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Article *in* Physical Review Letters · May 2008

DOI: 10.1103/PHYSREVLETT.100.217403 · Source: PubMed

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Decreased Surface Tension of Water by Hard-X-Ray Irradiation

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(Received 4 November 2007; published 29 May 2008)

We discovered that intense irradiation by hard-x-ray strongly decreases the effects of natural surface tension of water in droplets and capillary tubes. The effect was revealed by direct experimental observations with phase contrast microradiology. A model based on ionization and surface charging explains this so far undetected phenomenon. The effect can impact the results of many experimental techniques based on x rays. This is an example of the largely unexplored effects that can be produced by extreme intense x-ray irradiation—an important issue due to current development of x-ray free-electron-lasers with unprecedented brilliance.

DOI: 10.1103/PhysRevLett.100.217403 PACS numbers: 78.70.Dm, 68.03.Cd, 82.50.Kx

Hard x rays are used in a variety of experimental studies of liquids and in particularly of water [1–11]. The present synchrotron sources allow very high levels of irradiation that could conceivably alter basic parameters such as the surface tension, and the corresponding effects. In spite of its potential impact, this issue is still largely unexplored [1–11].

Using phase contrast microradiology [12–14], we discovered that intense hard x rays do decrease the effects of the surface tension of water, in particular, for droplets. The evidence was obtained with three different types of experiments at the 7B2 beam line of the PLS 2.5 GeV, 150 mA storage ring in Pohang, Korea [13]. Spatially coherent synchrotron x rays in the photon energy range 10–60 keV were used to irradiate water and simultaneously to image the induced effects [12–14].

The first series of tests was conducted by injecting pure water droplets (18 MΩ, Millipore) in a container with olive oil as schematically shown in Fig. 1. Some droplets stayed suspended at the upper oil surface [15] forming small water-air interfaces. During x-ray irradiation, these droplets were imaged using a $CdWO_4$ scintillator crystal and a CCD camera. The scintillator-specimen distance was set at 150 mm to optimize phase contrast [12–14]. The beam spot size was $0.58 \times 0.44\ \mathrm{mm}^2$ and the microradiology spatial resolution was 0.5 μm. Sequential microradiographs were taken with an acquisition time of 100 ms.

Figure 1(c) shows that the hard-x-ray irradiation (dose rate $\approx 10^3\ \mathrm{Gy\ s}^{-1}$) causes a gradual decrease of r, the radius of the contact surface between air and the water droplet, until the droplet detaches. This indicates a decrease in the water-air surface tension γ_w. Figure 2 illustrates how r and the oil-air and water-oil contact angles θ and ϕ [defined in Fig. 1(b)] evolve with the irradiation time. The x rays marginally affect θ, indicating only limited effects on the oil-air surface tension γ_o—whereas ϕ markedly increases.

For a quantitative analysis, we used the horizontal and vertical balance of forces:

$$\gamma_w = 2(\gamma_o \cos\theta + \gamma_{\mathrm{wo}} \cos\phi); \tag{1}$$

$$\gamma_g = \gamma_o \sin\theta - \gamma_{\mathrm{wo}} \sin\phi. \tag{2}$$

Here γ_{wo} is the water-oil surface tensions and γ_g the surface tension equivalent of gravity, given by Tate's law:

