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Stress-strain curves of aluminum nanowires: Fluctuations in the plastic regime and absence of hardening

L. Pastor-Abia,[1] M. J. Caturla,[1,2] E. SanFabián,[1,3,4] G. Chiappe,[1,2] and E. Louis[1,2,3]

[1]*Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*
[2]*Departamento de Física Aplicada, Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*
[3]*Unidad Asociada of the "Consejo Superior de Investigaciones Científicas," Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*
[4]*Departamento de Química Física, Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante, Spain*

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The engineering stress-strain curves of aluminum nanowires have been investigated by means of molecular dynamics. Nanowires were stretched at constant strain rate and at a temperature of 4.2 K. Atoms at fixed positions with velocities randomly distributed according to Maxwell distribution were taken as initial conditions. Averaging over at least 1500 realizations allows the conclusion that, beyond the yield point, the system does not harden, in line with experimental results for larger nanowires of gold measured at room temperature. Fluctuations of the heat exchanged in the nonlinear regime have been investigated by analyzing around 1.5 million data. The results indicate the presence of non-Gaussian tails in the heat probability distribution.

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One of the most subtle issues in the increasingly broad area of nanoscience concerns the mechanical response of small systems. Mechanical devices are getting so small that quantum limits are already reachable.[1] Understanding how materials respond at such small scales is a need for the design of electromechanical devices and a challenge for scientists involved in basic research. Although technical difficulties inherent to the measurement of the mechanical response of small systems are enormous, nowadays tools are allowing the investigation of both inorganic[2–9] and organic (biological)[9,10] systems. Several issues are of particular interest to researchers, among which we mention the size dependence of mechanical moduli,[9] fracture at the nanoscale,[5] and whether small systems do or do not harden.[7,8] No complete agreement has yet been attained on these questions.

In regard to hardening, it could be argued that as soon as the system becomes smaller than the characteristic length of interaction among dislocations,[11,12] no hardening is expected. Actually, molecular-dynamics (MD) calculations on a single, albeit large, copper nanowire indicate that no hardening occurs beyond the yield point.[13] However, experiments are still far from giving an unambiguous answer. Measurements on nanowires of diameters as small as 40 nm (Ref. 8) indicate that dislocation pileup is still operative at such small sizes. Contrarily, experiments on gold nanowire forests with wire diameters in the range of 30–80 nm (Ref. 6) show a constant engineering stress beyond the yield point. On the other hand, atomic force microscope (AFM) indentation experiments on lead surfaces gave a constant true stress (which means a decreasing engineering stress) for contact radii in the range of 4–14 nm.[2] The absence of hardening observed in bulk nanocrystalline copper[7] certainly has an origin different from that outlined above. It is also interesting to note that, while the authors of Ref. 7 observed no significant necking up to the breaking point, simulations on metallic nanowires have clearly shown that it actually occurs.[13,14] These facts show that one should not expect similar behaviors in nanostructured and nanosized materials. Size, shape, and temperature may affect the mechanical response at the nanoscale too. In particular there is experimental evidence which shows that the elastic moduli increase as the size goes down,[6,9] with metallic chains being substantially stiffer than bulk material.[4] An additional issue that is being investigated, mainly on organic molecules (polymers), is how fluctuations in the plastic regime are distributed.[10,15] Experimental data indicate that the work probability distribution has a Gaussian component plus long non-Gaussian tails. The origin of this deviation from the Gaussian distribution predicted by the central limit theorem (CLT) (Ref. 16) is a matter of fundamental interest that is being intensively investigated.[15,17–19] Whether this kind of deviations from the CLT is a characteristic common to all small systems is something that has yet to be settled.

The aim of this work is to discuss the results of molecular-dynamics calculations of stress-strain curves of aluminum nanowires. The paper focuses on two issues: whether the nanowire hardens or not upon stretching and which is the distribution followed by fluctuations in the nonlinear (plastic) regime. Standard MD calculations[20,21] were carried out on aluminum samples stretched along the [001] direction at a constant rate of 0.01 Å/ps which for a nanowire 30 Å in length gives a strain rate of $\dot{\epsilon}\approx 4\times 10^{8}\ \mathrm{s}^{-1}$. This strain rate is far above that commonly used in experiments, of the order of $10^{-6}\ \mathrm{s}^{-1}$, but unfortunately, no molecular-dynamics simulation can be performed at such low strain rates.[22] Consequently, no one-to-one comparison can be done between experiments and simulations. However, general trends can be observed. As initial conditions we took fixed atomic positions and the velocity at each atom randomly distributed according to Maxwell distribution. No viscous term was explicitly included in the equations of motion, as this is not expected to be operative in very small systems.[23] Although most simulations were done on single-crystal nanowires containing 463 atoms, clusters containing up to 2645 atoms were also investigated. The initial shape of the nanowire has diameters at the narrowest point of 8 and

