Statistical Characterization of the Yield Stress of Nanoparticles

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ABSTRACT Atomistic simulations are performed to study the statistical mechanical properties of gold nanoparticles. It is demonstrated that the yielding behavior of gold nanoparticles is governed by the dislocation nucleation around surface steps. Since the nucleation of dislocation is an activated process with the aid of thermal fluctuation, the yield stress at a specific temperature should vary statistically rather than being a definite constant value. Molecular dynamics simulations reveal that the yield stress follows a Gaussian distribution at a specific temperature. As the temperature increases, the mean value of yield stress decreases while the width of distribution becomes larger. Based on the numerical analysis, the dependence of mean yield stress on temperature can be well described by a parabolic function. This study illuminates the statistical features of the yielding behavior of nanostructured elements.

KEY WORDS Yield stress, Gold nanoparticle, Molecular dynamics, Gaussian distribution

1. Introduction

The mechanical properties of nanostructured elements usually exhibit extraordinary size-dependent characteristics [1]. For example, the experimentally measured moduli of metallic nanowires increase dramatically with the decrease of diameter [2, 3]. The compressive strength of gold nanopillar is about 800 MPa, close to its ideal shear strength [4]. Experiments revealed that the hardness of silicon nanoparticles is more than three times that of bulk silicon [5, 6]. The yielding behavior of nanoparticles has also been widely explored. For example, the yield stress of gold nanoparticles is much higher than that of bulk gold [7], and governed by the particle radius and surface steps together [8]. It was reported that the strength of CdS nanoparticles extracted from \textit{in-situ} mechanical tests could approach to the ideal yield strength [9]. In addition, the yield strength of nanostructures often displays some stochasticity in experiments [10, 11], which was usually attributed to experimental errors or sample nuance. To quantify the yield strength of nanosized elements, the maximum value or the mean value with standard deviation is commonly used.

Owing to the small volume and high surface-to-volume ratio, the nonuniform energy distribution is associated with the nanosized elements [12, 13]. The initiation of yielding of nanowires [14–16] or nanoparticles [8, 17–19] is closely related to the state of local atoms around surfaces or surface defects. It is well-known in the statistical thermal dynamics that the kinetic energy of a collection

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of atoms at a specific temperature follows some statistical distribution. Therefore, it is expected that
the thermal fluctuations of atoms around surfaces may lead to the stochasticity of the yield stress for
nanostructured elements consisting of a small cluster of atoms. Recently, Mordehai et al. [20] calculated
the yield stress of faceted Mo nanoparticles at different temperatures and proposed a method to extract
the activation free-energy barrier for dislocation nucleation. However, the statistical feature of the yield
stress has not been fully understood, which is of critical importance to study the mechanical properties
of nanoparticles.

In this paper, based on the large-scale molecular dynamics (MD) simulations, we mainly study
the yielding behavior of defect-free gold nanoparticles and focus on the statistical feature of the yield
stress. Furthermore, the dependence of yield stress on temperature is also discussed.

2. Computational Methods

The uniaxial compressions of gold nanoparticles are performed by using the open-source MD sim-
ulation package, LAMMPS [21]. A well-tested embedded atom method (EAM) potential is utilized to
describe the atomic interactions among gold atoms. The simulation results using the EAM potential
show good agreement with such experimental data as lattice constant, elastic constants, and stack-
ing fault energy [22]. All nanoparticles are carved out of single-crystalline bulk gold with a lattice
constant of 4.08 Å. The nanoparticle radius is denoted by the radius of its corresponding spherical
cutting surface. In our simulations, nanoparticles with radii of 8 nm, 12 nm, and 20 nm are inves-
tigated. The deformation behaviors at different temperatures are studied, from low temperature (10
K) to room temperature (300 K). At each temperature, the simulations are repeated 100 times for
each sized nanoparticle. Nanoparticles with the same radius have identical geometrical profiles and
are assigned with random seeds to initialize the velocities of atoms. The initial velocities of atoms in
one nanoparticle follow the Maxwell–Boltzmann distribution, while the initial velocity of a specific
individual atom in different simulations varies randomly. Canonical ensembles (NVT) are adopted to
describe the atomic systems, and the Nosé–Hoover thermostat is utilized to control the temperature
of the system. The time integration is implemented based on the velocity-Verlet algorithm with a time
step of 0.002 ps.

