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# Molecular statistical thermodynamics – A distinct and efficient numerical approach to quasi-static analysis of nanomaterials at finite temperature

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ABSTRACT

This paper briefly reviews a distinct and efficient numerical approach to quasi-static analysis of nanomaterials at finite temperature: molecular statistical thermodynamics (MST), especially its various applications and efficiency. Different from molecular dynamics (MD) based on Newton equations, MST is a half-analytical numerical method based on the minimization of Helmholtz free energy. The applications of MST to compression of nanorods, nanoindentations and tension of nanowires show that MST is capable of characterizing the nucleation, propagation and interaction of dislocations as well as phase transformations involved in quasi-static deformations. Not only the mechanical responses and properties calculated with MST are in agreement with MD simulations, but the size effect of Young's modulus of zinc oxide nanowires calculated with MST are also in good consistency with experimental results. All these results justify the reliability of MST. Furthermore, the efficiency analysis indicates that MST is dramatically faster than MD for quasi-static processes and is expected to be capable of simulating nanomaterials at larger scales with high efficiency.



## 1. Introduction

With high surface-to-volume ratios, nanomaterials always show unique structures and properties as compared with their bulk components. It inspires people to investigate those structures and properties for specific applications. In particular, mechanical properties involved in the deformation of nanomaterials have attracted more and more attentions recently, because these properties underlie the external loading conditions under which these nano-components can work effectively. More especially, both experimental observations and numerical calculations indicate that most of the mechanical properties of nanomaterials are size-dependent [1–5]; while this effect is not so prominent for bulk ones. This size-dependence effect requires a wider size range of nano-components to be studied in order to fully understand the variations of mechanical properties. However, the experimental measurements are not fully competent for this task so far, and numerical simulations are expected to play an important role in predicting the mechanical properties of nanomaterials as complement. Molecular dynamics (MD) simulations, with the ability to trace each atom's movement during microscopic processes, pervade the work of elucidating microscopic mechanisms involved in nanomaterials. However, the time scale involved in MD is usually about $10^{-12}$ s, which is determined by the intrinsic time scale of atomic vibrations. Apparently, it is not suitable for quasi-static deformation analysis of nanomaterials as in experiments. Furthermore, despite ever-increasing computer power, tremendous computational consumptions of MD restrict it for atomistic simulations of large-scale samples, which can be measured in experiments. As a result, many efforts [6–9] have been done to seek alternatives, which can permit the quasi-static analysis of nanomaterials with larger spatial dimensions.

One of the remarkable approaches for quasi-static deformation is the quasi-continuum (QC) method proposed by Tadmor et al. in 1996 [6], which is a mixed continuum and atomistic approach. However, it is applicable at 0 K, and researchers are trying to extend this method to finite temperatures [8,10,11] or to take the temperature effect into account in a dynamic and multi-spatial scale scheme yet with reduced computational cost [12,13]. Alternatively, Hu et al. and Wang et al. proposed the molecular statistical thermodynamics (MST)/cluster statistical thermodynamics (CST) as well as the hybrid MST and CST (HMCST) computational frameworks [14,15]. This group of methods is designed for quasi-static analyses of micro- or nano-materials with different spatial scales and representation at finite temperature. Specifically, the MST is an atomistic representation based method; while the CST is continuum representation based and the HMCST is a hybrid with

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**Table 1**
Similarities and differences between MD and MST.

| | MD | MST |
|---|---|---|
| Similarities | Atomistic or molecular potential<br>Atomic or molecule mass | |
| *Differences* | | |
| 1. Governing equation | Newton's equation of motion | Formulation of Helmholtz free energy |
| 2. Independent variables | Time step ($t$) | Average atomic positions ($\bar{r}_i$) |
| | Atomic positions ($r_i$) | Boltzmann constant ($k$)<br>Planck constant ($h$) |
| 3. Algorithm | Finite difference solution of Newton's equation of motion | Numerical minimization of Helmholtz free energy |

atomistic and continuum representation based multi-scale approach. The core of this group of methods is MST, which is based on the statistical thermodynamics formulation of Helmholtz free energy of atoms and its minimization, and MST can also be used as a separate approach to analysis of nanomaterials at finite temperature. Though both MST and MD are atomistic frameworks, there are some similarities and distinct differences between them as listed in Table 1. The characteristics of MST indicate that it is suitable for quasi-static processes, whereas it is very hard for MD. Now the MST method has already been applied to investigate structure transformations and mechanical properties of some nanomaterials successfully [15–17]; but how well the ability of MST to capture the microstructure deformation and temperature effects involved in nanomaterials and how good the efficiency of MST are should be carefully examined. More importantly, these examinations can also be used as a reference in choosing between MST and MD for a specific problem.

