The minimal nanowire: Mechanical properties of carbyne

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Abstract – Advances in molecular assembly are converging to an ultimate in atomistic precision —nanostructures built by single atoms. Recent experimental studies confirm that single chains of carbon atoms —carbyne— exist in stable polyyne structures and can be synthesized, representing the minimal possible nanowire. Here we report the mechanical properties of carbyne obtained by first-principles–based ReaxFF molecular simulation. A peak Young's modulus of 288 GPa is found with linear stiffnesses ranging from 64.6–5 N/m for lengths of 5–64 Å. We identify a size-dependent strength that ranges from 11 GPa (1.3 nN) for the shortest to a constant 8 GPa (0.9 nN) for longer carbyne chains. We demonstrate that carbyne chains exhibit extremely high vibrational frequencies close to 6 THz for the shortest chains, which are found to be highly length-dependent.

Introduction. – Synthetic assembly of molecular structures with mono-atomistic control represents a milestone in materials physics, enabling the exploration of new nanoscale architectures. Carbon is a natural choice for building material due to both the natural abundance and chemical stability. Recently, the superlative properties and potential applications of synthetic carbon, particularly fullerenes [1–4], nanotubes [5] and graphene [6], have motivated significant research efforts. Amongst the remaining theoretical forms of carbon allotropes [1–4], the existence of stable forms of single chains of carbon, carbyne, has remained elusive and a subject of debate. This carbon structure has caused significant interest due to the possibility of electron transport, motivated by the prospect of using carbyne as components in atomic-scale circuits. Carbyne represents the ultimate limit of synthetic nanoscale structures: the absolute minimal nanowire consisting of only a one-dimensional chain of atoms. Naturally occurring carbon is believed to exist predominantly in two allotropes, diamond and graphite, consisting of sp^3- and sp^2-hybridized carbon atoms.

Carbyne is a one-dimensional structure carbon atoms composed of sp-hybridized carbon atoms (fig. 1(a)). Theoretically, stable carbon chain structures may be double-bonded (polycumulene), $[=(=C=)=]_n$ or alternating single-triple bonded (polyyne), $[-(-C\equiv C-)-]_n$ [7], and it has been suggested that carbyne exists in interstellar dust and meteorites [8,9]. Single chains of carbon have recently been produced linking graphene sheets [10] as well as within carbon nanotubes [11], potentially leading to new methods of structurally assembling bulk graphene or nanotube systems. Most importantly, recent reports of successful synthesis of long chains of conjugated carbon provide a protocol for controlled production of carbyne in the polyyne state [12]. Due to their potential use in atomic-scale circuits, there has been particular interest in their novel electronic properties, motivating previous theoretical and quantum-scale studies [13–17]. However, the mechanical properties of carbyne, essential to their successful incorporation in the design of novel devices, have yet to be determined. This poses fundamental questions about the physics of deformation and failure of carbyne, which have not yet been addressed.