Uniaxial compression is performed along [111] crystal orientation, as depicted in Fig. 1. Two rigid
planar indenters are adopted to conduct the uniaxial compression on a nanoparticle. The origin of
the coordinate system is set at the center of the nanoparticle, with the z-axis along [111] orientation.
The top and bottom indenters are parallel to {111} facet. A repulsive potential is used to describe the

![Fig. 1. Schematic of the uniaxial compression of a gold nanoparticle in MD simulation](image-url)
interaction between rigid indenter and gold atoms, which is the same as the setup in our previous study on gold nanoparticles [8]. Prior to compression, the nanoparticle is initially relaxed using a conjugate gradient method to achieve a stable configuration with minimum cohesive energy, and then the whole system is dynamically equilibrated at a specific temperature for about 30 ps. Uniaxial compressions are accomplished by moving the two rigid planar indenters simultaneously towards the center of the nanoparticle at a constant speed of 0.05 Å/ps.

The compressive load $P$ is obtained from the reactive force acting on the indenter, and the compression depth $\delta$ is given by the displacement of indenter. In our simulations, the atoms in contact are those which experience repulsive force from the indenter. The real contact area $A$ is calculated from the contacted atoms by using the Delaunay triangulation algorithm. In this method, the positions of contacted atoms are first projected to the indenter plane and recorded as a set of points. Then, a collection of triangles is constructed based on the point set so that no point lies inside the circumcircle of any triangle. The sum of areas of all triangles gives the current total contact area. The average contact stress $\sigma$ is defined as the compressive load divided by the current contact area. To analyze the atomic process inside the nanoparticle during compression, an open-source package OVITO is used to identify and visualize the characteristics of the nucleated defects [23], and a dislocation extraction algorithm is used to calculate the total dislocation length [24].

3. Results and Discussions

To precisely quantify the yield point, we first examine the deformation behavior of a gold nanoparticle with radius of 12 nm at temperature 100 K. Owing to the symmetry of the atomic model, only half of the nanoparticle needs to be considered. The compressive load-depth curve is shown in Fig. 2. It is shown that the contact response can be divided into elastic and plastic stages. In the elastic stage, the compressive load increases linearly with the increase of the compression depth. When yielding occurs, the continuous building-up of the load is abruptly punctuated, indicating the onset of plasticity. In the stage that follows, the compressive load fluctuates with the increase of compression depth because of the dislocation activities inside the nanoparticle. The contact area in the elastic stage keeps constant. Soon after the yield point, the contact area first abruptly jumps to another constant value and then keeps increasing with further compression. Consequently, the average contact stress can be calculated with the obtained load and contact area. It is found that the contact stress drops prominently from a local peak to a low level after the yield point.

Atomic surface steps play a key role in the elastic deformation of nanoparticles. In the initial elastic stage, the planar indenter touches the outmost surface step. Thus, the contact area keeps constant, and the load-depth response follows the elastic flat punch model [25]. When yielding occurs, the indenter just flattens the outmost surface step and gets into contact with the second step. Simultaneously,
Fig. 3. a The distribution of yield stress of gold nanoparticles with radius of 12 nm at 100 K; b characteristic dislocations beneath surface steps at the onset of plasticity (Atoms in perfect lattice are not shown for clearness; atoms in red represent surface and dislocation cores; atoms in blue are dislocation embryos; and atoms in green are stacking faults.)

Partial dislocations nucleate heterogeneously around the fringes of the first surface step. The trailing partial dislocation emits shortly after the nucleation of the leading partial dislocation, forming an extended full dislocation with a stacking fault ribbon. After the critical yield point, the total length of dislocations $L_{\text{disl}}$ starts to increase from zero. Therefore, the local peak of the contact stress right before dislocation nucleation can be reasonably defined as the yield stress of the gold nanoparticle.

