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Molecular/cluster statistical thermodynamics methods to simulate quasi-static deformations at finite temperature

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Abstract

The rapid evolution of nanotechnology appeals for the understanding of global response of nanoscale systems based on atomic interactions, hence necessitates novel, sophisticated, and physically based approaches to bridge the gaps between various length and time scales. In this paper, we propose a group of statistical thermodynamics methods for the simulations of nanoscale systems under quasi-static loading at finite temperature, that is, molecular statistical thermodynamics (MST) method, cluster statistical thermodynamics (CST) method, and the hybrid molecular/cluster statistical thermodynamics (HMCST) method. These methods, by treating atoms as oscillators and particles simultaneously, as well as clusters, comprise different spatial and temporal scales in a unified framework. One appealing feature of these methods is their "seamlessness" or consistency in the same underlying atomistic model in all regions consisting of atoms and clusters, and hence can avoid the ghost force in the simulation. On the other hand, compared with conventional MD simulations, their high computational efficiency appears very attractive, as manifested by the simulations of uniaxial compression and nanoindentation.

Keywords: Inter-atomic potential; Finite temperature; Quasi-static; Multiscale; Statistical thermodynamics

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1. Introduction

The 21st century is witnessing an unprecedented growth of nanotechnology. The rapid evolution of this new science and its exciting applications have necessitated novel, sophisticated, and physically based approaches for design and performance prediction. The most direct and popular simulation approach is the molecular dynamics (MD) method (Leach, 1996), in which one chooses an appropriate inter-atomic

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potential to describe the interaction between atoms and then integrates the classical equations of motion with suitable boundary conditions. An appealing feature of MD is that it follows the actual dynamical evolution of all atoms. However, for realistic systems, it is practically impossible to track all atoms by solving the equations of motion. In addition, to resolve individual motion of atoms requires a time step of approximately femtoseconds, i.e. a fraction of atom oscillation period, in the integration of the equations of motion, so that even on today's fastest supercomputers, to simulate a process lasting microseconds is very difficult. Therefore, a number of multiscale methods have been proposed to link MD to meso- or macroscale simulation approaches (Kohlhoff et al., 1991; Tan and Yang, 1994; Wagner and Liu, 2003; Broughton et al., 1999; Shilkrot et al., 2002; Dupuy et al., 2005; Rudd and Broughton, 1998). Connections between these length scales are achieved either by a parameterization or by a coarse-graining procedure. However, the inherent short time-scale limitation of MD cannot be surmounted, since the coarse graining is not applicable over temporal scales.

Being more specific in this paper, we focus our attention on the simulations of deformations under quasistatic loading at finite temperature, as commonly undergone in many standard test procedures. In this type of processes, at least two temporal scales are typically involved: atomic oscillation on time scale of shorter than picoseconds, while the atomic re-arrangement as a result of external loading takes place on much longer time scales: seconds to years. Obviously, the enormous time-scale gaps between them are thus unmanageable by conventional MD simulation.

A well-known multiscale approach for quasi-static deformation at 0 K is the quasicontinuum (QC) method developed by Shenoy et al. (1998). The key idea of QC is kinematic slavery in which by virtue of finite element method (FEM), the positions of the majority of atoms are entirely constrained and determined only by the displacements of those nodes (repatoms) tied to the element that includes the atoms. The positions of all nodes at zero temperature can be obtained by minimizing the coarse-grained potential energy of the system. They also applied the idea of kinematic slavery to MD simulation at finite temperature and proposed finite-temperature quasicontinuum method (Dupuy et al., 2005). It is shown that although the simulation can be considerably sped up at finite temperature, the total simulation time is usually limited to nanoseconds. On the other hand, based on the statistical thermodynamics formulation of Helmholtz free energy of atoms and its minimization, Hu et al. (2005) and Wang et al. (2005) reported molecular statistical thermodynamics (MST)/cluster statistical thermodynamics (CST) methods. These short papers noticed their results just provided an encouraging first step, "there are a variety of interesting issues still to be explored" (Dupuy et al., 2005).