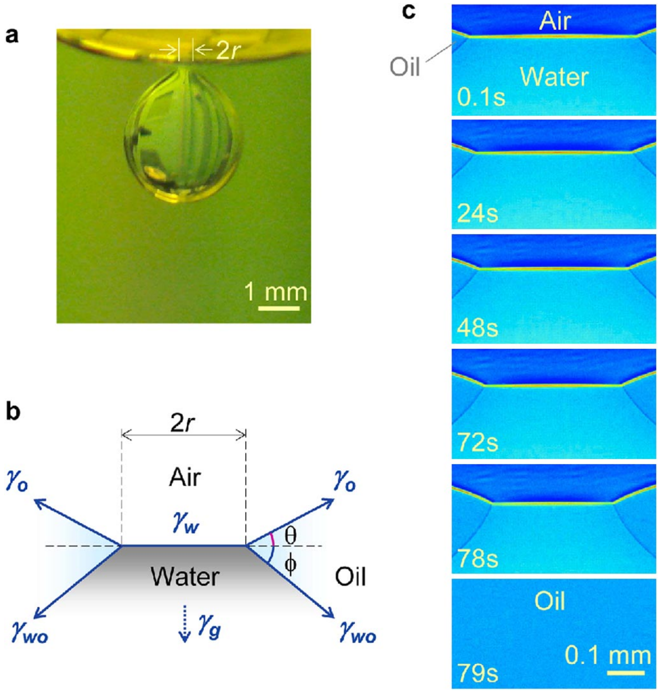

FIG. 1 (color online). First series of tests: (a) the experimental specimen, a water droplet suspended at an interface between oil and air. Scale bar: 1 mm. (b) force balance; (c) representative microradiology image sequence during x-ray irradiation (Scale bar: 100 μm). The x-ray dose rate was $\approx 10^3\ \mathrm{Gy\,s}^{-1}$.

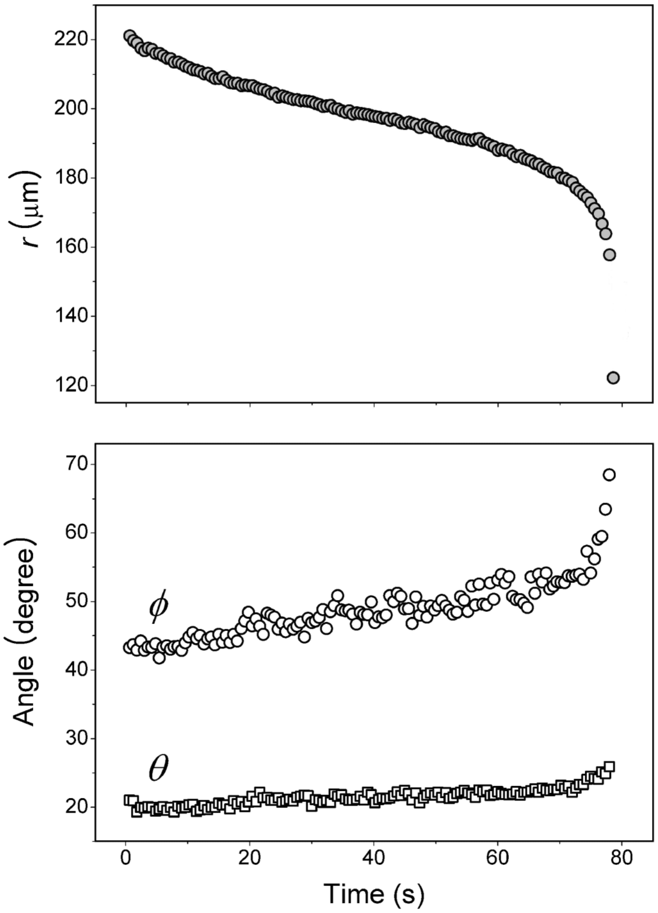

FIG. 2. Evolution of the contact radius and of the contact angles with the irradiation time, again with an x-ray dose rate $\approx 10^3$ Gy s^{-1}.

$\gamma_g = \Delta\rho g V/(2\pi r)$—where V is the droplet volume, $\Delta\rho$ the water-oil density difference and g the gravity acceleration. Thus, assuming an approximately constant value $\gamma_o = 35.3$ mN m^{-1}, γ_w and γ_{wo} can be derived from the r, V, θ, and ϕ values measured in the micrographs. The corresponding dependence of γ_w on the irradiation time is shown in Fig. 3, revealing a strong decrease; note that this qualitative conclusion is not affected by the above assumptions. Similar results were consistently obtained for 28 quantitative tests (plus several more qualitative tests).

The second set of experiments explored the impact of x-ray irradiation on water capillarity as shown in Fig. 4(a). Ultrapure water was injected into a hydrophilic capillary tube (Suprasil, VitroCom, radius $a = 300$ μm). The concave water meniscus was again imaged with x-ray microradiography.