Figure 3a shows the distribution histogram of the yield stress, which approximately follows the Gaussian distribution. As a result, the probability density function of the yield stress can be characterized by

$$
\phi(\sigma_Y) = \frac{1}{\sqrt{2\pi}w} \exp \left[ -\frac{(\sigma_Y - \sigma_m)^2}{2w^2} \right]
$$

where $\sigma_m$ and $w$ are the mean value and the standard deviation of the sample data set, respectively. For nanoparticles with radius of 12 nm at 100 K, $\sigma_m$ is 11.67 GPa and $w$ is 0.54 GPa.

The characteristic dislocations of the nanoparticles with low, medium, and high yield stress are shown in Fig. 3b from left to right, which are evidently different from one another. It is noted that the fringes of the first atomic surface step are the preferential dislocation nucleation sites. Due to the thermal motion of atoms, dislocations of geometrically identical nanoparticles may nucleate at different locations, even at the same temperature. Consequently, the yield stress varies stochastically.

Furthermore, we consider the 12-nm-radius nanoparticle at different temperatures to obtain more information about the distribution of yield stress. At each temperature, the simulation is also repeated 100 times. The distribution histograms of yield stress are displayed in Fig. 4b. It is shown that the yield stress at a higher temperature exhibits a wider distribution and has a lower mean value. The atomic energy supplies a thermal assistance to the surface dislocation nucleation, and hence, to the critical yielding behavior. At a higher temperature, both the average atomic energy and the thermal
fluctuation become larger, leading to the decrease of the mean yield stress and the increase of the distribution width.

To confirm that the distribution of yield stress is an inherent character, nanoparticles with different radii are considered as well. Based on our previous research, atomic surface steps under the indenter play an important role in the yield process and cause great changes of yield stress [8]. In order to eliminate the influence of atomic surface steps, we compress nanoparticles with similar surface morphology so that the yield stress of nanoparticles with different radii can be compared directly. The distributions of the yield stress of nanoparticles with radii of 8 and 20 nm at different temperatures are shown in Fig. 4a, c. From these distribution histograms, similar conclusions can be drawn as the case of 12-nm-radius nanoparticles. The yield stress of each set exhibits an approximate Gaussian distribution. To characterize the variation of yield stress with respect to temperature, the coefficient of variation (CV) is calculated as the ratio of standard deviation to the mean value. As shown in Fig. 4d, the value of CV monotonically increases from ~2% to ~7% for all the three sized nanoparticles as the temperature increases from 10 K to 300 K. The deviations of CV between different sized nanoparticles are slight.

Overall, our simulations demonstrate that the yield stress of a group of identical nanoparticles is indeed not a constant value, but exhibits a Gaussian distribution. It is reasonable to quantify the yield stress by the mean value with standard deviation. Figure 5 shows the variations of yield stress versus temperature. For all the three sized nanoparticles, the mean yield stress declines with the increase of temperature. Nevertheless, the trend that “smaller is stronger” is still satisfied at a given temperature.

To understand the temperature-dependent feature of the mean yield stress, a simple model is utilized. The dislocation nucleation from the surface is mainly governed by two factors: the athermal
stress and the thermally activated stress [26, 27]. The former is associated with the elastic limit of material at zero-K temperature, at which dislocation nucleates spontaneously without the assistance of thermal fluctuation. The thermally activated stress originates from the thermal vibrations of atoms. As in the previous study [26, 27], the yield stress $\sigma_Y$ of a nanoparticle with these two factors considered can be given by

$$\sigma_Y = \sigma_a - \sigma_t$$  \hspace{1cm} (2)

