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Nanoscale Mechanical Drumming Visualized by 4D Electron Microscopy

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ABSTRACT

With four-dimensional (4D) electron microscopy, we report in situ imaging of the mechanical drumming of a nanoscale material. The single crystal graphite film is found to exhibit global resonance motion that is fully reversible and follows the same evolution after each initiating stress pulse. At early times, the motion appears “chaotic” showing the different mechanical modes present over the micron scale. At longer time, the motion of the thin film collapses into a well-defined fundamental frequency of 1.08 MHz, a behavior reminiscent of mode locking; the mechanical motion damps out after ∼200 µs and the oscillation has a “cavity” quality factor of 150. The resonance time is determined by the stiffness of the material, and for the 75 nm thick and 40 µm square specimen used here we determined Young’s modulus to be 1.0 TPa for the in-plane stress-strain profile. Because of its real-time dimension, this 4D microscopy should have applications in the study of these and other types of materials structures.

Structural, morphological, and mechanical properties of materials have different length and time scales. The elementary structural dynamics, which involve atomic movements, are typically of picometer length scale and occur on the time scale of femto (fs) to picoseconds (ps). Collective phenomena of such atomic motions, which define morphological changes, are observed on somewhat longer time scale, spanning the ps to nanosecond (ns) time domain, and the length scale encompasses up to micrometers. When the membranelike mechanical dynamics have high frequencies and complex spatial-mode structures, imaging becomes of great value in displaying the spatiotemporal behavior of the material under stress (see refs 1–5).

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extraordinary thinness, large surface area, low mass density, thicknesses reaching the one atomic layer, graphene remains graphene a new type of nanoelectronmechanical system the 2D basal planes. More recently, with the rise of displays anisotropic electromechanical properties of high strength, stiffness, and thermal/electric conductivity along the 2D basal planes. More recently, with the rise of graphene a new type of nanoelectronmechanical system (NEMS) has been highlighted with a prototypical NEMS being a nanoscale resonator, a beam of material that vibrates in response to an applied external force.

Graphite was chosen because of its unique material properties; it is made of stacked layers of 2D graphene sheets, in which the atoms of each sheet are covalently bonded in a honeycomb lattice, and the sheets separated by 0.335 nm are weakly held together by van der Waals forces. It displays anisotropic electromechanical properties of high strength, stiffness, and thermal/electric conductivity along the 2D basal planes. More recently, with the rise of graphene a new type of nanoelectronmechanical system (NEMS) has been highlighted with a prototypical NEMS being a nanoscale resonator, a beam of material that vibrates in response to an applied external force.

With the thicknesses reaching the one atomic layer, graphene remains in a high crystalline order, resulting in a NEMS with extraordinary thinness, large surface area, low mass density, and high Young’s modulus.

All measurements were performed with our second-generation microscope, UEM-2, the operations of which in the fs single-electron mode and ns single-pulse mode have been described in detail elsewhere.

Because here the visualization is that of the mechanical modes with resonances on the MHz scale, the ns resolution was sufficient. The electrons are accelerated to 200 kV with a de Broglie wavelength of 2.5079 pm. Two laser pulses were used, one as the clocking, excitation pulse at 532 nm and another at 355 nm for the generation of the electron pulse for imaging. The time delay was controlled by changing the trigger time for electron pulses with respect to that of clocking pulses. The delay can be made arbitrarily long and the repetition rate varies from a single shot to 200 kHz, to allow complete heat dissipation in the specimen. The experiments were carried out with a natural single crystal of graphite flakes on a TEM grid. Graphite flakes were left on the surface, covering some of the grid squares completely. The observed dynamics are fully reversible, retracing the identical evolution after each initiating pulse; each image is constructed stroboscopically, in a half-second, from typically 2500 pulses of electrons.

Panels A and B of Figure 1 show the UEM (bright field) images of graphite, and in panel C a typical electron diffraction pattern is given. The Bragg spots are indexed according to the hexagonal structure of graphite along the [001] zone axis, with the lattice dimension of \( a = b = 2.46 \) Å \( c = 6.71 \) Å. In Figure 1A, and at higher magnification in Figure 1B, contrast fringes are clear, typically consisting of linear fringes having \( \sim 1 \) µm length and a few hundred nm spacing. These contrast fringes are the result of physical buckling of the graphene layers by constraints or by nanoscale defects within the film. In the dark regions, the zone axis (the crystal [001]) is well aligned with the incident electron beam and electrons are scattered efficiently, whereas in the lighter regions the alignment of the zone axis deviates more and the scattering efficiency is lower. With these contrast patterns, changes in image provide a sensitive visual indicator of the occurrence of mechanical motions.