The meniscus surface shape is related to the surface tension by the Young-Laplace equation [16]:

$$\Delta p = 2\gamma_w/R, \tag{3}$$

where Δp is the pressure difference between the fluids and R is the harmonic mean of the two principal radii of curvature of the surface. In our case, the capillary tube is sufficiently narrow (i.e., a is smaller than the capillary length $[\gamma_w/(\rho g)]^{1/2}$, where ρ is the water density [17]) to produce a spherical meniscus: thus, R is the radius.

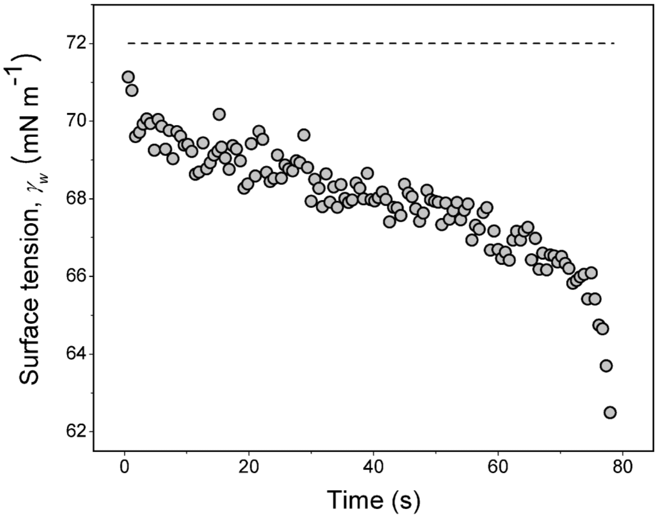

FIG. 3. Experimental x-ray-induced (dose rate $\approx 10^3$ Gy s^{-1}) decrease of the water-air surface tension, starting from the standard value of 72 mN m^{-1}.

Figure 4(b) shows that R (estimated from the micrographs with the Image-Pro Plus software) is reduced by the 10–60 keV x-ray irradiation. According to Eq. (3), this confirms the decrease of the water surface tension. Figure 4(c) shows the corresponding dependence of R and γ_w on the irradiation time.

The contact line between the meniscus and the capillary tube did not move during the irradiation. Thus, the decrease of R corresponds to a reduction of the total water volume due to evaporation. The evaporation enthalpy is related [18] to the surface tension, thus the presence of evaporation confirms again a decrease in γ_w.

Evaporation effects were studied in detail by the third set of tests, similar to the second except that both ends of the capillary tube were sealed. This complicated the quantitative analysis since Δp was no longer a constant. Qualitatively, x-ray irradiation induced both a reduction in the meniscus radius and a decrease in the water volume—confirming the induced decrease in the surface tension.

Our newly discovered phenomenon raises two critical questions: first, why was it not discovered by the many previous experiments conducted with x rays on water systems [1–11]? Second, what is the underlying mechanism and, in particular, could heating by x-ray irradiation trivially explain it?

The key point in the first question is flux. We used broadband, unmonochromatized synchrotron radiation with a much higher flux than most experiments that are conducted with monochromatized beams. Figure 5 shows for different x-rays dose rates the irradiation-induced

