{\pi}{8}}\frac{V_0}{h}\right)^{2/3} \propto K_I^{-2/3}, \qquad (4)$$

which is plotted in continuous lines in Fig. 3 for different values of V_0. This relation is clearly in contrast with the trend of the data.

Equilibrium condition and critical condensation distance.—It is mentioning that the equilibrium modeling represents a static open crack, while the crack in the experiments is propagating, though at very low velocity (generally well below 10^{-9} m/s), and it is consuming water from the condensation in order to propagate by stress corrosion. The quality of the fit to the equilibrium relations means that condensation is able to feed the liquid reservoir in order to maintain its equilibrium length independently of propagation velocity, except perhaps at the highest velocities, reaching 10^{-8} m/s in the four points at higher K_I on the right-hand side of Fig. 3, where the fit is less effective. Equilibrium is also confirmed by the fact that the data obtained while rising or decreasing the force are consistent.

We can thus fit the three data series in Fig. 3 with Eq. (3) in order to extract the critical condensation distance H_c for different values of relative humidity, reported in the inset of Fig. 3. The incertitude of 0.8 nm on the values of H_c was estimated in order to include 68% of the data in the confidence interval in all conditions. The critical distance is shown to increase with relative humidity as expected from the theory of capillary condensation. Although more measurements are needed in order to discuss the details of the adsorption isotherms, we can already state that the observed values, ranging between 16 and 19 nm, are quite large in relation to what we expected theoretically. Since the fresh crack surfaces of glass are totally wetted by water, the critical distance can be expressed as a sum of two terms: $H_c = 2|r_k| + 3e$, respectively, related to the Kelvin radius r_K of the liquid phase and the thickness e of the thin wetting layers on the crack surfaces, both of which are (in absolute value) increasing functions of relative humidity [15]. Using the properties of pure water and fused silica glass, $|r_K|$ should not exceed 1.5 nm for a relative humidity below 70% and the thin water films on the sidewalls should not exceed 1 ML (~ 0.3 nm) [15]. However, since this equation only takes into consideration the van der Waals interaction between water molecules and bulk silica glass, it dismisses important properties of the glass fracture surfaces, which are naturally covered of hydrophilic SiOH terminations, leading to the development of a negative charge density on wetted surfaces [17]. Taking into consideration electrostatic interactions, the thickness of the adsorbed water films is expected to rise with surface charge density and pH of the liquid phase [15]. For very thin films, hydration forces and charge recombination should also be taken into account, as well as the effect of the weak (but finite) roughness of the crack surfaces and especially the subtle role of confinement [4,5]. The relative importance of each contribution is presently far from being understood [15]. Experimental adsorption isotherms of water on flame polished silica surfaces (involving only SiOSi bonds on the external surface) were found to be in good agreement with the van der Waals expectations [18]. However, the measurements of film thickness on hydrated glass surfaces present larger values than expected from any of the previous modeling [19,20].

Mechanical effect.—The pressure inside the liquid condensate can be strongly negative due to the Laplace pressure difference $\Delta P = \gamma/r_K$ originated by the surface tension on the air-liquid meniscus with (negative) nanometric radius of curvature. Water cavitation is not possible due to extreme confinement. It is difficult to separate the contribution of r_K and e to H_c in the present measurements. However, we can reasonably limit the domain of variation of r_K between 1 nm (the typical curvature radius at the crack tip) and 10 nm ($\sim H_c/2$). Using $\gamma_{water} = 72$ mJ/m^2, we obtain a negative pressure in the condensate

between 72 and 7.2 MPa, respectively. This induces a reduction of the crack opening in the condensate region, which can in principle alter the functional expression of Eqs. (3) and (4). Through a detailed experimental and numerical study [16] we showed that for condensate length less than 2 μm, as in the present work, the corrected equations still fit accurately the data in the equilibrium hypothesis and the most pessimistic effect on the measure of the critical distance H_c (occurring for $r_K = 1$ nm) is a reduction of 10%. The mechanical effect can become very strong when the condensation length grows to hundreds of microns, i.e., for weakly loaded cracks.

Conclusion.—The importance of the present result is twofold: on one side we showed that cracks in fused silica glass are filled with a liquid condensate, the extension of which is determined by an *equilibrium* condition. On the other side we presented here a new powerful technique to access the critical condensation distance of a liquid confined between the rigid surfaces of a crack in a brittle solid as a function of the partial pressure of the condensing molecule in the atmosphere. Several efforts have been made in literature in order to access this measurement with surface force apparatus [21]. However, such measurements become very difficult for analyzing water condensation between glass surfaces at low humidity, due to the elevated stiffness of the capillary bridges causing the jump to contact between the test sphere and the sample surface. Thanks to the extreme rigidity of the crack tip walls in glass, our technique allows us to measure the evolution of the critical condensation distance down to very low humidity. This approach also presents important advantages in relation to the studies in porous silica, since the degree of confinement can be changed dynamically with great care, thus making it possible to access transitory properties. Thanks to the achievement of a great control in the local *in situ* measurements, the wet crack tip can become a new "laboratory" for studying physicochemical phenomena in confined nanoscale liquids, such as nanochemical reactions and nanofluidics.

Going back to glass fracture, the present new technique is very promising in order to clarify the subtle role of the physicochemistry of fresh crack surfaces on the stress-corrosion mechanisms. Because of the small size of the condensate, the slow crack propagation in moist atmosphere is quite different than when the sample is immersed in water. Chemical exchanges with atmosphere and glass corrosion products can significantly alter the pH and composition of the condensate. Preliminary results show that the measured critical distance is very sensitive on the condition of initiation, propagation, and aging of the crack

in fused silica glass. These effects are still more pronounced in more complex glasses where ion exchange at the crack tip causes the enrichment of the condensate in alkali species [22]. Since the liquid condensate constitutes the local environmental condition for the corrosion reaction at the crack tip, we believe that this study will shed new light on modeling the complex relation between glass composition and fracture properties.

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