Actually, to further explore various aspects of the approaches is badly needed, including its foundation and essence, limitations, comparisons with other molecular simulations and its applications to some challenging nano-mechanical problems. Nevertheless, it seems that the strict framework of statistical thermodynamics can guarantee a solid basis for the endeavors in these directions.

In order to achieve sophisticated and efficient simulations of quasi-static deformation at finite temperature, in this paper, we propose a group of statistical thermodynamics methods, that is, molecular statistical thermodynamics (MST) method, cluster statistical thermodynamics (CST) method, and the hybrid molecular/cluster statistical thermodynamics (HMCST) method in detail. These methods are named since they base on the findings of statistical thermodynamics to deal with various spatial and temporal scales. One attractive feature of these methods is their "seamlessness" or consistency, in which the same underlying atomistic model is used in all regions consisting of atoms and clusters, regardless of additional constitutive relations, and hence can avoid the ghost force in simulation. On the other hand, compared with conventional MD simulations, their high computational efficiency appears very desirable, as well manifested by the simulations of uniaxial compression and nanoindentation.

The rest of this paper is organized as follows. In Section 2, we first introduce the molecular statistical thermodynamics (MST) method, its application to molecular clusters to form cluster statistical thermodynamics (CST) method, and the hybrid molecular/cluster statistical thermodynamic (HMCST) method. In Section 3, we will validate these methods by comparing the simulations of uniaxial compression obtained from these methods with conventional MD simulation. In Section 4, we will demonstrate the practical performance of the HMCST method in the studying of quasi-static nanoindentation. And, summary is made in Section 5.

2. Method

2.1. Molecular statistical thermodynamics (MST)

At nonzero temperature, the atoms in a solid merely oscillate about their equilibrium positions when no external load is applied. If an external load is applied, the equilibrium positions of atoms will alter, resulting in the deformation of the solid. As we stated earlier, there exist enormous time-scale gaps between the oscillations of atoms and the deformation of the solid. However, the traditional MD simulation treats the oscillations and the deformation indifferently. Both are calculated via the integration of the motion equations of atoms with time steps of femtoseconds, leading to very time-consuming computations. Hence, to manage the computational burden and establish a reliable computational scheme, one must describe the oscillation of atoms and the deformation of the solid discriminatingly and then couple the descriptions judiciously.

The core of MST method (Wang et al., 2005) is the particle–oscillator duality, that is, we treat the atoms as particles at their equilibrium positions when we examine the mechanical deformation of the atomic lattice, while treat the atoms as oscillators with various frequencies when we examine the contribution of the thermal oscillations of atoms to deformation. According to statistical thermodynamics (McQuarrie, 1976) and solid state physics (Born and Huang, 1954; Kittle, 2005), the oscillating frequencies are governed by the current positions of atoms, which couples the two descriptions of particles and oscillators. In addition, when a solid is quasi-statically deformed, the equilibrium positions of the atoms can be obtained by minimizing the free energy of the atomic system.

Since the free energy is one of the most fundamental thermodynamic functions, substantial efforts have been expended in developing methods to determine the free energy. In MST method, we adopt some approximations to calculate the free energy, since they can provide a reasonable compromise between computational accuracy and expense (Rickman and LeSar, 2002; Najafabadi and Srolovitz, 1995).

One assumption is that the oscillations of atoms in the solid are harmonic (Born and Huang, 1954; Kittle, 2005). This means the amplitude of these oscillations is small, compared with typical inter-atomic distances in the solid. Therefore, the Helmholtz free energy of a solid can be represented by a sum of the inter-atomic potential energy and the contribution of harmonic oscillation of atoms as:

$$A = \Phi + kT \sum_{i=1}^{N} \sum_{\xi=1}^{3} \ln \left[2 \sinh \left(\frac{1}{2} \frac{\hbar \omega_{i\xi}}{kT} \right) \right] \tag{1}$$

where Φ is the static lattice energy (inter-atomic potential energy), T is the temperature, N is the total number of atoms, ħ is Planck's constant, k is Boltzmann's constant, $\varpi_{i\xi}$ $(\xi = 1, 2, 3)$ are the three oscillating frequencies of atom i. As Born and Huang (1954) pointed out that in many aspects the behavior of an atomic system are identical to a system of oscillators, for which the total of oscillations should be equal to three times of the total atoms, i.e. $3N$.

