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chondrule formation took place in the weakly ionized “dead zone,” which contains gas poorly coupled to local magnetic fields and occurs within ~3 gas scale heights of the midplane (35). Our measurements therefore indicate that a substantial magnetic field (yet still well below the ~400 μT equipartition field strength (35)) existed in the dead zone, potentially as a result of fields inherited from the collapse of the solar system’s parent molecular cloud. Given our measured field strengths, mass accretion driven by the MRI or magnetic braking at 2.5 AU would have been <0.04 × 10−8 to <3.5 × 10−8 M⊙ year−1, where M⊙ is the Sun’s mass (supplementary text). Meanwhile, the MCW model would predict mass accretion rates of 0.3 × 10−7 to 30 × 10−7 M⊙ year−1 or less. The inferred age of Semarkona chondrules is 2 to 3 My after the first calcium aluminum-rich inclusions (36). Given that protoplanetary disks are observed to have accretion rates of 10−9 to 10−7 M⊙ year−1 at 2 to 3 My after collapse of their parent molecular clouds (2), both magnetic mechanisms could fully account for the expected accretion rates. This suggests that magnetic fields govern the observed rapid transformation of protoplanetary disks into planetary systems around Sun-like stars.

REFERENCES AND NOTES

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MATERIALS SCIENCE

Dynamic mechanical behavior of multilayer graphene via supersonic projectile penetration

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Multilayer graphene is an exceptionally anisotropic material due to its layered structure composed of two-dimensional carbon lattices. Although the intrinsic mechanical properties of graphene have been investigated at quasi-static conditions, its behavior under extreme dynamic conditions has not yet been studied. We report the high–strain-rate behavior of multilayer graphene over a range of thicknesses from 10 to 100 nanometers by using miniaturized ballistic tests. Tensile stretching of the membrane into a cone shape is followed by initiation of radial cracks that approximately follow crystallographic directions and extend outward well beyond the impact area. The specific penetration energy for multilayer graphene is ~10 times more than literature values for macroscopic steel sheets at 600 meters per second.

Graphene, the atomic monolayer building block of graphite, is known for its exceptional high intrinsic strength and stiffness arising from the two-dimensional (2D) hexagonal lattice of covalently bonded carbon atoms. Recently, graphene’s in-plane Young’s modulus (Y) was measured to be more than 1 TPa using atomic force microscopy nanoindentation (1). Because tensile mechanical stresses in a material cannot be transmitted faster than the speed of sound (c ~ 22.2 km s−1), implying that concentrated stresses applied under extreme conditions can rapidly be delocalized. Nanoindentation has served as an effective technique to study the tensile mechanical properties of monolayer graphene. It is inherently a low-speed test (<1 m s−1), but strain rates can reach ~104 to 105 s−1 for very thin samples (4), whereas most high-speed, high–strain-rate mechanical characterization techniques, such as split-Hopkinson pressure bar (5) and ballistic tests (6), are inappropriate for testing very thin specimens. To address high-speed and high–strain-rate tensile-dominated penetration of thin films, we improved our laser-induced projectile impact test (LIPIT) (7). In this advanced LIPIT (or “c-LIPIT”), a single micrometer-size solid silica sphere (or “μ-bullet”) is fired at a high speed