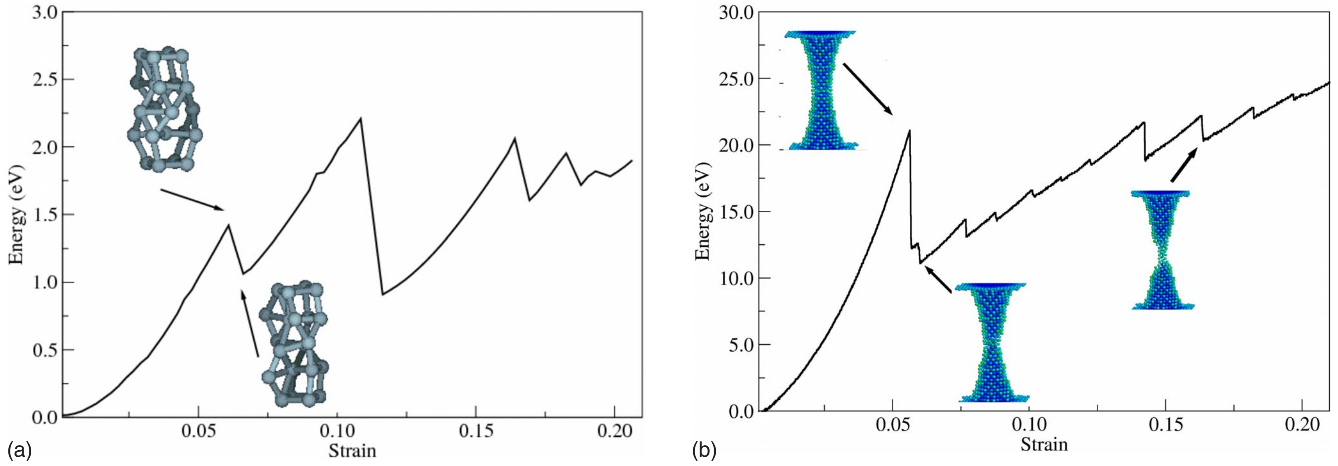

FIG. 1. (Color online) Energy vs engineering strain, calculated using either density-functional theory (a) or molecular dynamics (b), for aluminum nanowires containing 22 and 2645 atoms, respectively. Atomic arrangements at different stages of the stretching process are shown. The results correspond to a single realization (see text).

12 Å, respectively. Averaging was done over at least 1500 realizations (initial conditions). The interatomic potential used in the simulations was taken from Ref. 24. Simulations were done at a constant temperature of 4.2 K, which amounts to assuming thermal contact, with a bath large enough to absorb all heat generated. This assumption was implemented in the simulations by rescaling every ten MD steps along all atom velocities.[25] The change in kinetic energy upon scaling gives the heat evolved ΔQ.

The stress tensor can be easily derived from MD,[26]

$$\sigma_{\alpha\beta} = \frac{1}{V}\left(\sum_{i=1}^{N} m_i v_{i\alpha} v_{i\beta} + \frac{1}{2} \sum_{i \neq j}^{N} r_{ij\beta} F_{ij\alpha} \right), \tag{1}$$

where V is the volume of the sample, $v_{i\alpha}$ is the component α of the velocity vector at atom i, $r_{ij\beta}$ is the component β of the vector that joins atoms i and j, and $F_{ij\alpha}$ is the component α of the force that atom i exerts on atom j. As seen in Eq. (1) both the kinetic and the potential energies contribute to the stress tensor [first and second terms on the right-hand side of Eq. (1)]. Calculations have been done, replacing V by its initial value. This gives what is known as engineering stress. Accordingly, we have used as variable in characterizing deformation the increment in length divided by the initial length, again known as engineering strain. If the external force is applied in the z direction, the stress is given by σ_{zz} in Eq. (1).