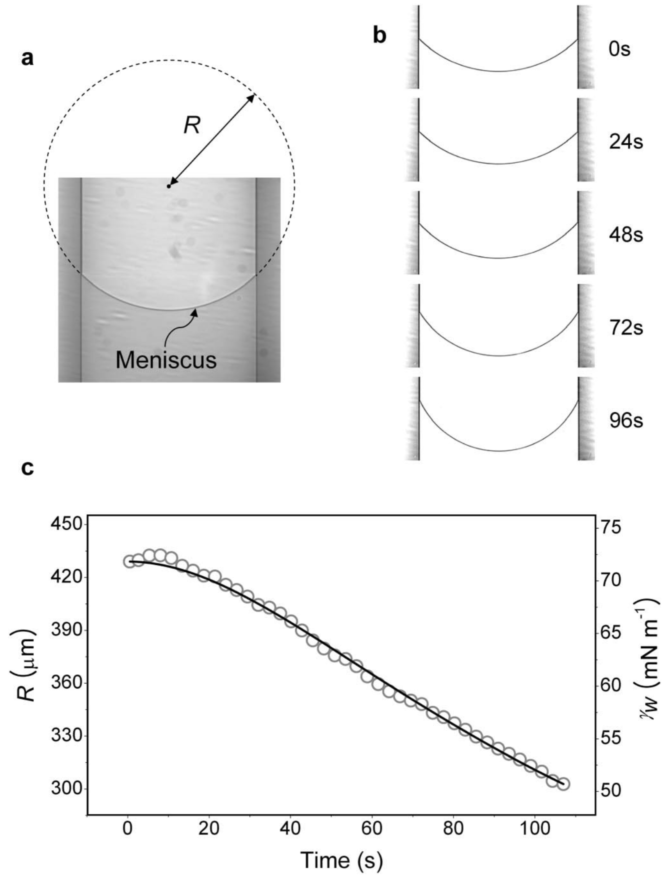

FIG. 4. Second series of tests: (a) microradiology image of the spherical meniscus of water in a capillary tube with radius $a = 300\ \mu\text{m}$, sealed at the bottom and open at the top; (b) change in the meniscus radius during x-ray irradiation (dose rate $\approx 10^3\ \text{Gy}\,\text{s}^{-1}$); (c) corresponding time evolution of the radius and of the water-air surface tension; the solid line is the best fit with the theoretical Eq. (9).

changes of the meniscus radius in a 1.6 mm diameter sealed capillary tube. These tests were performed with an x-ray microfocus facility (Hamamatsu, L9191) and the dose rate was measured with a previously calibrated ion chamber. The meniscus radius was derived in this case from digital pictures: the accuracy was lower than in microradiology but adequate for this test.

The surface tension decrease is clearly visible in Fig. 5 for high dose rates. For comparison, the dose rate in the previously discussed three test series was $\approx 10^3\ \text{Gy}\,\text{s}^{-1}$ and the irradiation time up to 100 s; the highest dose rate ($166\ \text{Gy}\,\text{s}^{-1}$) in Fig. 5 and the 10 min of irradiation produce a similar total dose in the 10^5 Gy range. The surface tension decrease can no longer be detected for $3\ \text{Gy}\,\text{s}^{-1}$—comparable to the dose rate produced by experiments with monochromatic beams. This explains why the phenomenon was not previously reported.

Concerning the causes, we found that heating during x-ray irradiation is negligible. In the droplet experiments, measurements by an infrared thermometer detected only a small temperature increase <1.0 K. In the capillary-tube tests, the increase was <1.0 K ± 0.08 K—a result corroborated by parallel observations of the expansion of a 200 μm diameter mercury droplet.

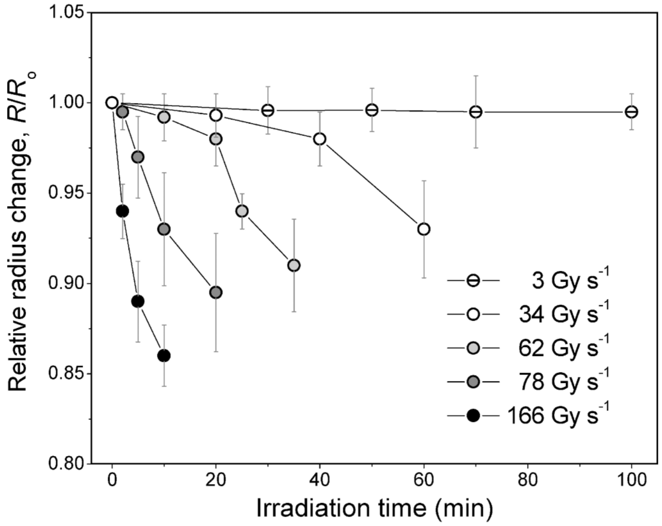

FIG. 5. Relative decrease at different x-ray dose rates of the meniscus radius (R_o = initial value) for water in sealed 1.6 mm diameter capillary tubes.