In this paper we firstly considered the face-centered-cubic (FCC) single crystals under specific quasi-static loadings using MST. In this consideration, the stress–strain curves of compressed nanorods and the depth-force curves of nanoindentaion are compared with that of MD simulations for verification. Dislocation distributions in the simulated nanosystems excited by external loadings are also analyzed to see whether MST could characterize the dislocation nucleation, propagation and interactions. The work of Wang et al. [17] applying MST to zinc oxide (ZnO) nanowires is introduced to exhibit how well MST can handle phase transformations involved in nanomaterials. Furthermore, Young's modulus of ZnO nanowires calculated using MST is combined with experimental data to analyze the size effects. Characterization of temperature effects by MST are also examined by analyzing the Young's modulus of 2-dimensional (2D) and 3-dimensional (3D) nanorods at different temperature. And finally the efficiency of MST with comparison to MD is discussed in details.

## 2. Method

Here we consider a solid system in a thermal equilibrium state containing $N$ atoms at volume $V$ and temperature $T$. Statistically the temperature are contributed by the atomic vibrations. In particular, the atoms in an equilibrium solid system at finite temperature just vibrate around their equilibrium positions and can be treated as an ensemble of oscillators. In the quasi-harmonic approximation, all the oscillators are assumed to be harmonic [18]; and the Helmholtz free energy of the considered system can be expressed as

$$F = \Phi + kT\sum_{j=1}^{N}\sum_{\alpha=1}^{3}\ln\left[2\sinh\left(\frac{\hbar\omega_{j\alpha}}{2kT}\right)\right]. \tag{1}$$

In this expression, $\Phi$ is the total potential energy, $k$ is Boltzmann constant, $\hbar$ is the reduced Plank constant, $\omega_{j\alpha}$ ($\alpha = 1, 2, 3$) are the three oscillating frequencies of atom $j$ in Cartesian coordinate system. The second term on the right hand side in Eq. (1) accounts for the contribution of temperature or thermal vibrations of the atoms to the free energy. In the classical approximation ($\hbar\omega \ll kT$), Eq. (1) can be simplified to

$$F \approx \Phi + kT\sum_{j=1}^{N}\sum_{\alpha=1}^{3}\ln\left(\frac{\hbar\omega_{j\alpha}}{kT}\right). \tag{2}$$

In practical calculations, $\Phi$ is determined by summing the interatomic potential over all the atoms in the system, and then the key point is how to calculate the frequencies. According to lattice dynamics theory [19,20], the vibration frequencies $\omega_{j\alpha}$ are the $3N$ eigenvalues obtained from the diagonalization of the dynamical matrix $\boldsymbol{D}$

$$D_{ij}^{\alpha\beta} = \frac{1}{\sqrt{m_i m_j}}\left(\frac{\partial^2\Phi}{\partial r_{i\alpha}\partial r_{j\beta}}\right), \tag{3}$$

where $m_i$ is the mass of atom $i$ and $r_{i\alpha}$ is the $\alpha$th coordinate of atom $i$. Specifically if we rewrite the Eq. (2) by taking the summation inside the logarithmic function as product

$$F = \Phi + kT\ln\left[\left(\frac{\hbar}{kT}\right)^{3N}\prod_{i=1}^{3N}\omega_i\right], \tag{4}$$

then the frequencies can be connected with the dynamic matrix elements in a more direct form

$$|D| = \prod_{i=1}^{3N}\omega_i^2. \tag{5}$$

The term on the left hand is the determinant of the dynamic matrix. However, for a system containing large amount of atoms, it is rather difficult to accurately calculate the determinate of a $3N \times 3N$ dimensional dynamic matrix as the computational complexity is proportional to $N^2$. As a matter of fact, the most contributions of the interaction between atoms to the oscillations come from the nearest atoms. Hence, to strike a balance between accuracy and efficiency like those in references [18,21–23], the local harmonic approximation is applied. This approximation neglects the coupling of oscillations of different atoms. As a result, the calculation of the determinate is reduced from a full $3N \times 3N$ dynamic matrix to $N$ $3 \times 3$ local dynamic matrices, and the complexity now is proportional to $N$. Substituting the frequencies into Eq. (4), the free energy can be rewritten as

$$F = \Phi + 3kT\sum_{i=1}^{N}\ln\frac{\hbar|D_i|^{1/6}}{kT}, \tag{6}$$

where $D_i$ is the local dynamical matrix of atom $i$. The Helmholtz free energy in Eq. (6) is expressed as a function of atomic coordinates. The equilibrium state of a given system can be obtained by minimizing the free energy with respect to the atomic coordinates and then thermodynamic properties of the system can be calculated based on the equilibrium configuration.