In Figure 2A, we display several time-framed images of graphite taken at a repetition rate of 5 kHz and at delay times indicated with respect to the clocking (heating) pulse with fluence of 7 mJ/cm². At positive times, following \( t = 0 \), visual changes are seen in the contrast fringes. With time, the contrast fringes change their location in the images, and with these and other micrographs of equal time steps we made a movie of the mechanical motions of graphite following the ns excitation impulse (see Supporting Information). To more clearly display the temporal evolution on the nanoscale, image-difference frames were constructed.

In Figure 2B, depicted are the images obtained when referencing to the \( -1 \) µs frame, that is, \( \text{Im}(-1 \: \mu s; \: t) \). In the difference images, the regions of white or black indicate locations of surface morphology change (contrast pattern movement), while gray regions are areas where the contrast is unchanged from that of the reference frame. Care was taken to ensure the absence of long-term specimen drifts as they can cause apparent contrast change; note that in the difference images, the static features are not present. As
mentioned above, image changes are fully reproducible, retracing the identical evolution after each initiating laser pulse. The reversal of contrast with time in Figure 2B directly images the oscillatory behavior of the drumming.

The image change was quantified by using the method of cross-correlation. The normalized cross correlation of an image at time \( t \) with respect to that at time \( t' \) is expressed as

\[
\gamma(t'; t) = \frac{\sum_{x,y} C_{x,y}(t)C_{x,y}(t')}{\left(\sum_{x,y} C_{x,y}(t')^2 \sum_{x,y} C_{x,y}(t')^2\right)^{1/2}}
\]

where the contrast \( C_{x,y}(t) \) is given by \([I_{x,y}(t) - \bar{I}(t)]/\bar{I}(t)\), and \( I_{x,y}(t) \) and \( I_{x,y}(t') \) are the intensities of pixels at the position of \((x,y)\) at times \( t \) and \( t' \); \( \bar{I}(t) \) and \( \bar{I}(t') \) are the means of \( I_{x,y}(t) \) and \( I_{x,y}(t') \), respectively. This correlation coefficient \( \gamma(t'; t) \) is a measure of the temporal change in “relief pattern” between the two images being compared, which can be used as a guide to image dynamics as a function of time. Shown in Figure 3 are cross-correlation values between the image at each measured time point and a reference image recorded before the arrival of the clocking pulse.

Over all pixels, the time scale for image change covers the full range of time delays, from ten ns to hundreds of \( \mu \)s, indicating the collective averaging over the sites of the specimen. Upon impulsive heating at \( t = 0 \), the image cross-correlation changes considerably with an appearance of a “chaotic” behavior, in the \(~5 \mu s\) range (regime I in Figure 3). After 10 \( \mu \)s, for example, regime II, the cross correlation change begins to exhibit periodicity, and at longer time, a

**Figure 2.** Representative image snapshots and difference frames. (A) Images recorded stroboscopically at different time delays, indicated at the top right corner of each image \((t_1, t_2, t_3, t_4, \text{ and } t_5)\), after heating stress with the initiating pulse (fluence = 7 mJ/cm\(^2\)); \( t_1 = 200 \text{ ns}; t_2 = 500 \text{ ns}; t_3 = 10 \mu \text{ s}; t_4 = 30 \mu \text{ s}; t_5 = 60 \mu \text{ s}; \) and the negative time frame was taken at \(-1 \mu \text{ s}\). Note the change in position of fringes with time, an effect that can be clearly seen in panel B. (B) Image difference frames with respect to the image taken at \(-1 \mu \text{ s}, \text{ that is, } Im(-1 \mu \text{ s}; t)\), which show the nm-scale image change with time. The scale bar is the same (Figure 1A). The reversal in contrast clearly displays the oscillatory (resonance) behavior, as discussed in the text.
well-defined resonance oscillation emerges (regime III). This is also evident in the selected-area image dynamics (SAID) in several regions (noted as 1 to 5) where the temporal behavior is of different shapes at early time but converges into a single resonance transient after several tens of $\mu$s. The shape of image cross correlation dynamics was robust at different fluences from 2 to $\sim 10$ mJ/cm$^2$, but the amplitude varies.

The overall decay of the transients is on a time scale shorter than the separation between pulses. In fact, we have verified the influence of repetition rate and could establish the full recovery at the time intervals indicated. Heat transfer must occur laterally. With an initial $z$-independent heat profile by absorption of the heating pulse in graphite, we estimated, using a 2D heat diffusion in a homogeneous medium, the time scale for an in-plane transfer, with thermal conductivity $\lambda = 704$ (Â5000 for graphene) W/(m·K) for natural graphite flakes, density $\rho = 2260$ kg/m$^3$, and specific heat $c_v = 700$ J/(K·kg). For the radius at half-height of the initial pulse heat distribution $r_0 = 30 \mu$m, $t_{1/2}$ the time for the axial temperature to drop to a half of its initial value is deduced to be $\sim 720$ ($\sim 100$ for graphene) ns, certainly much shorter than the 200 $\mu$s time interval between pulses. It follows that the decay of the oscillation $[Q/(\pi f_0)]$, as derived below, is determined by the damping of mechanical motions.

