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Non-Gaussian tails in the probability distribution function of heat exchanged during isothermal stretching of aluminum and gold nanowires

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The heat exchanged upon isothermal (0.5–200 K) stretching of aluminum and gold nanowires has been calculated by means of molecular dynamics. Atoms at fixed positions with velocities randomly distributed according to Maxwell distribution were taken as initial conditions. The results clearly reveal the presence of non-Gaussian (exponential) tails in the heat probability distribution function at low temperatures, both in gold and aluminum. As temperature is raised, tails rapidly disappear.

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Systems in which fluctuations of characteristic magnitudes have amplitudes similar to their average values are attracting an increasing interest [1–8]. Nanosystems are an obvious example as average values of most physical magnitudes characterizing these systems are that small that thermal fluctuations induced even at low temperatures may have comparable values [9,10]. Two are the issues most widely investigated in this field. First there is much concern about the kind of fluctuation theorems (FTs) that apply in this case [1–4]. Experimental and theoretical analyses indicate that while work fluctuations follow standard FT, the heat exchanged between the system and the environment does actually follow extended FT [5] applicable to systems arbitrarily far from equilibrium. The second question concerns the existence of long non-Gaussian tails in the distribution of fluctuations. Spontaneous processes (as opposed to standard stimulated processes), independent of the thermal bath, seem to be responsible for those tails [2]. The most concluding experimental analysis of this question was reported in Ref. [5] on an electrical dipole driven out of equilibrium by means of a small constant electric current. After having measured the work performed on the system and the exchanged heat, the authors analyzed the distribution or probability density function (PDF) of those two magnitudes averaged over time intervals of width τ. The heat PDF strongly depended on the latter parameter: (i) for $\tau < \tau_0$ (τ_0 being the time constant of the *RC* circuit) it was almost centered around zero (very small average heat) and showed long exponential tails and (ii) for $\tau > \tau_0$ the heat PDF gradually became a Gaussian with a finite average heat. Instead, the mean work was always finite and the work PDF was Gaussian for all τ. An important conclusion is that long non-Gaussian tails in the heat PDF show up only when dissipation is weak.

Of particular interest to the present work are the experiments on RNA unfolding of Liphardt *et al.* [3]. The results clearly indicate that the PDF for the dissipated work at low switching rates (unfolding-refolding) is always a Gaussian and that the average dissipated work is very small or zero no matter the extension. Instead, at high switching rates, while for low extensions the mean dissipated work is still zero, as soon as the extension increases the mean work increases with the switching rate. In all cases the dissipated work PDF was a Gaussian. Unfortunately, the data obtained in Ref. [3] were too scarce to allow a thorough analysis of non-Gaussian tails. The results are similar to those discussed above for the *RC* circuit in the sense that when dissipation mechanisms are not operative (time interval τ less than circuit time constant in the first case and low switching rates in the second) the mean heat or the mean dissipated work is close to zero. In the two cases [3,5] the measured PDFs were used to evaluate performance of extended FT.

We have recently shown, by means of molecular dynamics (MD) simulations, that the PDFs of work and heat exchanged during isothermal stretching of Al nanowires were as expected, namely, Gaussian in the first case and Gaussian for low values of heat plus non-Gaussian exponential tails in the second [10]. In addition, as the nanowire temperature was equated to the bath temperature after a few MD steps, the average exchanged heat $\langle \Delta Q \rangle$ was negligible. The aim of the present work is to present concluding evidence regarding the existence of those tails in the heat PDF. To this end, extensive molecular dynamics simulations of stretching of Al and Au nanowires at temperatures in the range of 0.5–200 K were carried out. Our results conclusively prove the existence of those tails at low temperatures which disappear as the testing temperature is increased. In addition, at 0.5 K an exponential fitting of the tails over a rather wide range was possible in the case of Al. Instead gold required two exponentials, suggesting two types of spontaneous processes or atomic rearrangements during stretching.

