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Observing Liquid Flow in Nanotubes

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Advances in microfabrication have led to the emergence of the field of nanofluidics, which studies fluid transport in nanometer-scale structures [1-2]. Nanoscale confinement may considerably modify the properties and dynamics of a liquid. For example, the flow of water through carbon nanotubes has been reported to be enhanced by several orders of magnitude [3-4]. However, the magnitude of the enhancement has remained a point of contention [5]. A particular obstacle to settling this controversy is the great challenge of studying flow in a single nanotube [6]. Here, we demonstrate how this can be achieved by using 4D Electron Microscopy, which combines the spatial resolution of a Transmission Electron Microscope with the (ultra)fast time resolution of modern laser systems [7]. We directly image the flow of liquid lead through individual ZnO nanotubes to capture a range of flow phenomena and to characterize the nanoscale viscous friction involved [8].

Lead filled ZnO nanotubes [9] on a graphite thin film were studied at 363 K, well below the melting point of lead at 600.64 K. Experiments were performed with the UEM-1 instrument [7]. Briefly, a laser pulse was used to melt the lead core *in situ*, and the ensuing dynamics of the hot, pressurized liquid were imaged with a short electron burst, fired a short instant later.

Figure 1A shows a micrograph of a typical nanotube after exposure to several laser pulses. On the left, lead has leaked through an imperfection in the tube wall and formed a spherical particle, while voids are visible in the remaining lead core on the right. It is evident that the laser fluence is sufficiently high to melt the lead core and to initiate dynamics that are driven by the expansion of the liquid. Among the many flow phenomena that we observe is the process displayed in Fig. 1B-F. When the continuously filled tube in (B) is irradiated with a laser pulse, part of the molten lead column is forced through a leak in the tube wall. A single-shot image recorded at 96 ns (C) shows that a spherical extrusion has formed. After the tube has cooled, the extrusion is slowly reabsorbed on the timescale of several minutes [(D) to (F)]. This suggests that the lead atoms on the surface of the extrusion and in the channel connecting it to the inside of the tube are sufficiently mobile to allow this slow diffusion process to occur.

For the partially filled nanotube in Fig. 2A (55 nm inner diameter), laser-heating simply triggers the expansion of the lead column. The complete expansion dynamics, obtained from over 100 individual single-shot experiments, are shown Fig. 2B. During the first 30 ns, the meniscus advances rapidly with a speed of about 4 m/s and then recedes more slowly within another 300 ns, which agrees well with the typical cooling timescales that we measure for similar nanotubes. To analyze the expansion dynamics, we developed a simple model, using an approach similar to Washburn's law for the dynamics of capillary filling [10], but assuming that the expansion of the lead column drives the dynamics, not the capillary force. From a fit of the initial expansion with an expression thus obtained (blue line and dots), we determine that the flow is enhanced by at least one order of magnitude.

We believe that the approach developed here will find fruitful application in the study of a range of nanoscale flow phenomena and will greatly benefit the emerging field of nanofluidics [11].

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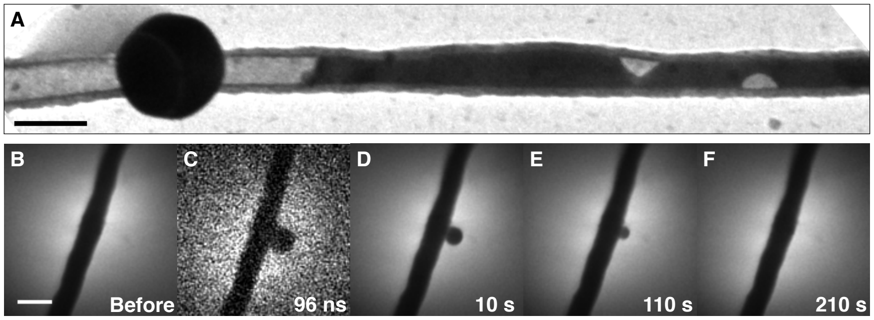

Figure 1. A lead-filled ZnO nanotube and the temporal evolution of an extrusion. (A) Micrograph of a lead-filled ZnO nanotube after irradiation with several laser pulses. Scale bar, 100 nm. (B to F) When the filled nanotube in (B) is laser-heated, molten lead forces its way through a leak in the tube wall. At 96 ns, an extrusion is visible (C), which is slowly reabsorbed on a time scale of several minutes after the tube has cooled [(D) to (F)]. Scale bar, 200 nm.

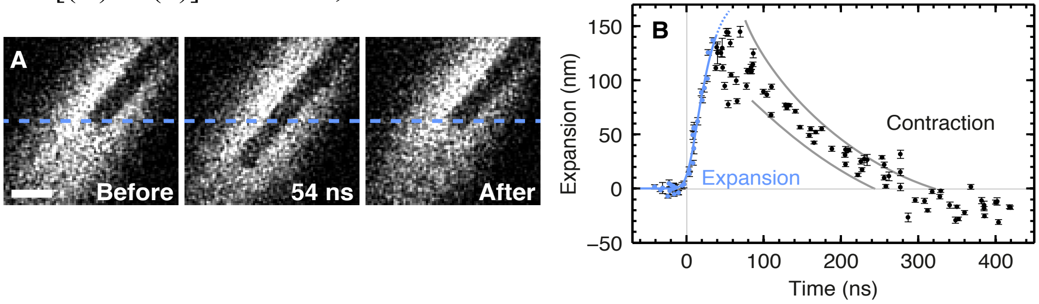

Figure 2. Expansion dynamics of liquid lead in a single nanotube. (A) Single-shot images of a partially filled tube with an inner diameter of 55 nm. At a delay of 54 ns after the heating laser pulse, the lead column has expanded by 140 nm, before returning to its original length at long times. Scale bar, 100 nm. (B) The complete dynamics obtained from a series of such experiments. The gray lines have been inserted to guide the eye. From a fit of the initial expansion using a simple model of the dynamics that we developed in analogy to Washburn's law (blue line and dots), we estimate that viscous friction is reduced by at least one order of magnitude.