## 3. Numerical simulations and discussions

Compared with elastic properties (Young's modulus for example), some important microstructure rearrangements, such as dislocation nucleation and propagation, phase transformations, are always been greatly concerned. A computational method designed for nanomaterials should have the capability to handle these rearrangements properly. To demonstrate the capability of MST method, we considered FCC single crystal nanosystems and ZnO

nanowires subjected to various external loadings. The stress–strain curves, distributions of dislocations, phase transformations and Young's modulus involved in these nanosystems are analyzed in details, and the results obtained with MST simulations are compared with those of MD. Furthermore, the temperature effects and efficiency of MST are also addressed.

### 3.1. Analysis of FCC single crystal under mechanical loadings

Firstly, an FCC single crystal nanorod subjected to uniaxial compression loading is studied using MST, since it is also the simple test to evaluate MST with comparison to MD. The concerned FCC single crystal is Cu nanorod with lattice constant $a = 3.615$ Å, as illustrated in Fig. 1a, and the nanorod is along [1 0 0] crystal orientation with {1 0 0} surfaces. It contains 5155 atoms with dimensional size ($lx$, $ly$ and $lz$ in Fig. 1a) to be $10.8 \times 2.2 \times 2.2$ nm, and a Lennard–Jones potential [24] with parameters $\varepsilon = 0.4912$ eV and $\sigma = 2.3276$ Å is used to model the interatomic interactions. Atomic layers at the end sides with thickness of 1.0 nm are fixed to perform displacement-controlled compression loading. The thickness is a little larger than the cutoff radius of 0.7 nm for the interaction calculations to ensure that unfixed atoms near the fixed layers have the same number of interaction neighbor atoms as that of atoms far away from the fixed layers. The same configuration is also used to MD simulations for comparison. The concerned system temperature in both MD and MST simulations is maintained at 100 K. The as-prepared nanorod configuration is relaxed enough to get rid of initial stresses before compression loading is applied, and similar relaxed configurations are adopted to both MST and MD. Since each MST load step relates to a quasi-static state, for comparison, each load step in MD is followed by a 25 ps relaxation to make sure that a statistical thermal equilibrium state is reached.

The stress–strain curves obtained with both MST and MD simulations are illustrated in Fig. 2. For elastic compression stage, the calculated Yong's modulus is 330.78 GPa from MST, which is quite close to 330.19 GPa from MD. The first precipitous drop in stress of either MST (point B in Fig. 2) or MD results is corresponding to a dislocation slip in the nanorod. The dislocation distribution of MST result after the slip is demonstrated in Fig. 1b in which atoms near the dislocations are identified by centro-symmetry parameters [25]. Apparently, most of the slips predicted by MST occur along {1 1 1} planes, which coincides well with the most favorable slip systems of FCC crystals according to the dislocation theory. The dislocation distribution observed in MD is similar to that in MST; however the first slip initiates at the strain of 7.69% in MST, which is a little bit later than 6.70% predicted by MD

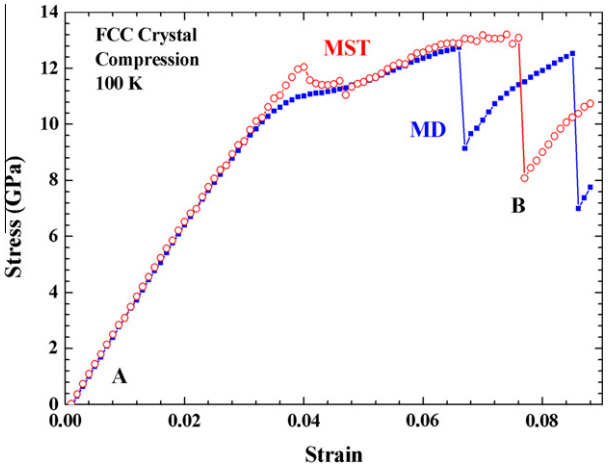


**Fig. 2.** Compressive stress–strain relations of FCC single crystal nanorod obtained with MST (open circles) and MD (solid squares) simulations.

results. This delay can be attributed to the different algorithm used in MD and MST for locating atoms to their equilibrium states. In MST atomic equilibrium positions are obtained through energy minimization procedure which is corresponding to a quasi-static process and the atomic vibration is characterized by oscillator hypothesis. While in MD, atoms find their equilibrium positions through a dynamic process and vibrate randomly around them. It is these random vibrations that may lead to an earlier nucleation and subsequent propagation of dislocations which, ultimately, results in stress drops. The mechanical response and details of dislocation are correctly captured by MST in this simple test, yet a more complex system should be considered to fully examine the capability of MST.