tensile loading (2). In this regard, the relatively low density (~2200 kg m−3) of graphene (3), along with its high modulus, leads to a superior in-plane speed of sound (c ~ 22.2 km s−1), implying that concentrated stresses applied under extreme conditions can rapidly be delocalized. Nanoindentation has served as an effective technique to study the tensile mechanical properties of monolayer graphene. It is inherently a low-speed test (<1 m s−1), but strain rates can reach ~104 to 105 s−1 for very thin samples (4), whereas most high-speed, high–strain-rate mechanical characterization techniques, such as split-Hopkinson pressure bar (5) and ballistic tests (6), are inappropriate for testing very thin specimens. To address high-speed and high–strain-rate tensile-dominated penetration of thin films, we improved our laser-induced projectile impact test (LIPIT) (7). In this advanced LIPIT (or “c-LIPIT”), a single micrometer-size solid silica sphere (or “μ-bullet”) is fired at a high speed
(<3 km s\(^{-1}\)) with a high aiming accuracy (<1.1° deflection) toward a thin film. The velocity of the \(\mu\)-bullet is measured before and after penetration to determine the energy lost during the test. We employed multilayer graphene (MLG) membranes in a range of thicknesses (10 to 100 nm, equivalent to 30 to 300 graphene layers) to apply localized, very–high–strain–rate tensile deformation (~107 s\(^{-1}\)) at a specific area. As the thickness of the MLG membranes \(h\) is always considerably less than the diameter \(D\) of a \(\mu\)-bullet \((D/h \geq 40)\), the high-strain-rate in-plane tensile behavior of MLG can be assessed from the thickness-dependent characteristics of the energy required for projectile penetration through the membrane.

The MLG membranes are prepared by mechanical exfoliation of highly ordered pyrolytic graphite (grade SPI-1, SPI Supplies; fig. S1), as shown in Fig. 1A. A silica \(\mu\)-bullet \((D = 3.7 \pm 0.02 \mu\text{m}, \text{based on imaging by scanning electron microscopy (SEM)})\) is propelled by expanding gases created by the laser ablation of a gold film (~50 nm thick). A 20-\(\mu\text{m}\)-thick elastomeric layer of cross-linked polydimethylsiloxane is used to confine the ablation products, eliminates the temperature rise of the \(\mu\)-bullet, and diminishes the strength of the shock waves propagating through air. The impact speed \((v_i)\) is measured (with the reproducibility of \(v_i\) within \(\pm 2\%\)) using a triple-exposure photograph of the moving \(\mu\)-bullet with \(\pm 10\) m s\(^{-1}\) error, where the time gap between the three exposures is achieved by employing different travel distances for each laser pulse (fig. S2). The residual speed \((v_f)\) of the \(\mu\)-bullet is similarly measured after the \(\mu\)-bullet has traveled a certain distance \((d)\) beyond the membrane (Fig. 1B). An average thickness \((h_{\text{ave}})\) of the impact area was determined using a thickness-dependent optical transmittance measurement (fig. S3) given by an analytical formula (8) and the optical parameters of graphite (9). An additional postpenetration image allowed identification of the penetration area (Fig. 1C).

The schematic in Fig. 1D depicts the series of events during penetration accompanying the kinetic energy loss of a \(\mu\)-bullet \((\Delta E_k)\). As the \(\mu\)-bullet impacts a strike face area \((A_s = \pi D^2/4)\), an elastic wave radially propagates at \(c_e\) and a conic deformation of the MLG membrane follows with a radial speed of its base, \(v_c\), which is generally slower than \(c_e\) (step ii). The primary force is axisymmetric tension with a strong radial gradient and results in the cone shape. Typically, three to six cracks are initiated near the center of \(A_s\) and propagate outward in the radial direction (step iii), resulting in the creation of the same number of petals. The transferred momentum to the MLG membrane induces creasing and folding of each triangular-shaped petal at its base while the elastic extension of the membrane is rapidly relaxed along the radial direction via snap-back (step iv). The longest crack from the impact center is defined as the maximum crack distance, \(L_{\text{max}}\), which we use as the estimation of the final radius of the conic deformation due to the reduction of the tangential stress. \(\Delta E_k\) is composed of two terms, the net energy to penetrate a membrane \((E_p)\) and the energy loss due to air drag \((E_{\text{drag}})\). \(E_p\) depends on various energy dissipation mechanisms including elastic stretching of the membrane, fracture, and heating, as well as the kinetic energy transfer to the membrane petals and membrane debris.