MD calculations [11] of aluminum and gold nanowires stretched along the [001] direction at a constant strain rate of 0.03%/ps were performed using the interatomic potentials in Refs. [12,13], respectively. As pointed out by Ikeda *et al.* [14] these large strain rates are only achieved experimentally in shock wave and high velocity impact studies. The nanowires were 30 Å in length and a section gradually reduced from its ends to the center (actual diameters being 8 and 12 Å, respectively) with a total of 463 atoms. Initial random velocities were assigned to all atoms resulting in a Maxwell

distribution. No viscous term was explicitly included in the equations of motion since this is not expected to be operative in very small systems [15]. Averaging was done over a large number of realizations (initial conditions) that was varied in order to check convergence and trustability of the results. Simulations were done keeping the nanowire at a constant temperature that was varied over the range of 0.5–200 K, which amounts to assume perfect thermal contact with a bath large enough to absorb all heat generated, a supposal that is justified in systems as small as those investigated here. Thus, velocity scaling was done after a few number of MD steps N_{MD}^{T} (taken equal to ten in this work). The heat evolved ΔQ is calculated from the change in kinetic energy upon scaling.

The stress-strain curve was calculated using the Virial theorem [16]. These curves have been described and analyzed in detail in a previous article [10]. Calculations using similar procedures have been performed by other authors [14,16–19]. We focus here on the heat exchange between the thermal bath and the nanowire during deformation. The PDFs for the heat exchanged were obtained for those deformations in the stress-strain curve beyond the yield point and before breaking. In this region, the curves show steps composed by elastic regimes where the nanowire is stretched, followed by plastic deformation, where atomic rearrangements occur.

Heat PDFs were derived from the stress-strain curves as follows. First it was checked that the yield point occurred at an extension that was similar for all realizations. Breaking, however, although in most cases occurred for extensions within a narrow range, some samples broke either much earlier or much later. Then, only those realizations leading to extensions within that range were used. For the nanowires and testing conditions described above, the number of points in the stress-strain curves used to produce the PDF varied in the range of 800–1000 (depending on material and temperature) which gives a total over half million points as in most cases the number of realizations was in the range of 600–1500.

Numerical results for the exchanged heat PDF in stretching aluminum and gold nanowires at several temperatures are depicted in Figs. 1 and 2. Results for different numbers of realizations do not vary appreciably indicating good convergence. It is noted that all PDFs are centered around zero, which implies a negligible average exchanged heat (actually, two orders of magnitude smaller than $k_B T$) in accordance with the isothermal character of our simulations. Around $\Delta Q=0$ all PDFs admit a Gaussian fit, although over a range that depends on temperature and to a less extent on material. For instance, the PDF for aluminum tested at 200 K follows a Gaussian over the whole heat range. This range is greatly reduced when stretching is done at 0.5 K (top panels in Figs. 1 and 2). The FWHM of the fitted Gaussians increases with temperature and it is larger in Al than in gold (see caption of Figs. 1 and 2). Figure 3 shows the numerical results for FWHM versus temperature and the best fittings we have found. The results are rather conclusive: the FWHM versus T follows a power law whose exponent is slightly larger in Au than in aluminum. Although the actual power law may depend on details of the calculation, such as parameter N_{MD}^{T}, the results of Fig. 3 are rather illustrative.