Nanoindentation technique is commonly used to measure mechanical properties of nanomaterials, and it is a rather complex micro/nano structure transformation process in which contacts of different materials, nucleation, propagation and interactions of dislocations are involved. So it is always selected as a benchmark to examine new computational methods for micro/nanomaterials [7,8,15]. Here we considered a nanoindentaion to examine whether MST method can handle such a complex process. As shown in Fig. 3, the substrate is FCC single crystal containing 73,800 Cu atoms with dimensions ($lx \times ly \times lz$) of $10.8 \times 10.8 \times 7.2$ nm. It is indented by a triangular pyramid-shaped diamond-structured tip which contains 888 C atoms. The tip has {0 0 1} side surfaces and its height is about 2.3 nm. The top surface of the substrate is (0 0 1) crystal plane

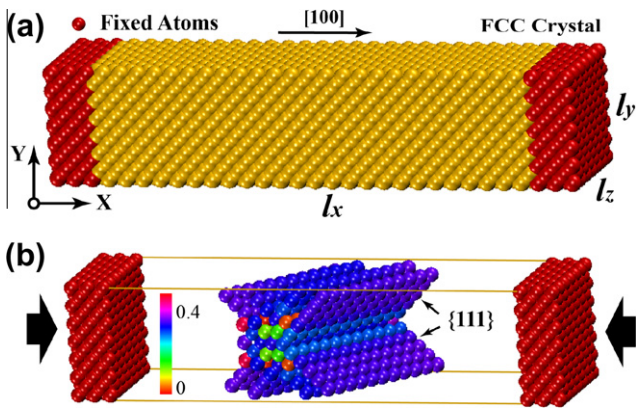


**Fig. 1.** (a) FCC single crystal nanorod with fixed ends. (b) Dislocation distributions in the nanorod after compressive loadings, atoms near the dislocations are colored by centro-symmetry parameters.

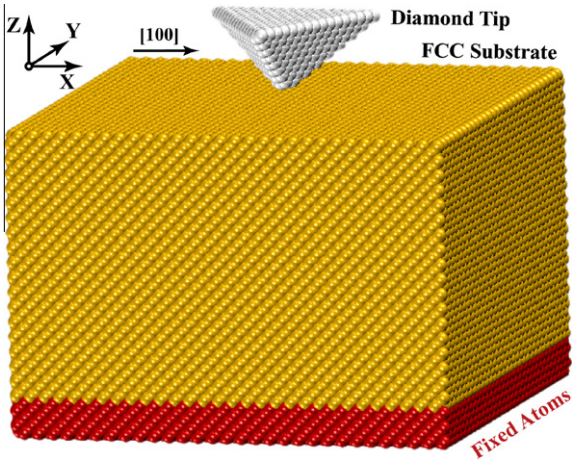


**Fig. 3.** An FCC single crystal substrate indented by a diamond-structured tip.

and the other two side surfaces are (1 0 0) and (0 1 0) planes, respectively. The top surface is traction free and the bottom layers of the substrate with thickness of 0.8 nm are fixed. Periodic boundary conditions are imposed against the side surfaces to approximate a nanofilm with infinite width. Interatomic interaction of the substrate is the same as that of the nanarod discussed previously. The atomic type of the tip is different from that of the substrate, and interactions between tip and substrate atoms are described by a Morse potential [26] with parameters $D_0 = 0.087$ eV, $\alpha = 5.14$ Å$^{-1}$ and $r_0 = 2.05$ Å. We assume that the tip is rigid or relative motion of the tip atoms is prohibited during indentation. Again MD simulations are performed to the same system for comparison. The whole configuration is relaxed enough before indentation and the temperature is maintained at 100 K. The tip force curves obtained with both MST and MD simulations are plotted against indentation depth in Fig. 4. In both simulations, the tip forces are calculated by directly adding all the interaction acting on the tip atoms along the indenting direction. As expected, the two curves coincides with each other very well in either loading (A → B → C) or unloading (C → D → A) stages. Sawtooth jumps in the curves are corresponding to dislocation events such as nucleation, propagation and interactions. Fig. 5 shows the dislocation distribution at point C, represented by atoms near dislocations colored by their centro-symmetry parameters. Similar to the simple slips in the previous nanorod test, the main slip systems here are the {1 1 1} planes along the [1 1 2] directions. All these results suggest that the MST method is capable of handling these complex dislocation processes.