\[
\Delta E_k = \frac{1}{2}m(v_f^2 - v_i^2) = E_p + E_{\text{drag}}(d) \tag{1}
\]

As the mass of a \(\mu\)-bullet, \(m\) is calculated to be \(5.0 \pm 0.1 \times 10^{-14}\) kg, based on the measured diameter \(D\) and the density of silica (1900 kg m\(^{-3}\)) provided by its vendor (microParticles GmbH). The incident \(E_k\) is 9 nJ at 600 m s\(^{-1}\) and 21 nJ at 900 m s\(^{-1}\) while \(\Delta E_k\) is in the range of 1 to 5 nJ. The measured deceleration by air drag \((a_{\text{drag}})\) is \(-0.6 \times 10^3\) m s\(^{-2}\), assuming constant deceleration, which yields \(E_{\text{drag}} = ma_{\text{drag}}d \sim 1.07\) nJ for \(d \approx 350\) \(\mu\text{m}\) (the travel distance of a \(\mu\)-bullet after penetration when we take the triple exposure). Therefore, the primary contribution to the kinetic energy loss is the net energy to penetrate a MLG membrane \((E_p)\) under our experimental conditions.

The MLG membranes had a typical lateral grain size of ~10 \(\mu\text{m}\). Due to the stress concentration at the impact site, the grain boundary effects \((10, 11)\) (if any; see the supplementary materials) would occur only if the grain boundaries exist within \(A_s\). As the ratio, \(D/h\) is quite large (40 to 350), the mechanical response of the MLG film depends primarily on its in-plane tensile strength under a high strain rate. A typical penetration hole features a set of petals (Fig. 2). The area directly beneath the \(\mu\)-bullet impact shows extensive damage through complex, fine-scale fractures, folding, delamination, and loss of parts of the membrane (indicated by the yellow arrowheads). As the initiation of the radial cracks may not be exactly at the impact center, asymmetrically shaped petals are often observed (e.g., Fig. 2, A and D). The damage area is thus much wider than \(A_s\), in strong contrast to the observed behavior of polycrystalline gold and amorphous, glassy poly(methyl methacrylate) (PMMA) membranes,
in which penetration results in a circular hole with an area of \( \sim A \) (see figs. S6 and S7). Correspondingly, a much smaller penetration energy is measured.

Many independent penetration experiments (47 events for \( v_i = 600 \, \text{m s}^{-1} \) and 43 events for \( v_i = 900 \, \text{m s}^{-1} \)) were carried out for statistical analysis (figs. S4 and S5). The average apex angles (\( \theta_A \) in Fig. 1D) of petals for the 600– and 900–m s\(^{-1}\) projectile velocities are 83 \( \pm \) 21\(^\circ\) (for 107 cracks) and 70 \( \pm \) 23\(^\circ\) (for 93 cracks), respectively, indicating that the higher tangential stresses induced at 900 m s\(^{-1}\) were relaxed through more radial cracks. Despite the in-plane isotropic elastic nature due to the approximate sixfold symmetry of graphene (J2), the preferential crack propagation

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**Fig. 2. Representative penetration features of MLG membranes.** (A and B) SEM images of petals, radial cracks, folds, and snap-back damage to the petal tips and (C) the adjacent crack-pair angle distribution for \( v_i = 600 \, \text{m s}^{-1} \). (D and E) SEM images and (F) the adjacent crack-pair angle distribution for \( v_i = 900 \, \text{m s}^{-1} \). The inset in (F) shows the armchair (red) and zigzag (green) directions. The circles in the SEM images show \( A_s \). Scale bars in (A), (B), (D), and (E), 5 \( \mu \text{m} \).