Methods. – Here we report a first analysis of the nanomechanical properties of carbyne chains, obtained by implementing mechanical test cases via molecular dynamics with the first-principles–based ReaxFF force field [18,19], providing an accurate account of the
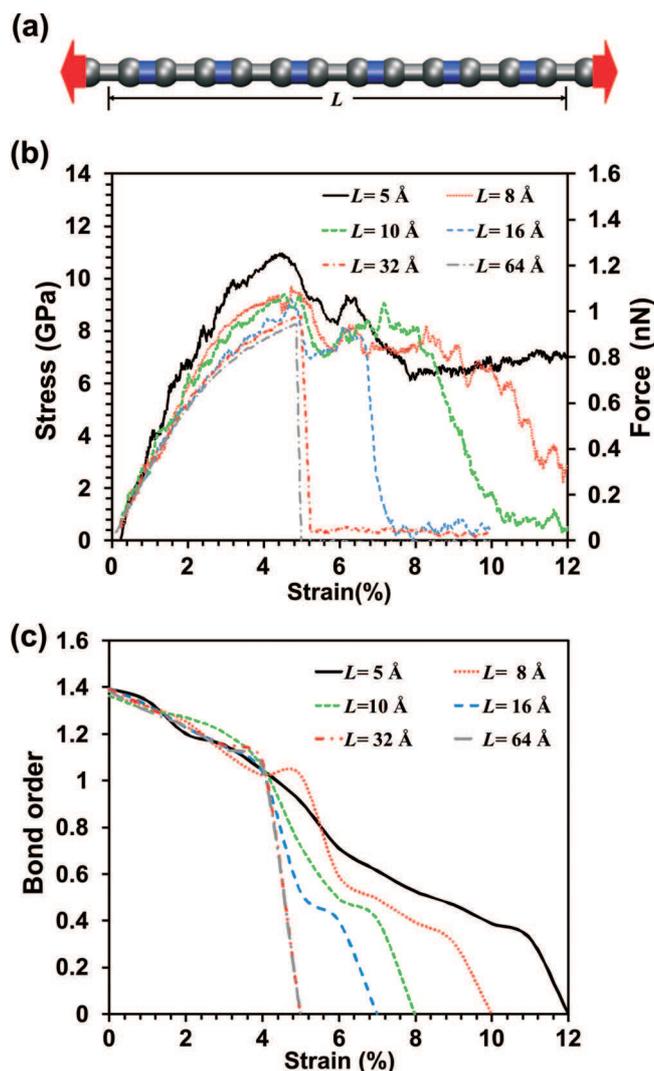

Fig. 1: (Colour on-line) Mechanical testing of carbyne chains with different lengths. (a) Carbyne chain used for simulation with alternating single and triple *sp*-hybridized bonds. Arrows indicate the pulling direction for the uniaxial tension test with initial length L. (b) Stress-strain curves for carbyne chains of lengths $L = 5$ Å, 8 Å, 10 Å, 16 Å, 32 Å, 64 Å with 4, 6, 8, 12, 24 and 48 atoms, respectively. (c) Bond order *vs.* strain for different lengths of carbyne chains.

chemical and mechanical behavior of hydrocarbons, graphite, diamond, and other carbon nanostructures [20–22] while being capable of treating thousands of atoms with near quantum-chemical accuracy and at long time-scales of several nanoseconds. Simulations are carried out under a microcanonical (NVT) ensemble (temperature control by a Berendsen thermostat [23], time step of 0.5×10^{-15} s), implemented in LAMMPS [24]. Stress is computed using the virial theorem [25]. Calculation of stress using the virial theorem requires an estimate of volume, and we hereby assume a uniform cross-section of 3.35×3.35 Å (an approximation corresponding to the thickness of a graphene sheet [26]). These dimensions

are selected to enable a quantitative comparison between carbyne and graphene.

Carbyne chains of varying lengths (5 Å, 8 Å, 10 Å, 16 Å, 32 Å, 64 Å) containing 4, 6, 8, 12, 24 and 48 atoms are generated with alternating single and triple bonds that are *sp*-hybridized (fig. 1(a)), motivated by recent findings [12] suggesting polyyne-like structures and associated length-scales. The ambiguity for the thickness of mono-atomic structures such as graphene [27] suggests the stress and moduli of monolayer graphene be reported in force per unit length (N/m) rather than force per unit area (N/m^2 or Pa). Similarly, here, the mono-atomistic cross-sectional area of a carbyne is difficult to define. Thus, along with a conventional engineering modulus calculated by an approximate area, we report the stiffness as a length-independent constant, $E^0 = EA$, irrespective of attributed area. All chains are first energy minimized and then equilibrated at a temperature of 300 K to ensure structural stability; followed by a reduction of the temperature to 10 K during mechanical characterization to limit fluctuations induced by temperature.