### 3.2. Phase transformation of ZnO nanowire induced by tensile loading

Besides dislocations, MST is also capable of handling phase transformations in nanomaterials under loadings. Wang et al. [27,28] has reported a tensile stress-induced phase transformation from wurtzite phase to a tetragonal phase of [0 0 0 1] oriented ZnO nanowire by making use of MD simulations. Recently they used MST method to analyze this transformation as well as mechanical properties of ZnO nanowires with larger diameters. To validate the MST method, the tensile response of a nanowire with diameter of 2.0 nm was obtained with MST simulations and compared with that from MD. As expected, similar to the results of MD, the results of MST simulations also show three-stage stress–strain relations: elastic stretching of the original wurtzite structure, transformation from wurtzite phase to a tetragonal phase and elastic stretching of the new tetragonal phase. Furthermore, the lattice parameters of the two phases obtained with three different methods: MST, MD and density functional theory (DFT), are compared with each other. The results from MST are well consistent with those from MD and DFT, with errors less than 3%. These comparisons confirm that MST can effectively simulate phase transformations of nanomaterials.

In the study of the size effect on Young's modulus of ZnO nanowires, the smallest diameter of nanorods tested experimentally is limited to about 17 nm [3]. Since MST is much faster than MD (this will be discussed in details in Section 3.4), it gives us a very good tool to calculate the Young's modulus of nanowires with diameters comparable with experimental samples. As shown in Fig. 6 (the experimental data are from Ref. [3]), the Young's modulus obtained with calculations and experiments increases as the diameter is decreased. This size enhanced elasticity arises from the skin of several atomic layers where the bond becomes shorter and stronger [2,29,30]; the elasticity and strength is proportional to the binding energy density. As the diameter is decreased, the ratio of the number of surface atoms to total atoms of the sample increases and eventually the Young's modulus is enhanced. For the largest sample with diameter of 23.4 nm in MST simulation, the calculated Young's modulus is 210.37 GPa. And for the sample with diameter close to the smallest sample (about 17.5 nm diameter) tested in experiments, the calculated Young's modulus is 217.14 GPa which is in good agreement with the experimentally measured value of 221 GPa. These values calculated from MST provide a very good reference for analyzing the size effect on Young's modulus of ZnO nanowires.

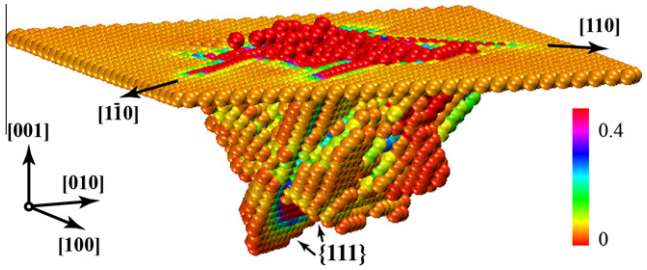


**Fig. 5.** Dislocation distributions in the substrate after indentation, where atoms near the dislocations are indicated by their centro-symmetry parameters.

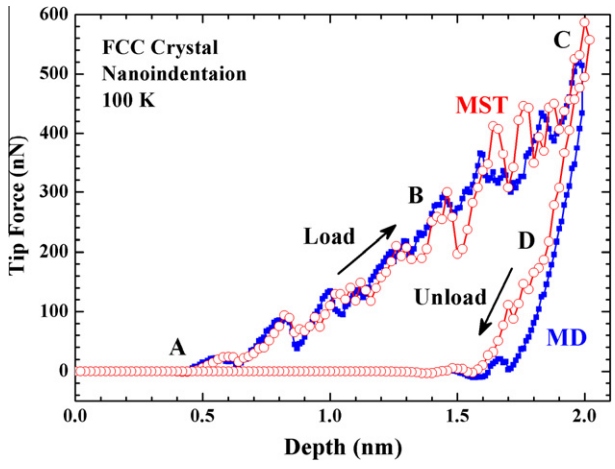


**Fig. 4.** The tip force vs. indentation depth curves for FCC single crystal during indentation and retraction obtained with MST (open circles) and MD (solid squares), respectively.

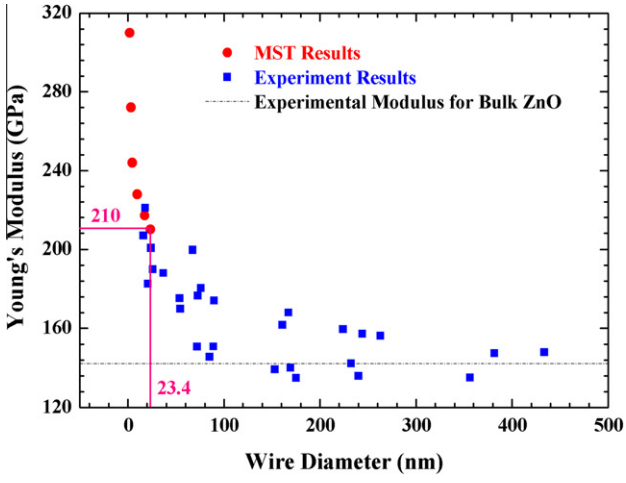


**Fig. 6.** Variation of Young's modulus of ZnO nanowire with its diameter obtained with MST calculations and experiments, and the dash-dotted line denotes the experimentally reported bulk ZnO value of about 140 GPa.