In the classical limit, Eq. (1) can be simplified to

$$A = \Phi + kT \sum_{i=1}^{N} \sum_{\xi=1}^{3} \ln \left(\frac{\hbar \omega_{i\xi}}{kT} \right) \tag{2}$$

Now, the key to the expression of Helmholtz free energy A is how to determine the oscillators' frequency. In fact, to understand the thermal and mechanical properties of solids, we need two representations of atoms: oscillators and particles, simultaneously. On the other hand, we have to properly deal with the duality of atoms and find a proper way to bridge the gap between the two representations, according to the concerned problems. Einstein assumed that all oscillators have the same frequency, however, this can represent the isotropic oscillation of independent atoms only. After considering the constraint of atoms in lattice, Debye proposed that the $3N$ frequencies could be taken as the $3N$ lowest frequencies of a continuum, which possesses the same elastic constants as the atomic lattice. Debye's theory has had great success in the explanation of thermal properties of solids. However, recently we found that either Debye or Einstein approximation is unable to simulate severely localized deformation. As noted by Tsien (1962) that Debye's theory is still not an accurate approximation, once there are differences between Debye's approximation and facts, one should resort to other formulations. In order to simulate severe deformation, we turn to dynamical matrix of lattice. According to Born and Huang (1954) and Kittle (2005), $\varpi_{i\xi}$ are the $3N$ eigenvalues obtained from the diagonalization of the dynamical matrix D:

$$D_{ij}^{\xi\eta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 \Phi}{\partial x_{i\xi} \partial x_{j\eta}} \tag{3}$$

where m_i is the mass of atom i, $x_{i\xi}$ is the ξth coordinate of atom i.

For a system consisting of thousands of atoms or more, the diagonalization of the $3N \times 3N$ dynamical matrix becomes extremely difficult. Therefore, we turn to the other approximation, the local harmonic (LH) approximation (Zhao et al., 1993). This approximation neglects the coupling of oscillations of different atoms, and hence, the terms in the dynamical matrix that couple one atom to another are assumed to be zero. Therefore, the full $3N \times 3N$ matrix is decomposed into N 3×3 local dynamical matrices. And, the diagonalization of these matrices can easily yield $3N$ local oscillating frequencies. Substituting the frequencies into Eq. (2), we obtain

$$A = \Phi + 3kT \sum_{i=1}^{N} \ln\left(\frac{\hbar \mid D_i|^{1/6}}{kT}\right) = A\{(x_{i1}, x_{i2}, x_{i3}),\ i = 1, \ldots, N\} \tag{4}$$

where D_i is the determinant of the local dynamical matrix of atom i. By minimizing the free energy expressed by Eq. (4) with respect to the atomic coordinates, the equilibrium positions of atoms and corresponding thermodynamic properties can be calculated.

2.2. Cluster statistical thermodynamics (CST) method

By treating atoms as oscillators and particles simultaneously, the MST method bridges the temporal gaps between the oscillation of atoms and the deformation of the crystal lattice. However, in the case of even large systems, the MST method still has the limitation of data storage requirement since too many atoms need to be dealt with individually. Therefore, a coarse-grained MST method, namely, cluster statistical thermodynamics (CST) method is developed (Hu et al., 2005).

In the CST method, the system is partitioned into clusters characterized by their nodes like FEM. Each cluster is assumed to consist of a number of atoms and is treated as a subsystem in equilibrium. Therefore, the Helmholtz free energy of each cluster as a subsystem of atoms can be expressed with the positions of the corresponding nodes. And hence, the coordinates of the nodes can be determined by minimizing the free energy of the whole system.