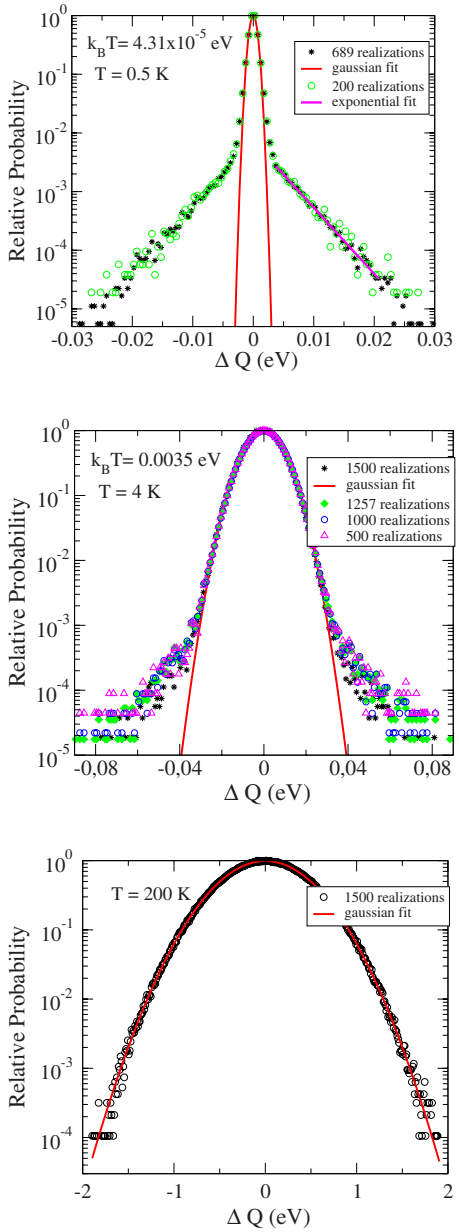

FIG. 1. (Color online) Probability distributions of the heat evolved (ΔQ) in the nonlinear regime derived from MD simulations of stretching of Al nanowires containing 463 atoms. The simulations were carried out at a constant strain rate and keeping the nanowire temperature constant, namely, 0.5 K (upper), 4 K (middle), and 200 K (lower). Numerical results for different numbers of realizations (each one containing around 900 points along the stress-strain curve) are depicted. The (red) continuous curves are Gaussian fits to the numerical data over the ranges of $[-0.0025, 0.0025]$, $[-0.03, 0.03]$, and $[-2, 2]$ eV for 0.5, 4, and 200 K, with full widths at half maximum (FWHMs) of 0.00168, 0.0192, and 1.035 eV, respectively. For 0.5 K an exponential fit to the non-Gaussian tail is also shown (magenta straight line).

The most appealing features, however, of the results reported in Figs. 1 and 2 are without doubts the long non-Gaussian tails that show up at low temperatures. The results for Al at 0.5 K are particularly conclusive. The tail admits a fitting with an exponential, in agreement with what it is ex-

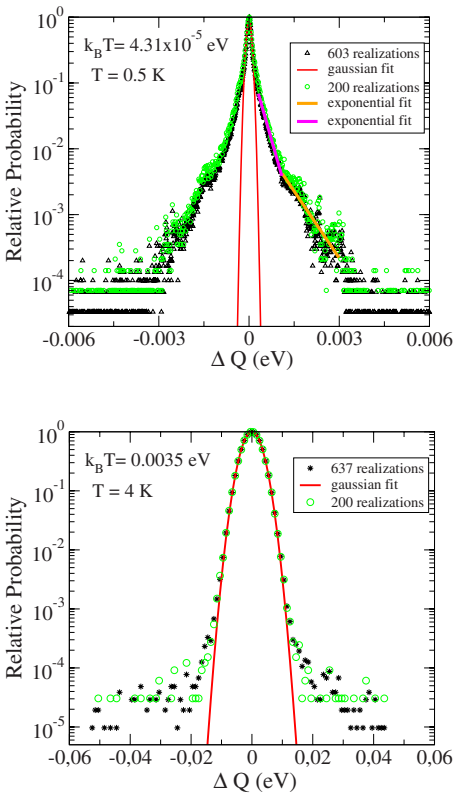

FIG. 2. (Color online) Same as Fig. 1 for gold nanowires. In this case results correspond to 0.5 K (upper panel) and 4 K. The (red) continuous curves are Gaussian fits to the numerical data over the ranges of $[-0.000\,15, 0.000\,15]$ and $[-0.012, 0.012]$ eV for 0.5 and 4 K, with FWHMs of 0.0002 and 0.007 eV, respectively. For 0.5 K two exponential fits to the non-Gaussian tails are also shown (blue and orange straight lines).

pected in these systems [2,5]. Increasing the temperature up to 4 K sharply narrows the heat range over which tails span and, in addition, the PDF is much noisier in that region. At 10 K the tails are restricted to less than 10% of the covered heat range and apparently disappear for the largest temperature shown in Fig. 1 (note that the Gaussian law is followed down to a value of the relative probability of 10^{-4}). Similar

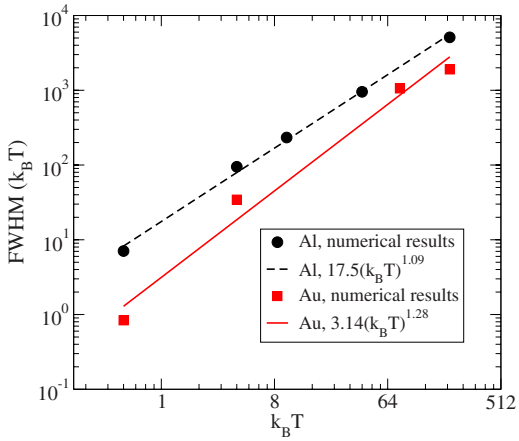

FIG. 3. (Color online) FWHM of the Gaussians fitted to Al and Au heat PDFs (Figs. 1 and 2) versus temperature.