**Fig. 3. Damage features of a thin MLG membrane.** (A) Bright-field TEM micrograph of the impact region (\( h_{\text{ave}} \sim 10 \, \text{nm} \)) for \( v_i = 900 \, \text{m s}^{-1} \). (B) Higher magnification of the petal apex area indicated by the red arrowhead in (A). (C) Three dark-field TEM micrographs are overlaid to show bend contours, rotation-tilt moiré fringes, and a fine-scale mosaic texture resulting from snap-back and membrane folding. The two diffraction patterns show (C1) a typical hexagonal spot pattern of the undeformed film and (C2) the altered, multireflection-satellite spot pattern from near the impact region. The red and blue regions correspond to imaging with \( \mathbf{g} = (01\overline{1}0) \), and the green region corresponds to \( \mathbf{g} = (\overline{2}110) \). Scale bars, (A) 5 \( \mu \text{m} \); (B) and (C), 0.5 \( \mu \text{m} \). The voidlike features at the upper left in (A) are a result of residual water-soluble polymer from film preparation.
Transmission electron microscopy (TEM) was carried out on snap-back portions of the petal regions of thin (h_{ave} ~ 10 nm) fractured membranes (Fig. 3). The bright-field TEM image shows complicated local folding of the membrane near the penetration (Fig. 3, A and B). The higher magnification dark-field image shows bend contours and moiré fringes (upper left and left center regions in Fig. 3C), resulting from the interference of electrons scattered from superposed folded MLG regions; see diffraction pattern insets in Fig. 3C). In the extensively folded region nearest the impact origin, a fine-scale mosaic structure is evident in both the electron diffraction pattern and dark-field images due to the deformation resulting from the rapid elastic relaxation (i.e., petal snap-back).

Despite a relatively wide fluctuation in L_{max}, its lower limit is well fit by 0.1 h_{ave} + D/2 (Fig. 4A). The film thickness inhomogeneity is represented by the coefficient of variation (CV) of the local thicknesses measured over a circular area (radius r = L_{max}). MLG membranes that have CV > 10% in the impact area clearly lead to a greater fluctuation of L_{max}. The radial speed of the circumferential base of the expanding cone-shape deformation region of a membrane can be approximated by v_{r} \approx 1.23c_{1}(v_{i}^{2}h_{ave})^{1/2} and thus scales with the cube root of the in-plane speed of sound in the material (14). Values for v_{r} correspond to 1950 and 2500 m s^{-1} for impacts of 600 and 900 m s^{-1}, respectively. An empirical estimation of deformation parameters is then possible by setting the lower limit of L_{max} to the maximum radius of the cone, because the tangential tensile stress (Fig. 1D) is the origin of the radial cracks. For example, assuming a simple 1D model for a 900-m s^{-1} impact to a 50-nm-thick MLG membrane, we estimate the penetration time t_{p} \approx L_{max}/v_{r} \sim 3 ns; the 1D-approximate average maximum tensile strain \varepsilon_{max} \approx (v_{r}^{2}/L_{max})^{2}/2 \sim \varepsilon_{0}(h_{ave})^{2}/2 \sim 8\%, close to the lower boundary of the reported failure strain range, 5 to 25\% (1, 15, 16); and the 1D-approximate average tensile strain rate as given by the maximum strain divided by the penetration time or \dot{\varepsilon}_{max} = (v_{r}/L_{max})^{2}/2 \sim 10^{-7} s^{-1}. A further discussion of the estimation of strain and strain rate is available in the supplementary materials.