Since heating can be ruled out, what is the cause of the phenomenon? We argue that intense x-ray bombardment creates by ionization [19] a surface charge that affects the surface tension [20,21]. Consider Lippmann's equation [22]:

$$\frac{d\gamma_w}{d\Phi} = -\sigma, \tag{4}$$

where Φ is the potential and σ the surface charge density; this equation can be written as

$$\frac{d\gamma_w}{d\sigma} = -\left(\frac{d\Phi}{d\sigma}\right)\sigma; \tag{5}$$

on the other hand, $\Phi = \sigma R/(\varepsilon_o\varepsilon_r)$, where $(\varepsilon_o\varepsilon_r)$ is the dielectric permittivity. The Young-Laplace Equation, Eq. (3), gives then $\Phi = 2\sigma\gamma_w/(\varepsilon_o\varepsilon_r\Delta p)$ and

$$\frac{d\Phi}{d\sigma} = \frac{2}{\varepsilon_o\varepsilon_r\Delta p}\left(\gamma_w + \sigma\frac{d\gamma_w}{d\sigma}\right). \tag{6}$$

Together with Eq. (5), this leads after a few simple steps to

$$\frac{d\gamma_w}{\gamma_w} = -\frac{\sigma d\sigma}{\frac{\varepsilon_o\varepsilon_r\Delta p}{2} + \sigma^2}. \tag{7}$$

After integration, this equation gives: $\ln(\gamma_w/\gamma_{wi}) = -(1/2)\ln\{1 + [2\sigma^2/(\varepsilon_o\varepsilon_r\Delta p)]\}$, where γ_{wi} is the initial value of the surface tension, or [since Eq. (3) gives $\Delta p = 2\gamma_{wi}/R_o$, where R_o = initial radius of curvature],

$$\gamma_w = \frac{\gamma_{wi}}{\sqrt{1 + \frac{R_o}{\varepsilon_o \varepsilon_r \gamma_{wi}} \sigma^2}}. \tag{8}$$

Assuming a time-dependent charge building towards an asymptotic value σ_F of the type $\sigma = \sigma_F[1 - \exp(-t/\tau)]$, Eq. (8) can be used to derive the time dependence of the surface tension. Note that σ cannot exceed the Rayleigh instability limit [23] (for Coulomb fragmentation) $\sigma_R = 2(\varepsilon_o \varepsilon_r \gamma_{wi}/R_o)^{1/2}$—and Eq. (8) can be written as

$$\gamma_w = \frac{\gamma_{wi}}{\sqrt{1 + 4\{(\frac{\sigma_F}{\sigma_R})[1 - \exp(-t/\tau)]\}}}. \tag{9}$$

The solid line of Fig. 4(c) shows by best fitting that Eq. (9) and therefore the charging effects can explain our experimental data. Here $\varepsilon_r \approx 80$ for water and the best-fitting parameters were $\sigma_F/\sigma_R = 1.40$ and $\tau = 240$ s. Note that since $\sigma_F/\sigma_R > 1$ the charge buildup would lead in this case to the Rayleigh instability before reaching the asymptotic value σ_F. On the other hand, the minimum value of $\gamma_w \approx 0.7\gamma_{wi}$ in Fig. 4(c) does not yet reach the Rayleigh limit: Eq. (8) gives indeed $\sigma_F/\sigma_R = [(\gamma_{wi}/\gamma_w)^2 - 1]^{1/2}/2 \approx 0.51$.

Our newly discovered effect can have a so far neglected impact on many other experiments. Its magnitude in our tests was quite large because of the unusually high flux of x rays. However, scaled-down phenomena of the same kind could still significantly affect the results of other experimental techniques involving the interaction of synchrotron x rays with water (and other liquids)—and these problems could become more relevant with the next generations of synchrotron and free-electron laser sources. Furthermore, the possibility to tune the surface tension by x-ray irradiation can be exploited to study the many phenomena affected by this parameter in physics, chemistry, and biology [24,25]—such as, for example, the tendency of oil and water to segregate. Our phenomenon could possibly play a role in extreme atmospheric droplet charging cases such as thunderstorm clouds in the vicinity of lightning where intense gamma and x-ray emission occurs [26]. By and large, our newly discovered phenomenon should not be neglected *a priori* whenever water and x rays interact with each other.

This work was supported by the Creative Research Initiatives (Functional x-ray Imaging) of MOST/KOSEF. We would like to thank Dr. Jasper Kirkby for his suggestions on the physical mechanism and on atmospheric phenomena.

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