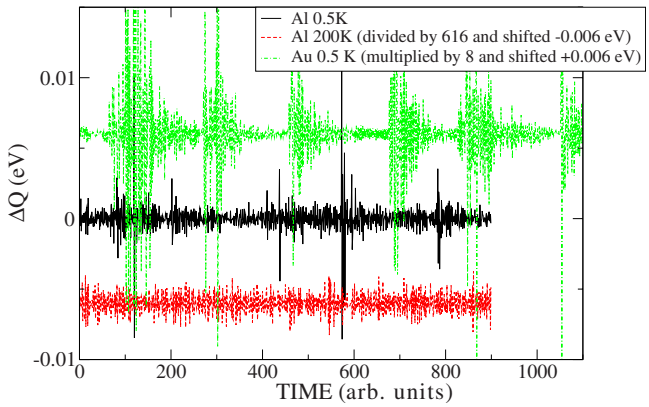

FIG. 4. (Color online) Time series of the heat exchanged with the environment during stretching of Al and Au nanowires at constant temperature. The distributions of Figs. 1 and 2 were derived from a large number of similar time series.

trends are observed in the results for gold shown in Fig. 2. Again long tails show up at 0.5 K which are noticeably reduced when the temperature is increased up to 4 K. The most striking feature now is the fact that the long tails that show up at 0.5 K cannot be fitted by a single exponential suggesting that two types of spontaneous processes are occurring (see Fig. 2). We have not been able to identify clearly the nature of those processes. Aiming, however, to throw some light on this result, we have plotted the exchanged heat time series for Al tested at 0.5 and 200 K and gold tested at 0.5 K (see Fig. 4). The results have been scaled with the corresponding ratios of their respective FWHM. Comparing the time series for Al tested at 0.5 and 200 K it is noted that while in the latter case the amplitude of fluctuations is rather uniform, that for 0.5 K shows large fluctuation events that are surely the origin of the non-Gaussian tails in Fig. 1. On the other hand the time series for gold nanowires tested at 0.5 K is highly irregular showing bunches and very large amplitude events. In order to understand the origin of these fluctuations we have examined the atomic configurations of the nanowires during deformation. We observe that after an atomic rearrangement occurs, a transversal vibration is transferred along the nanowire (see [20]). This vibration is particularly clear in the case of Au since it forms long and narrow structures during deformation which vibrate easily. For the higher temperature studied, 200 K, thermal vibrations overcome those vibrations induced by plastic deformation and therefore they are not observable. These vibrations of the gold nanowire may be the origin of the double tail structure in Fig. 2.

A relevant question is how these results depend on N_{MD}^{T}. If N_{MD}^{T} is small, as is the case of the results just discussed, negligible heating of the nanowire with respect to the thermal bath occurs. On the contrary, if N_{MD}^{T} is large the wire will suffer temporary heating. We have calculated the temperature versus elongation in the case that wire temperature is never equated to the bath temperature and found that, as expected, all heating occurs beyond the yield point and that the final temperature (just before breaking occurs) is approximately 100 K. Then, in view of the rapid elimination of tails as temperature is increased, one may safely ensure that the

non-Gaussian tails will be removed as N_{MD}^{T} is increased.

Summarizing, molecular dynamics calculations on aluminum and gold nanowires subjected to uniaxial stretching have allowed us to produce probability density functions for the heat exchanged with environment during the stretching process. A Gaussian can be fitted to the PDFs over a range which is very narrow at low temperature, increasing rapidly. The FWHM of the fitted Gaussians increases with temperature as a power law with an exponent slightly larger than 1. At low temperatures the probability density function of the exchanged heat shows long exponential tails. These tails rapidly disappear as the temperature is increased. While in the case of aluminum and at the lowest temperature explored here, 0.5 K, the tails can be nicely fitted with an exponential over a rather wide heat range, gold PDF shows two regions which require fittings with different exponentials. This suggests the existence of two types of spontaneous processes. The heat time series turns out to be far more irregular in gold than in aluminum. Vibrations of the gold nanowire when it gets thinner are suggested to be the origin of those irregularities and likely of the double tail structure observed in the PDF of this material. The fact that the tails rapidly disappear as the temperature is increased suggests that, if the nanowire is stretched under nonequilibrium conditions, i.e., if its temperature is allowed to increase during the deformation process, the tails will soon disappear. Preliminary results point in this direction.

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[20] See EPAPS Document No. E-PLEEE8-80-R03909 where videos showing the nanowire structural changes along the stretching process can be found. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.