From Eq. 1, \Delta E_{p}(h_{ave}) can be fit with a linear function (Fig. 4B), where the y-intercept value corresponds to E_{sp}. Therefore, the intrinsic energy dissipation of a MLG membrane is given by E_{p}(h_{ave}) = 0.026h_{ave} and 0.030h_{ave} for the two velocities we employed, and a similar trend is also found in macroscopic ballistic tests (17, 18). For D/h_{ave} >> 1, E_{p} can be expressed by two terms, E_{p} = (\rho A_{h}h_{ave})v_{r}^{2}/2 + E_{a}, where the first term represents the minimum inelastic energy transfer to target material within A_{h}, and E_{a} represents all of the other energy dissipation mechanisms. The specific energy dissipation, E_{p}^{*} = E_{p}((\rho A_{h}h_{ave})^{-1}, is which is insensitive to material density by taking account of the mass within A_{h}h_{ave} is given by E_{p}^{*} = v_{r}^{2}/2 + E_{a}^{*}, where E_{a}^{*} is the specific delocalized penetration energy. E_{a}^{*} is thus a figure of merit to evaluate the impact energy delocalization ability of a material by adding a simple mass beyond A_{h} contributes to the energy dissipation, whereas the material-independent energy dissipation term, v_{r}^{2}/2, serves as a baseline.

Statistical values of E_{p}^{*} for MLG, PMMA, and polycrystalline gold were determined from the fitted slopes of E_{p} versus h_{ave} (Fig. 4B and figs. S6E and S7C). From this data (see square data points in Fig. 4C), MLG exhibits the highest E_{p}^{*} (or E_{a}^{*}, namely 1.26 MJ kg^{-1} (or 0.86 MJ kg^{-1}) at 900 m s^{-1}, compared with 0.58 MJ kg^{-1} (or 0.19 MJ kg^{-1}) for gold and 0.52 MJ kg^{-1} (or 0.08 MJ kg^{-1}) for PMMA. We also calculated E_{p} from previous macroscopic ballistic tests of several materials: PMMA (19), aluminum (20, 27), steel (22, 29), and Kevlar KM2 polyvinyl butyral (PVB) composite fabric (24). These macroscopic tests used a millimeter-scale spherical steel projectile to penetrate a thin sheet (0.4 < h < 6 and 1 < D/h < 20) without appreciable deformation of the projectile (table S1). The overall trend of E_{p}^{*} is quite similar, despite the large differences in the macroscopic α-LIPIT and traditional macroscopic tests and the huge range in tensile modulus, strength, and density among PMMA, aluminum, and steel. This implies that the principal energy dissipation mechanism for the three macroscopic materials is the kinetic energy transfer from the projectile to the target material within A_{h} (i.e., to the mass \rho A_{h}), which results in a dressing process (25). This is why the E_{p}^{*} values of PMMA and gold from α-LIPIT also follow this trend and indicate a good correspondence between the micro- and macroscopic high–strain-rate evaluation methods for these materials, which also display localized penetration via a dressing process.

However, the two highly anisotropic layered materials—the Kevlar KM2-PVB composite fabric and the MLG membrane—deviate strongly from this trend. The Kevlar KM2-PVB composite is an armor-grade laminate made of strong, stiff polyaramid fibers (strength ~ 4 GPa, Y ~ 84 GPa, c ~ 7.6 km s^{-1}) embedded in PVB resin (26). The
planar fourfold symmetric high-stiffness woven polyaramid multilayer fabric shows an extensive coniclike deformation under ballistic impact, and the higher \( E_s \) (or \( E_l \)) values (see blue triangles in Fig. 4C) can be understood by the ability to simultaneously be stiff, strong, and elastic, stretching into a cone shape due to the force imparted by the forward moving projectile. As a result, the \( E_s \) values of the MLG membrane (0.92 and 0.86 MJ kg\(^{-1}\)) for 600 and 900 m s\(^{-1}\) substantially surpass those of steel (0.08 and 0.11 MJ kg\(^{-1}\)) at the same \( \nu_s \). Therefore, the MLG demonstrates specific delocalized penetration energy 8 to 12 times higher than that of steel due to the strong delocalization behavior at these impact speeds. As the higher delocalization effect results in a wider penetration hole, this tendency could be disadvantageous in certain aspects such as multi-hit capability. However, this potential weakness of MLG will be substantially relieved when the crack propagation is deflected by forming a composite.