Figure 1 shows the total energy as calculated by means of density-functional theory (DFT)[27] or MD for nanowires containing 22 and 2645 atoms, respectively. As discussed by other authors,[13,29] beyond the yield point the results of both approaches show short quasielastic events followed by sudden drops of the total energy associated to major atomic rearrangements. The significance of the fact that these drops occur in both calculations should not be minimized, as, while DFT calculations correspond to equilibrium at each stretching step or alternatively to an infinitely small strain rate, MD simulations are done at a very high strain rate. It is appealing to note that similar force-extension curves have been obtained for unzipping of DNA.[30,31] Aiming to carry out a statistical analysis as extensive as possible, all results discussed hereafter were derived from the much faster MD calculations. We have checked that, while the total volume of the sample steadily increases in the elastic regime and along the quasielastic episodes in the nonlinear regime, it drops steeply concomitantly with and proportionally to the just mentioned energy drops. Anyhow, there is an overall increase in volume as deformation proceeds. As expected, drops in total energy occur at strains which depend on the initial conditions. Atomic rearrangements in such small systems (see Fig. 1) are favored by the large proportion of surface atoms they contain. In order to understand the processes at the atomic level, we have used two standard methods of analysis: number of neighbors of each atom and common neighbor analysis.[32] These two methods reveal that, as expected for these very small sizes, no traces of dislocation activity are observed. The jumps in the stress-strain curves are associated to atoms that move from the bulk to the surface, such that at the early stages of deformation most of the atoms in the narrowest part of the nanowire are surface atoms. This high mobility allows for the accommodation of the stress by the nanowire as it deforms. As pointed out in Ref. 22 depending on the width of the nanowires, the deformation mechanisms change: at the largest structures the deformation is dominated by dislocations while at these small sizes it is dominated by surface effects. As shown in the lower panel of Fig. 1, MD simulations indicate that the nanowire undergoes necking well before breaking takes place, in line with other MD calculations.[13]

Numerical results for the average total energy and for the average engineering stress [as derived from Eq. (1)] vs strain, obtained from molecular-dynamics calculations, are reported in Fig. 2 [(a) and (b) panels, respectively]. In addition, results for three particular realizations are shown. We first note that, as expected and already remarked, drops (in energy and stress) occur at strains which depend on the particular realization (initial conditions). Although beyond the yield point, the stress-strain curve shows the short quasielastic events already reported by several authors,[13,14,28] averag-

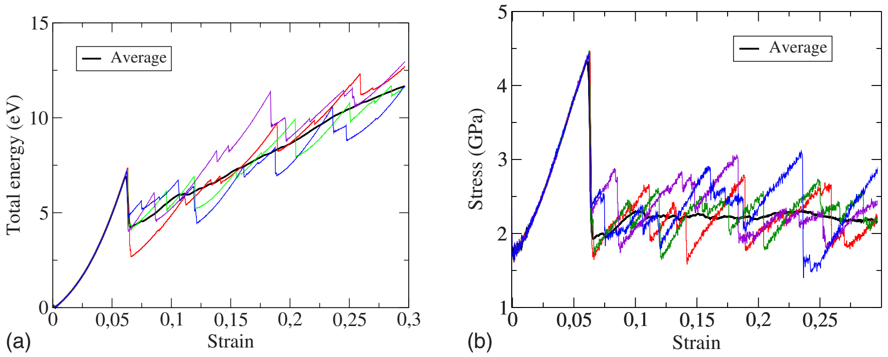

FIG. 2. (Color online) Total energy (a) and stress (b) vs engineering strain, as derived from molecular-dynamics calculations on aluminum nanowires containing 463 atoms stretched at a constant strain rate. The results correspond to three individual realizations (different initial distributions of atomic velocities) and to an average that includes over 1500 realizations (thick black line).