where $\sigma_a$ and $\sigma_t$ represent the athermal stress and the thermally activated stress, respectively. The athermal stress is only related to the material properties and structure. On the other hand, it is the thermally activated stress that results in the temperature dependence. At a finite temperature, atoms in a solid crystal could be regarded as independent simple harmonic oscillators vibrating around their equilibrium positions. The average kinetic energy per atom can be estimated by $E_K = \frac{3k_B T}{2}$, where $k_B$ is the Boltzmann constant, and $T$ is temperature. The thermal vibrations of atoms in the nanoparticles will be intensified with the rising of temperature. Assuming that the effective force constant of the metallic bonds is $k_s$, the magnitude of atomic vibration should be $\Delta = 2\left(\frac{E_K}{k_s}\right)^{1/2}$. It should be noted that the effective force constant of surface atoms may depend on the size of nanoparticles. The atomic thermal vibration induces an atomic-scale strain estimated by $\varepsilon_t = \Delta/a$, where $a$ is the lattice constant. Consequently, the thermally activated stress is on the level of $\sigma_t = E\varepsilon_t$, where $E$ is the material modulus. After substituting the thermally activated stress into Eq. (2), the relation between yield stress and temperature is expressed as

$$\sigma_Y = \sigma_a - \alpha T^{1/2}$$  \hspace{1cm} (3)

where $\alpha = \frac{E}{a}\left(\frac{6k_B}{k_s}\right)^{1/2}$. From Eq. (3), the yield stress shows a parabolic dependence on temperature. In Fig. 5, Eq. (3) is used to fit the MD simulation results. For the three nanoparticles with radii of 8 nm, 10 nm, and 12 nm, the fitted athermal yield stresses are 15.43 GPa, 13.19 GPa, and 10.02 GPa, respectively. In addition, we also calculate the yield stress at 0.01 K (approximately equal to the athermal yield stress) for the three sized nanoparticles, which are 15.74 GPa, 13.85 GPa, and 10.57 GPa, respectively, showing good agreement with the fitted athermal yield stresses by Eq. (3). Therefore, the applicability of this theoretical analysis can be confirmed.

In the present study, the compressive strain rate is in the range of $2.50 \times 10^8 \sim 6.25 \times 10^8$ s$^{-1}$, and all uniaxial compressions are exerted along the [111] orientation. In general, both the strain rate and the loading orientation could affect the yielding behaviors of nanostructures. Existing studies demonstrated...
that a higher strain rate usually leads to a higher yield stress [27, 28]. The yield stresses of nanoparticles under compression along different orientations could be conspicuously different [29, 30]. Since the stochasticity in yield stress primarily results from the thermal statistical nature, it is expected that similar statistical characteristics could be observed under compression along other loading orientations or at different loading rates. In addition, the statistical yielding feature of nanoparticles made of high-entropy alloys may become more pronounced [31].

Nanoparticles commonly yield with dislocation nucleation at the surface. Previous study showed that the critical stress for dislocation nucleation at the surface of nanovoids is size-dependent [32]. Similarly, by analyzing the dislocation nucleation at the surface of nanoparticles, i.e. the geometrically necessary dislocation under compression [33], a size-dependent yield stress may be deduced as well. Through molecular simulations, Yang et al. [8] summarized the influence of particle size on yield stress. More detailed theoretical work regarding such topics will be taken in the future.

4. Conclusion

In this paper, we investigate the statistical characterization of yield stress in the compression of gold nanoparticles. Under uniaxial compression, nanoparticles yield when partial dislocations nucleate at the fringe of surface steps. Since the dislocation nucleation is a thermally activated process, the atomic thermal fluctuation could significantly influence the yield stress. At a specified temperature, the yield stress of geometrically identical nanoparticles is not a constant value but approximately follows the Gaussian distribution. As the temperature increases from 10 K to 300 K, the mean value of yield stress decreases while the width of distribution becomes larger. In addition, the coefficient of variation increases and exhibits the same trend for all the three sized nanoparticles. Based on a numerical analysis, a simple model is proposed to explain the temperature dependence of yield stress. This study is helpful for understanding the statistical features of the yielding behavior of nanostructures.

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