Our microscopic ballistic results reveal that the superior in-plane speed of sound, high strength, stiffness, and structural anisotropy make MLG an extraordinary armor material exhibiting excellent impact energy delocalization under a supersonic penetration event. Because material far beyond the strike face area can also consume kinetic energy from the \( \mu \)-bullet while the MLG membrane sustains high dynamic tensile stress, the \( \mu \)-bullet effectively experiences a higher areal density material. As large-scale production of graphene-based composite materials is becoming possible (28), other graphene-like materials are being studied (29), and the results suggest opportunities for the use of ordered anisotropic nanocomposites for surprising mechanical applications. The good correspondence between the micro- and macroscopic projectile penetration tests, especially in the measured specific energy absorption, suggests that the microballistic method with its high-energy resolution may offer an effective means for the exploration of high-strain-rate physics of various materials, as well as practical advantages in rapid, high-throughput testing.

REFERENCES AND NOTES


Turning a surface superrepellent even to completely wetting liquids

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Superhydrophobic and superoleophobic surfaces have so far been made by roughening a hydrophobic material. However, no surfaces were able to repel extremely-low-energy liquids such as fluorinated solvents, which completely wet even the most hydrophobic material. We show how roughness alone, if made of a specific doubly reentrant structure that enables very low liquid-solid contact fraction, can render the surface of any material superrepellent. Starting from a completely wettable material (silica), we micro- and nanostructure its surface to make it superomniphobic and bounce off all available liquids, including perfluorohexane. The same superomniphobicity is further confirmed with identical surfaces of a metal and a polymer. Free of any hydrophobic coating, the superomniphobic silica surface also withstands temperatures over 1000°C and resists biofouling.

The ability to understand the extraordinary liquid repellency of natural surfaces (1, 2) has affected a wide range of scientific and technological areas, from coatings (3), heat transfer (4), and drag reduction (5) to biomimetics (6). Whereas the wetting-resistant surfaces developed since the 1960s (7–10) used only surface roughness to trap gas with no interest in the apparent contact angle, superhydrophobic surfaces created since the late 1990s (11, 12) combined the roughness with a hydrophobic material to superrepel water—that is, to display a very large apparent contact angle (\( \theta_o > 150^\circ \)) and a very small roll-off angle (\( \theta_{roll-off} < 10^\circ \)). For low-energy liquids such as oils or organic solvents, a roughness with overhanging topology was necessary to make the hydrophobic material superoleophobic (13, 14), omniphobic (14), or superomniphobic (15, 16). Despite the use of the prefix “omniphobic” (16, 15–18), however, no natural or man-made surface has been reported to repel liquids of extremely low surface tension or energy (i.e., \( \gamma < 15 \text{ mJ/m}^2 \)), such as fluorinated solvents, which completely wet existing materials (10, 19–21). Departing from the prevailing approach of roughening a hydrophobic material, we first propose that the material’s inherent wettability, depicted by the intrinsic contact angle \( \theta_{\text{intrinsic}} \), is irrelevant when dealing with a completely wetting liquid (\( \theta_{\text{intrinsic}} = 0^\circ \)). Focusing instead solely on the roughness details, we develop a surface that superrepels all available liquids, including fluorinated solvents—for instance, perfluorohexane (C6F13H, namely, 3M Fluorinert FC-72), whose surface energy (\( \gamma = 10 \text{ mJ/m}^2 \)) is the lowest known and which has never been observed to bead up, let alone roll off, on any surface.

To avoid the confusion with the petal effect (22), in which a droplet with large contact angles sticks to the surface, it helps to first clarify that “repelling” means that droplets not only bead on but also roll off the surface. To repel (i.e., \( \theta_o > 90^\circ \) with a small \( \theta_{\text{roll-off}} \) or superrepel (\( \theta_o > 150^\circ \) with \( \theta_{\text{roll-off}} < 10^\circ \)) a wetting liquid (\( \theta_o < 90^\circ \)) on a structured surface, two conditions must be met:

**REFERENCES AND NOTES**


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