Now, we use a two-dimensional system to illustrate the principle and application of the CST method in detail. Consider such a system of N atoms, whose positions are denoted by $\{\mathbf{x}\}$. As shown in Fig. 1, the system is partitioned into a number of clusters and the clusters are determined by their nodes (the big black circles in Fig. 1). Hence, the behavior and the properties of the whole system can be characterized by the coordinates of the nodes $\{\mathbf{X}\}$. Since the total number of nodes $N_{\text{node}} \ll N$, the degree of freedom of the system is significantly reduced.

Then, we assume that the total Helmholtz free energy of the whole system is the summation of the free energy of each cluster, i.e.

$$A = \sum_{\alpha=1}^{N_c} A_\alpha \tag{5}$$

where N_c is the total number of clusters, and A_α is the free energy of cluster α.

In addition, we take local mean field approximation, that is, we assume that all atoms in the cluster have the same oscillating frequencies and contribute equally to the free energy of the cluster. Therefore, similar to MST method, the free energy of cluster α can be expressed as:

$$A_\alpha = N_\alpha \Phi_{\alpha h} + 2N_\alpha kT \ln \frac{\hbar \mid D_{\alpha h}|^{1/4}}{kT} \tag{6}$$

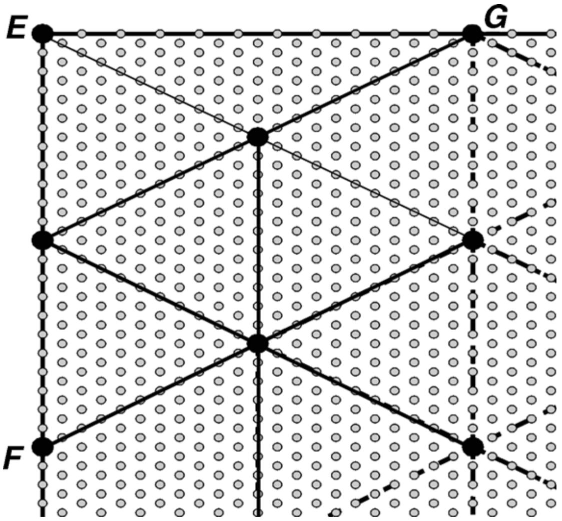

Fig. 1. Schematic figure of cluster construction. The small grey circles are atoms of the system and the big black circles, like E, F, and G, are the nodes that construct the clusters.

where atom h is the atom most adjacent to the center of cluster, N_α is the total number of atoms in cluster α, $\Phi_{\alpha h}$ is the contribution of atom h to the potential energy, $D_{\alpha h}$ is the determinant of the local dynamical matrix of atom h:

$$| D_{\alpha h} |= \frac{\partial^2 \Phi_\alpha}{\partial x_{h1}^2} \frac{\partial^2 \Phi_\alpha}{\partial x_{h2}^2} - \left(\frac{\partial^2 \Phi_\alpha}{\partial x_{h1} x_{h2}} \right)^2 \tag{7}$$

where $\{x_{h1}, x_{h2}\}$ are the coordinates of atom h in 1 and 2 directions, respectively.

With Eqs. (5)–(7), we can express the total Helmholtz free energy of the whole system A as a function of all the nodes positions $\{\mathbf{X}\}$, i.e.

$$A = A(\{(X_{i1}, X_{i2}),\ i = 1, \ldots, N_{\text{node}}\}) \tag{8}$$

We are now in a position to calculate the equilibrium configuration $\{\mathbf{X}_{\text{eq}}\}$ by minimizing A with respect to the coordinates of the nodes $\{\mathbf{X}\}$, so that the total area of clusters $S = \sum_{\alpha=1}^{N_c} S_\alpha$, keeps constant during the minimizing search.