When the specimen absorbs intense laser light, the lattice energy, converted from carriers (electron energy) by electron–phonon coupling, in a few ps builds up in the illuminated spot on the surface within the duration of the laser pulse. As a consequence, the irradiated volume will expand rapidly following phonon–phonon interaction on the time scale of tens of ps. The resulting thermal stress can induce mechanical vibration in the material, but a coherent oscillatory behavior, due to the thermoelastic stress, will only emerge in the image if the impulsive stress is on a time scale shorter than the period; to resolve the full dynamics, probing of images should be over the entire time scale of the process, in this case 100 $\mu$s. On the ultrashort time scale, we have observed the structural and morphological elastic changes.

The resonance modes in graphite are highlighted in Figure 4 by taking the fast Fourier transform (FFT) of image cross-correlation in the time regime of 0–100 $\mu$s. The FFT (Figure 4C) shows several peaks of different frequencies, among

Figure 3. Time dependence of image cross correlation. The whole scan for 100 $\mu$s is made of 2000 images taken at 50 ns steps. Also depicted are the zoomed-in image cross-correlations of three representative time regimes (I, II, and III). In each zoomed-in panel, the selected-area image dynamics of five different regions are included. Note the evolution from the “chaotic” to the global resonance (drumming) behavior at long times.
which the strongest one around 2.13 MHz is attributed to the overtone of 1.08 MHz. The overtones, due to the truncated nature of cross-correlation close to the value of 1, are greatly reduced in the FFT of selected-area image intensity (Figure 4E and F). In a few tens of µs, various local mechanical modes observed at early time damp out and one global mode around 1 MHz survives. The peak when fitted to a Lorentzian yields a resonant frequency of 1.08 MHz, and a “cavity” quality factor $Q = f_0/\Delta f \approx 150 \pm 30$. This dominant peak gives the fundamental vibration mode of the plate in graphite. Note that for a period of vibration, the contrast pattern of the image would recur twice to its initial feature.

A square mechanical resonator clamped at three edges has a fundamental resonance mode of $f_0$ which is given by

$$f_0 = A \frac{d}{L^2} \left[ \frac{Y}{(1 - \nu^2)\rho} \right]^{1/2} + f(T)$$

where $f(T)$ due to tension $T$ is taken to be zero in this case.24 $Y$ is the Young’s modulus, $\rho$ is the mass density, $\nu$ is the Poisson’s ratio, $L$ is the dimension of a grid square, $d$ is the thickness of the graphite, and $A$ is a constant, which in this case is equal to 1.103. We measured $d$ to be 75 nm from EELS in our microscope. With $\rho = 2260$ kg/m$^3$ (300 K), $21 \nu = 0.16$ for graphite,25 and $L = 40 \mu$m, we obtained from the observed resonance frequency the Young’s modulus to be 1.0 TPa, which is in good agreement with the in-plane average value of 1.02 TPa, obtained using stress–strain measurements.25 This value is different by more than an order of magnitude from the $c$-axis value we measured using the microscope in the ultrafast mode of operation.5

In conclusion, we have demonstrated a very sensitive 4D microscopy method for the study of nanoscale mechanical motions in space and time. With selected-area-imaging dynamics, the evolution of multimode oscillations to a coherent resonance (global) mode at long time is revealed in the mapping of local regions of the image, from nanometers to micrometers. The time scale of the resonance is directly related to the anisotropic elasticity (Young’s modulus), density, and tension, and as such the reported real-time observation in imaging can be extended to study mechanical properties of membranes (graphene in the present case) and other nanostructures with noninvasive probing. The emergent properties resolved here are of special interest to us as they represent a well-defined “self-organization” in complex macroscopic systems, and more on this subject will be forthcoming.

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Supporting Information Available: A movie showing the time-resolved drumming of graphite. The frames of this movie include those depicted in Figure 2A and are the basis for the image cross correlation plots in Figure 3. The movie

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**Figure 4.** Resonance dynamics and FFT of graphite. (Left) Time dependences of full image cross correlation over the indicated time (A) and image intensity of the selected area of $4 \times 6$ pixels (B) indicated by the arrowhead in Figure 3. (Right) Fast Fourier transforms of image cross-correlation (C; time range, 0–100 µs and D; time range, 60–100 µs). The FFT of image intensity is shown in E and F for the time range of 0–100 µs and 60–100 µs, respectively. Asterisks in the panels indicate overtones. Note the emergence of the resonance near 1 MHz in panel F.
has been slowed down by $\sim 10^6$ times with respect to real time so that the fast drumming motion can be observed. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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