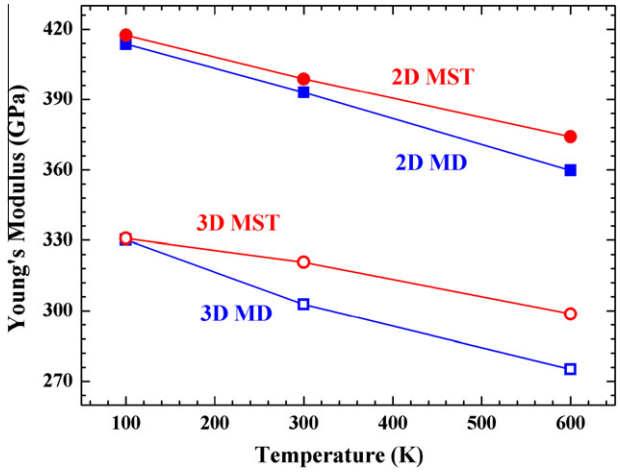


**Fig. 7.** Variation of Young's modulus with temperature obtained with MST and MD simulations.

### 3.3. Temperature effects on Young's modulus

As stated before, temperature effects are taken into account in MST method by taking the system's Helmholtz free energy as its objective function. As a basic part to the new HMCST multi-scale method, MST should characterize mechanical properties of nanomaterials in a normal temperature range effectively. Here 2D and 3D nanosystems are analyzed to examine the characterization of MST on temperature effects. The atomic arrangement in the initial 2D sample is similar to the close-packed or (1 1 1) plane of FCC lattice. It contains 2460 Cu atoms with dimensional size of 26.6 × 5.1 nm, and atoms at the left and right ends with thickness of 2.2 nm are fixed for performing displacement-controlled loadings. The 3D configuration is the same as that illustrated in Fig. 1. These 2D and 3D nanosystems are simulated using MD and MST, respectively, and Young's modulus at the temperature of 100, 300 and 600 K are plotted in Fig. 7. For the 2D case, as temperature increases from 100 to 600 K, the Young's modulus calculated from MST decreases from 417.47 to 374.08 GPa. Compared with that from MD, the errors are 0.91%, 1.45% and 3.97% (as listed in Table 2), respectively. For the 3D case, the Young's modulus are calculated to be 330.78, 320.73 and 298.66 GPa in MST simulations, and the errors are 0.18%, 5.93% and 8.56% in comparison with MD, respectively. Both MST and MD predict the reduction of Young's modulus in either 2D or 3D systems as the temperature is increased. Physically, thermal excitation will prolong and weaken the bonds throughout the sample which leads to the decrease of the binding energy density. As a result, a lower modulus is obtained with elevated temperature. The comparison in Table 2 also shows that the errors between MST and MD increase as temperature is increased. Perhaps this should be attributed to the local harmonic approximation applied in MST method. When atoms vibrate around their equilibrium positions with small displacement, local harmonic approximation is a good approximation to characterize these vibrations [18,22]. However, as temperature increases; the system expands and the average distances between atoms grow. As a result, atoms would vibrate with greater amplitudes in wider and gentler energy wells. Consequently, atoms would vibrate in a more non-harmonic way, so the real system becomes softer than that described by local harmonic approximation. Nevertheless MST can still well predict the temperature effects on Young's modulus with errors less than 9% at the temperature even close to 600 K.

**Table 2**
Variations of Young's modulus with temperature.

| Dimension | 2D | | | 3D | | |
|---|---|---|---|---|---|---|
| Temperature (K) | 100 | 300 | 600 | 100 | 300 | 600 |
| MD (GPa) | 413.71 | 393.04 | 359.79 | 330.19 | 302.77 | 275.10 |
| MST (GPa) | 417.47 | 398.74 | 374.08 | 330.78 | 320.73 | 298.66 |
| Errors (%) | 0.91 | 1.45 | 3.97 | 0.18 | 5.93 | 8.56 |