Results and discussion. – Uniaxial tension test is carried out by displacing both ends of the chain in opposite direction as shown in fig. 1(a), applying uniaxial strain at a constant rate. Stresses and strains are computed every 500 fs for individual chains and until failure occurs. A selection of different strain rates (0.025 fs^{-1}, 0.0025 fs^{-1}, 0.00025 fs^{-1}) shows negligible effects on the behavior of a 16 Å long carbyne chain, and thus an intermediate strain rate of 0.0025 fs^{-1} is chosen for all other simulations. The total simulated times are around 5 ns, well beyond the accessible scales of quantum-level simulation. Mechanical testing of longer chains as discussed here are not yet computationally feasible using other methods such as first-principles Density Functional Theory, but are easily accessible using ReaxFF at relevant time-scales that allows for relatively slow mechanical testing of carbyne. Relevant results are also expressed in terms of force (rather than stress), wherein definition of the effective cross-sectional area is unnecessary. The virial stress returns components of the macroscopic stress tensor, S_{ij}, over a volume Ω. To calculate the total stress, $\sigma_{ij} = S_{ij}\Omega^{-1}$, where Ω is taken as representative volume under stress. Noting that and $\Omega = AL$ and the uniaxial force is given by $F = \sigma A$. The force can be computed from the virial stress components independently from a properly defined cross-sectional area, A, where $F_{ii} = S_{ii}L^{-1}$.

From the force-strain data obtained from various simulations shown in fig. 1(b), we estimate E^0 to be 32.3 nN, or, expressed as a spring constant, $k_L = 64.6$ N/m for the 5 Å chain length ($k_L = E^0/L$) The equivalent stress-strain curves and approximation of area result in an estimate of Young's modulus from the linear elastic regime of the stress-strain curves (fig. 1(b)) to be ≈ 288 GPa. Thus, the modulus of carbyne is approximately one third that of graphene assuming a carbyne chain spacing of
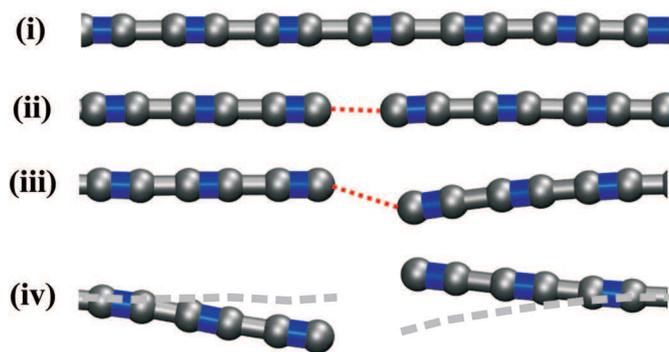
Fig. 2: (Colour on-line) Atomistic details of the deformation and failure mechanism of a carbyne chain of length 16 Å. The dashed line in snapshot (iv) indicates the shape of the carbyne chain in snapshot (iii), reflecting high-frequency oscillations induced after failure has occurred.
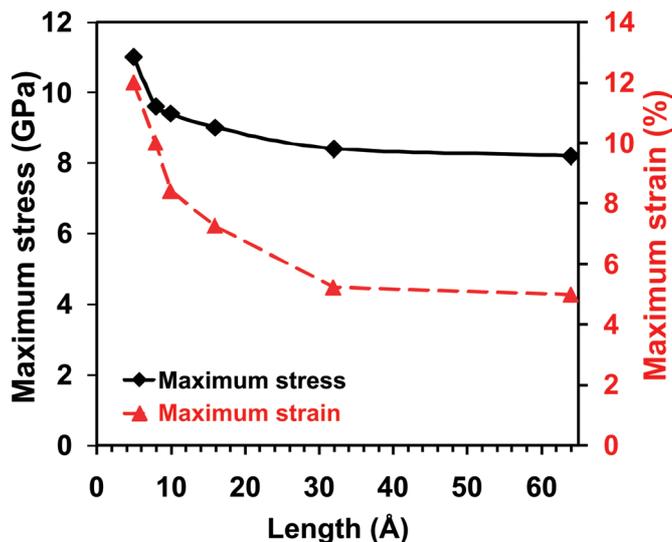

Fig. 3: (Colour on-line) Maximum stress and strain of carbyne chains with different lengths. The data shows that carbyne chains become stronger and stiffer and more extensible at shorter lengths. The values of maximum stress and strain reach an asymptotic value as the chain length approaches ≈ 60 Å.