It is worth noting that to implement the CST method, the size of clusters should meet two requirements. Firstly, the cluster should be large enough so that the interaction between different clusters can be neglected compared with the interaction within the cluster and hence the total free energy of the whole system can be assumed as the summation of that of each cluster. Secondly, the cluster should be small enough so that the fluctuation between different regions can be characterized. That is, the size of clusters should be much larger than the cutoff distance of inter-atomic force and much smaller than the scale of heterogeneous properties and deformation in the solid. Therefore, once severe, localized deformation appears, the CST method fails.

2.3. Hybrid molecular/cluster statistical thermodynamic (HMCST) method

As mentioned above, the MST method deals with atoms individually and cannot simulate very large systems, while CST method can simulate large scale systems but cannot deal with localized deformation. Therefore, we propose a hybrid molecular/cluster statistical thermodynamic (HMCST) method (Hu, 2006). The idea in the hybrid method is to merely coarse grain the regions that deform uniformly and use the CST method in these regions, while use MST method in the regions with severe deformation only. Like other multiscale methods, the key to the hybrid method is the connection between the molecular and cluster descriptions.

Again, we use a two-dimensional system to illustrate the HMCST method. Fig. 2 shows a 2D area divided into local, nonlocal and their handshaking regions. In a region with heterogeneous deformation, MST method is applied, that is, all atoms are treated as nodes. This region is named as nonlocal region and the nodes (atoms) in the region are named as nonlocal nodes. The energy of a nonlocal node depends on the nonlocal nodes within its cutoff distance only. In regions with uniform deformation, CST method is applied, that is, only those atoms on the boundary of the cluster are treated as nodes. This region is named as local region and the nodes are local ones. We assume that the local nodes interact with atoms in the cluster only. In the region between the local and nonlocal ones, the nodes interact with atoms in both local and nonlocal regions. Hence, we name it as handshaking region, but note that the nodes in this region are either local or nonlocal ones.

Let's calculate the free energy of such a hybrid system shown as Fig. 2. We suppose that the free energy of the system be the summation of free energy of three parts:

$$A^{\mathrm{tot}} = A^{\mathrm{LC}}\left(\{\mathbf{X}^{\mathrm{LC}}\}\right) + A^{\mathrm{NL}}\left(\{\mathbf{X}^{\mathrm{NL}}\}\right) + A^{\mathrm{SH}}\left(\{\mathbf{X}^{\mathrm{LC}},\mathbf{X}^{\mathrm{NL}}\}\right) \tag{9}$$

where $\{\mathbf{X}^{\mathrm{LC}}\}$, $\{\mathbf{X}^{\mathrm{NL}}\}$ are coordinates of local and nonlocal nodes, A^{LC}, A^{NL}, A^{SH} are free energy of the local, nonlocal and handshaking regions, respectively.

In the local region, we adopt the local mean field approximation as CST method. Hence, the free energy of the local region can be expressed as

$$A^{\mathrm{LC}}(\{\mathbf{X}^{\mathrm{LC}}\}) = \sum_{\alpha=1}^{N_{\mathrm{C}}^{\mathrm{LC}}} N_\alpha A_{\alpha h}^{\mathrm{LC}}(\{\mathbf{X}^{\mathrm{LC}}\}) \tag{10}$$

where $N_{\mathrm{C}}^{\mathrm{LC}}$ is the total of clusters in the local region, N_α is the total of atoms in cluster α, atom h is the atom most adjacent to the center of cluster α, $A_{\alpha h}^{\mathrm{LC}}$ is the contribution to free energy from the atom h of cluster α, which can be written as