### 3.4. Efficiency of MST and MD simulations

Despite ever-increasing computer power, it is still a challenge for MD to simulate larger systems, like micrometers. So the efficiency is a key point for new computational methods designed for micro- or nano-materials. Here a series of simulations are performed to compare the efficiency of MST and MD. All the nanorods simulated in this section have configurations similar to that illustrated in Fig. 1 except for the dimensional sizes. The ratio of the lengths of the unfixed body along $x$, $y$ and $z$ directions is set to be 4:1:1 for all these simulated samples. For MST simulations we considered 6 nanorods with $lx$ ranging from 18.0 nm to 36.9 nm (the following nanorods discussed will be denoted by $lx$) and with atoms from 20,507 to 246,103. As comparison, MD calculations are also carried out with the same size range. All these samples are compressed in terms of MST and MD methods, and the CPU consumptions are recorded at each load step for the analysis. In this work, the MD simulations are performed using the LAMMPS code which is an open source and commonly used MD simulation package distributed by Sandia National Laboratories [31], and the MST package is developed by the authors (the MST package has been registered in the Copyright Protection Center of China with registration No. 2011SR003778. This package is free and will be available online in the future). All these simulations are performed on the same hardware environment with a single Intel® Core™ 2 Duo CPU E6750.

The time consumptions per load step by MST simulation for the nanorod of 31.1 nm are plotted in Fig. 8, and this is also the typical time consumption pattern of MST. It is noticeable that the first step (point A in Fig. 8) consumes much more time than the other steps at the earlier stage. Actually, the first step is corresponding to the relaxation of the initial configuration. Since the initial configuration is truncated from a perfect bulk FCC crystal, atoms near the free surfaces after truncation are far away from their actual equilibrium positions. However, in the following elastic compression

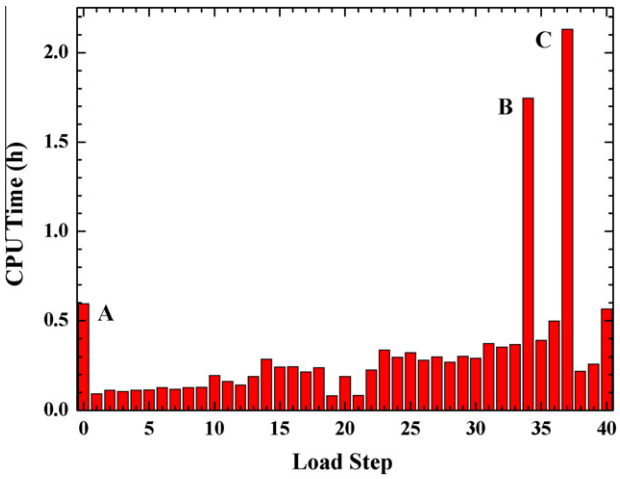


**Fig. 8.** CPU time consumptions at each loading step in MST simulation of FCC single crystal nanorod.

steps in which a little bit of strain is applied to the nanorod, atoms are not quite far away from their target positions after the previous minimization steps. Therefore, it takes less time for MST to relocate atoms in normal elastic loading steps than the first step. The two significantly higher bars at the 34th and 37th step in Fig. 8 (point B and C) are corresponding to large scale dislocation slips in the nanorod, and MST also spends more time to find the new equilibrium states under these loading conditions. Fig. 9 shows the time consumptions by MD and MST against the sample size (the total of atoms). Apparently, both MD and MST results show a linear relationship between the total CPU time and the sample size, and most importantly, in this comparison, the MST is about eight times faster than MD, suggesting its advantages for larger problems under quasi-static loadings at finite temperatures. It should be pointed out that the strain rate in the MD simulation is $1.25 \times 10^6\ s^{-1}$, which is much higher than real quasi-static loading rate. Normally the efficiency of MD simulation is linear proportional to the strain rate. This means, even if we set the strain rate in MD be $1.25 \times 10^5\ s^{-1}$ (still much higher than real quasi-static process), the efficiency of MST would be about 80 times higher than that of MD.

In fact, there are two key factors that may affect the efficiency of MST relative to that of MD. The first one is the type of the potential used to model the interatomic interactions. For the Lennard–Jones potential, the time consumption in either MD or MST simulations is proportional to the total of atoms $N$ of the system as discussed before. However, this is not the case for Buckingham-type potential that is commonly used to model ionic and some covalent solids, like ZnO. Besides short-range interactions between atoms, long-range Coulomb interactions are also involved between cations and anions. The calculations of the long-range Coulomb interactions are always carried out using the Ewald sum scheme, which makes the computational consumption growing as $N^{3/2}$. Wang et al. [17] carefully compared the efficiency of MST with that of MD for a nanowire with diameter of 2.0 nm using 32 processors on an Itanium® 2 based parallel cluster in their work (see Fig. 10). The result turns out that the efficiency of MST is approximately 60 times higher than that of MD for the same problem. It is worth noting in Fig. 10 that MST spends more time at the 44th step to find a new equilibrium state for the phase transformation from wurtzite to tetragonal structure. The other factor affecting the efficiency comparison is the loading rate used in MD simulations. As stated before, each loading step in MST simulations is a quasi-static process, while it is dynamic in MD. Since the time scale in MD simulation is governed by the intrinsic atomic oscillations (like