3.35 Å [28]. Alternatively stated, for equivalent stiffness, it would require three carbyne chains to replace a 3.35 Å width of graphene section of the same length. Notably, we find that carbyne chains of lengths 16 Å and below exhibit significant large deformation after the peak stress, with the smallest carbon chain of 5 Å strains reaching $\approx 12\%$ strain before ultimate failure. Such shorter carbyne chains exhibit an inelastic nonlinear behavior, and specifically the ability to sustain considerable stress post-yielding. For chain lengths of 32 and 64 Å, the failure is more sudden (brittle-like) when failure occurs at a strain of 5%.

Exploring the chemical details of the large-deformation inelastic regime in shorter carbyne chains, the bond order of the carbon atom at the location of failure is computed as a function of strain (fig. 1(c)). The bond order is a measure of bond stability and describes how many electrons participate in the bonding. We find that at 5% strain the 5 Å chain has a bond order of 0.90 compared to a 0.52 bond order for the 16 Å chain. At this same strain the bond orders of the 32 Å and 64 Å long chains are zero, thus explaining the presence of the large-deformation inelastic regime for short chains by the existence of residual covalent bonding even after the maximum stress has been reached. A simple geometric explanation is that, due to the displacement-controlled boundary conditions, shorter chains can relax over a smaller distance, and thereby the chain is not completely broken after reaching maximum stress. The observation of large deformation inelastic mechanisms at the ultimate monoatomic scale provides new insight into the physics of bond breaking in covalent materials, which may be directly tested in displacement-controlled experiments. Visualizations of the molecular deformation mechanism of the 16 Å carbyne chain are shown in fig. 2.

The maximum force at the breaking point for the 5 Å chain is 1.3 nN and 0.9 nN for the 64 Å long chain. With our assumption of cross-sectional area, the maximum stress reached by the shortest 5 Å chain is 11 GPa and

8.2 GPa for the longest 64 Å chain (fig. 3). The differences between maximum force and stress for longer chains such as 64 Å and 32 Å vanishes, indicating that the size effect is not a dominant factor for larger lengths ($L > 32$ Å and above). The maximum force attained by carbyne chain is dependent on the length of the chain; this could be due to the high axial strain energy for shorter chains. In addition, the probability of failure is likely to increase at a particular stress level for longer lengths which involves an increase in the number of individual bonds. The calculation of stress (and similarly, force) involves an averaging over the entire chain length, and thus local stress concentrations (and related, susceptibility to failure nucleation) are lost as the chain increases length. Simply put, the strength of individual carbon bonds does not decrease due to an increase in number, but rather the ultimate strength of the entire carbyne chain. The maximum stress of the shortest carbyne chain with 5 Å length is found to be one order of magnitude lower than that of graphene [28]. Such a drastic drop in strength (compared to graphene) can be attributed to the relatively weak single-carbon bonds. As stated above, approximately three carbyne chains can attain the equivalent stiffness as graphene (per 3.35 Å), yet they would fail at a stress of approximately 24 GPa (if spaced within the same 3.35 Å), still below the intrinsic strength of graphene. Thus, carbyne could potentially serve as sacrificial elements, ensuring localized failure at lower stress values, or stress-induced switches in atomistic circuits.