ing over a sufficiently large number of numerical experiments leads to the rather smooth averaged stress-strain curve, depicted in Fig. 2 as continuous black lines. The result is in our view conclusive: no hardening occurs in Al nanowires under the conditions studied. Moreover, beyond the yield point, the stress drops down to approximately its initial value. Although no experimental results exist for Al nanowires, it is interesting to note that absence of hardening has been observed experimentally in gold nanowires[4] and gold nanowire forests.[6] In addition, while in a single nanowire,[4] drops and fluctuations were observed, in the case of forests they were not,[6] surely due to the averaging inherent to a bunch of nanowires (both results in accordance with Fig. 2). The observation of hardening in larger nanowires[8] points to the existence of a transition when the system is sufficiently small. The crucial question is how small the system should be. The answer to this question will demand simulations on larger nanowires and more experiments on small systems. The second result, in turn, namely, the drop of the stress to the initial value, can be rationalized in terms of the large capability of the surface, dominant in such small systems, to absorb deformation. Some evidence of this behavior was also reported in the MD study of Wu.[13]

The results shown in Fig. 2 clearly indicate that fluctuations in the total energy and the stress are considerably large: the amplitude of fluctuations is similar to the average value of the magnitude. This is a characteristic of small systems[15,18] in which anomalies in the distribution of dissipative magnitudes are expected to show up. To explore this issue we have calculated the probability distribution of the stress and the exchanged heat in the nonlinear regime. The calculation was done on 1500 realizations and over 1000 points along the nonlinear part of the stress-strain curve, allowing the carrying out of statistical analysis over more than 1.5 million values of those magnitudes. The results are shown in Fig. 3. It is noted that the half width of the stress distribution is approximately 1 GPa, similar to the average value of the stress (approximately 2 GPa). The numerical results for the stress fluctuations closely follow a Gaussian up to approximately ±0.8 GPa. At larger stresses, deviations from the Gaussian fit become erratic. Quite different are the results for the exchanged heat [see panel (b) of Fig. 3]. Now, the numerical results follow a Gaussian down to probabilities around 0.001, and, thereon, a clear, systematic deviation is noted. Such non-Gaussian tails have been observed in many steady-state systems.[18]

Summarizing, extensive molecular-dynamics calculations on aluminum nanowires subjected to uniaxial stretching indicate that no hardening occurs beyond the yield point. It is interesting to note that absence of hardening has been ob-

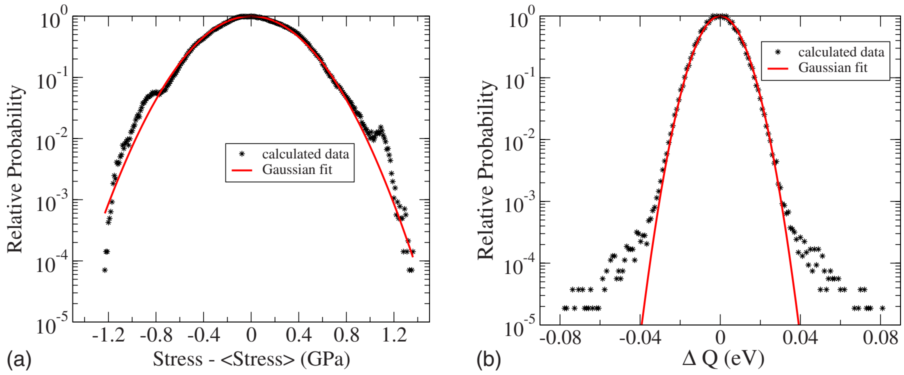

FIG. 3. (Color online) Probability distributions of the engineering stress and the heat evolved (ΔQ) in the nonlinear (plastic) regime derived from molecular-dynamics calculations on aluminum nanowires, containing 463 atoms, stretched at a constant strain rate. The distribution contains more than 1.5 million counts (1500 realizations by at least one thousand points along the stress-strain curve). The (red) continuous curves are Gaussian fits to the numerical data over the stress range of $[-0.5,0.5]$ GPa or the heat range of $[-0.02,0.02]$ eV.

served experimentally in gold nanowires of larger sizes measured at room temperature. Simulations (experiments) on increasingly larger (smaller) systems would be necessary to identify the critical size above which hardening begins to show up. In addition our results indicate that (i) the nanowire undergoes necking long before breaking occurs and (ii) beyond the yield point the stress steeply drops down to approximately its initial value. We have also investigated fluctuations of two magnitudes in the nonlinear regime: the stress and the heat evolved. While our results for the stress indicate that no deviations from a standard Gaussian behavior occur, fluctuations in the heat evolved along stretching unambiguously show the existence of long non-Gaussian tails, as found in many steady-state systems. Work is in progress to investigate how general this result is in the inorganic world. In particular we are investigating other metals as well as the effects of temperature and alloying.

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