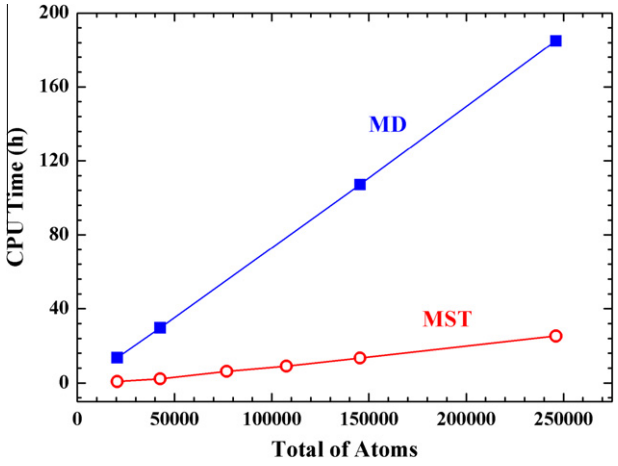


**Fig. 9.** CPU time consumptions in MD and MST simulations against the computational scale (the total of atoms). In this comparison, the MST is about eight times faster than MD.

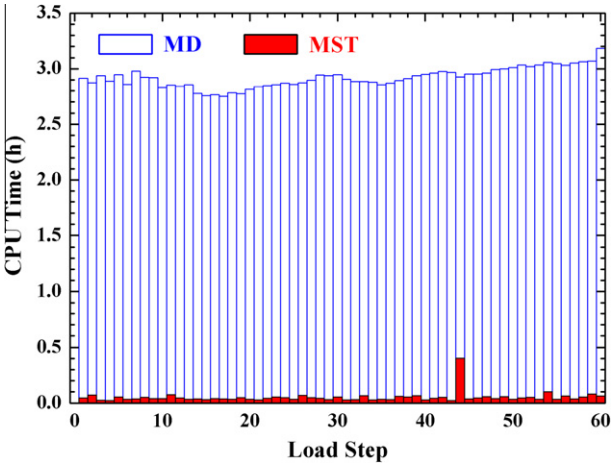


**Fig. 10.** Comparison of CPU time consumption in MD and MST simulations of ZnO nanowire under tensile loading. MST spends much more time at the 44th load step to handle the phase transformation event.

$10^{-13}$ s), it is hard to simulate a real quasi-static process (even in a few seconds) by making use of MD. Practically, in MD simulations quasi-static loading processes are always approximated by equilibrating the atomic system for a relatively long time ($10^{-12}$ s for example), yet the rate would still be at the order of $10^6\ s^{-1}$ even for a negligible small strain $10^{-6}$. Above all for a specific quasi-static problem, the more equilibration time steps are required for MD simulation, the more advantages in efficiency MST will bring us.

## 4. Summary

In this work we present a distinct and efficient numerical approach to quasi-static analysis of nanomaterials at finite temperature, the MST method. Theoretically, MST is used to analyze the quasi-static mechanical response of nanomaterials by minimizing its Helmholtz free energy, which is expressed as a function of the coordinates of all atoms in the system. In addition, temperature effects are taken into account in MST by evaluating the thermal vibrations with local harmonic approximation. Hence, this method greatly releases the restriction of time scale involved in molecular simulations, like ps in MD. In the analysis of single FCC crystals, like nanorods under uniaxial loadings and nanoindentations, both loading responses and dislocation distributions obtained with MST simulations agree quite well with that of MD simulations. In particular, the application to ZnO nanowires with long range interaction indicates that MST is capable of identifying the wurtzite-to-tetragonal phase transformation originally predicted by MD and DFT simulations. Furthermore, the Young's modulus of ZnO nanowires calculated with MST is in good agreement with experimentally measured values, this provides a useful reference for the analysis of size effects in nanomaterials. The calculations of Young's modulus of both 2D and 3D FCC nanosystems at different temperatures verify that temperature effects on the mechanical properties have been effectively introduced into MST method. More importantly, MST has a big advantage over MD in dealing with quasi-static problems. For the Lennard–Jones potential, CPU time consumptions in MST simulations show linear proportional to the size of the simulation system. For Buckingham-type potential, MST can be up to 60 times faster than MD calculations, therefore, potentially allowing larger size systems to be analyzed with MST. Since MST is an atomic simulation method in terms of free energy minimization, it can be seamlessly coupled with a quasi-continuum program, CST, in terms of the same free energy and then they form a new multi-scale method, the HMCST method

[15]. It is expected that the MST method combined with HMCST methods could handle more quasi-static problems at finite temperature with even larger systems properly up to several micrometers in the future.

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