Carbyne has potential application as ultrasmall beams that connect electronic or mechanical components, so —in addition to stiffness and ultimate stress and strain— it is essential to quantify the effective bending
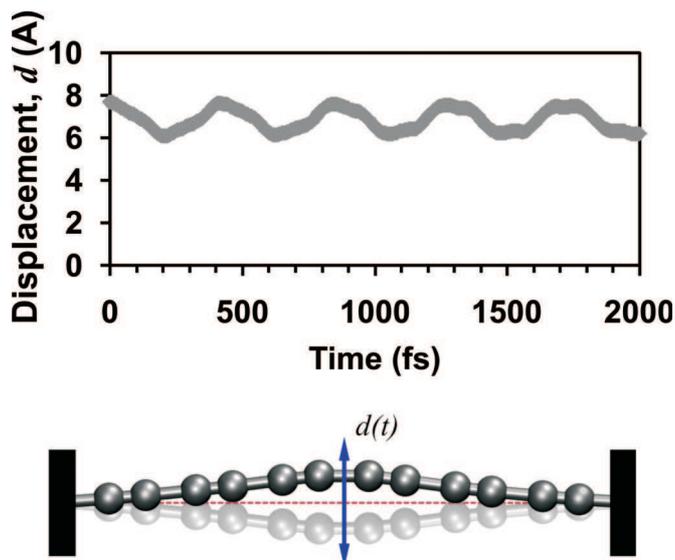
Fig. 4: (Colour on-line) Vibrational analysis of a carbyne chain. The inlay shows a fixed-fixed carbyne chain of length $L = 16\,\text{Å}$, displaced at the middle of the chain to find the frequency of vibration. The plot shows the displacement *vs.* time history for the carbyne chain of length $L = 16\,\text{Å}$. The frequency of vibration for this chain is 2.5 THz.

stiffness. Moreover, in addition to structural roles, the atomistic lengths, high stiffness and strength, low density, and large aspect ratio of such nanowires suggests a potential use as nanomechanical resonators. To isolate the frequency of vibrations, a simple test is constructed in which a fixed-fixed carbyne chain is excited by perturbing the center atoms and allowed to freely vibrate (see lower part in fig. 4). An analysis of the oscillations is performed via a discrete Fourier transform to extract the fundamental frequencies of vibration of the carbyne chains from the displacement-time history (fig. 4). The highest frequency is expressed by the shortest carbyne chains ($5\,\text{Å}$) and is $f = 6$ THz, which is larger than even the ultrahigh frequencies found in vibrating carbon nanotubes (on the order of 10 GHz to 1.5 THz [29]). The longest chain vibrates at a frequency of 0.625 THz, a difference in an order of magnitude. Thus the atom-by-atom control of carbyne chain length [12] can attain a large range of resonating frequencies. It could also be used to measure the length of carbyne chains from an analysis of the vibrations or be employed to develop highly sensitive sensors.

Assuming the chain behaves as an elastic beam, the frequency is related to the stiffness by the relation [30] $\omega = 2\pi f = \alpha^2 \sqrt{EI/mL^3}$, where m is the mass, L is the length, EI the bending stiffness, and α a constant determined by the boundary conditions (here, $\alpha = 4.43$ assuming a fixed-fixed beam with a load at the center as per the initial displacement conditions). Calculation of the bending stiffness via frequency analysis shows a variation of bending stiffness with respect to the length of the

carbyne chain, with the smaller chains ($16\,\text{Å}$ and below) exhibiting a lower bending stiffness than the larger chains. However, it is likely that higher-order vibrational modes are introduced at longer lengths (beyond the scope of the current investigation) and we limit the calculation of bending stiffness to intermediate carbyne segments, which yield bending stiffnesses of $1.36 \times 10^{-28}\,\text{Nm}^2$ and $2.02 \times 10^{-28}\,\text{Nm}^2$ for $8\,\text{Å}$ and $10\,\text{Å}$ lengths, respectively. We note this is several orders of magnitude lower than that of a (5,5) carbon nanotube ($EI = 6.65 \times 10^{-26}\,\text{Nm}^2$) [31], expected due to the wire-like properties of the single atomistic chains. It is expected that due to the interplay of thermal fluctuations and self-adhesion of carbyne chains interesting self-assembling phenomena may be observed.

Conclusion. – The mechanical properties of carbyne chains are promising for nanotechnology applications and provide further motivation to investigate the possibility of using this material as reinforcing agents in nanocomposites or in nanoelectronics applications. The knowledge of the physical basis for its mechanical properties as explored here is an important component towards functional use of this novel material, and the ReaxFF modeling approach reported here is a powerful tool that could be used for nanoengineering of this material for varied applications. Future work could focus on using this tool for studies of self-assembly of carbyne chains into larger-scale structures. Other work could emphasize on the use of quantum-mechanics approaches to elucidate the mechanical properties of carbyne, or to use these methods to explore electronic properties of the material under different applied strains.

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