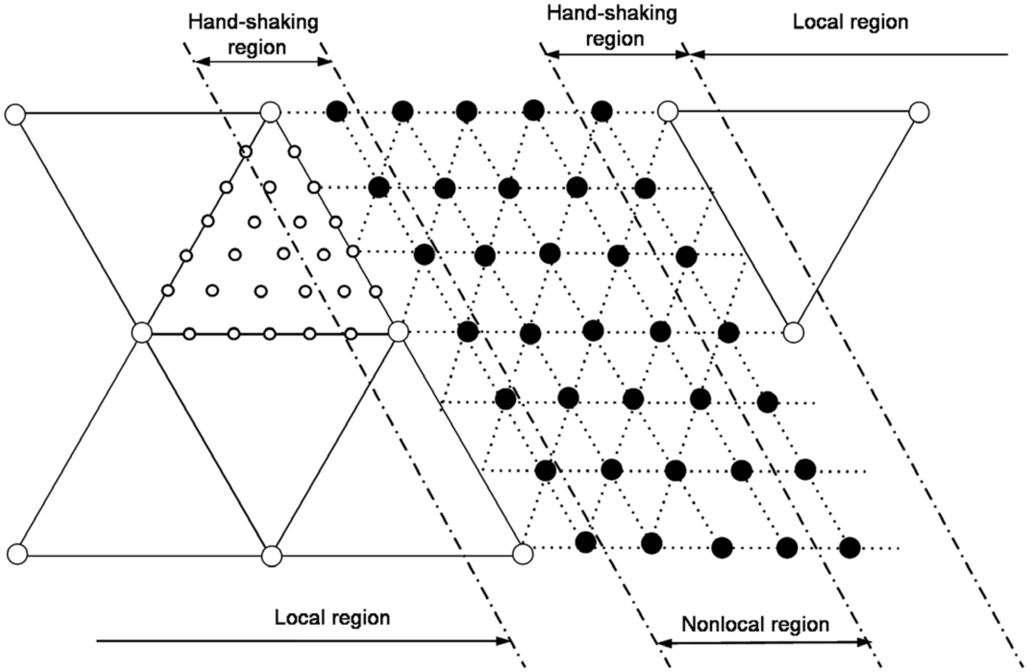

Fig. 2. Schematic figure of local, nonlocal, handshaking regions and nodes partition. The small hollow circles represent atoms, while the big solid and hollow circles are nonlocal and local nodes, respectively.

$$A_{\alpha h}^{\mathrm{LC}} = \Phi_{\alpha h}^{\mathrm{LC}} + 2kT\ln\frac{\hbar\mid D_{\alpha h}^{\mathrm{LC}}\mid^{1/4}}{kT} \tag{11}$$

where $\Phi_{\alpha h}^{\mathrm{LC}}$ and $D_{\alpha h}^{\mathrm{LC}}$ are the potential energy and the determinant of the local dynamic matrix of atom h in cluster α, respectively. $\Phi_{\alpha h}^{\mathrm{LC}}$ and $D_{\alpha h}^{\mathrm{LC}}$ are both functions of coordinates of local nodes in the cluster.

In the nonlocal region, the free energy can be written as:

$$A^{\mathrm{NL}}(\{\mathbf{X}^{\mathrm{NL}}\}) = \sum_{i=1}^{N_{\mathrm{node}}^{\mathrm{NL}}} A_i^{\mathrm{NL}}(\{\mathbf{X}^{\mathrm{NL}}\}) \tag{12}$$

where $N_{\mathrm{node}}^{\mathrm{NL}}$ is the total number of nodes (atoms) in the nonlocal region, A_i^{NL} is the free energy of the ith node (atom). And, A_i^{NL} can be expressed as:

$$A_i^{\mathrm{NL}} = \Phi_i^{\mathrm{NL}} + 2kT\ln\frac{\hbar\mid D_i^{\mathrm{NL}}\mid^{1/4}}{kT} \tag{13}$$

where Φ_i^{NL} and D_i^{NL} are the potential energy and the determinant of the local dynamic matrix of the ith nonlocal node (atom) and they are both functions of the coordinates of nonlocal nodes (atoms).

In the handshaking region, the free energy of this region can be written as the summation of that of all atoms in the region,

$$A^{\mathrm{SH}}(\{\mathbf{X}^{\mathrm{LC}}\},\{\mathbf{X}^{\mathrm{NL}}\}) = \sum_{i\in C_{\mathrm{SH}}} A_{i\mathrm{atom}}^{\mathrm{SH}}(\{\mathbf{x}^{\mathrm{NL}}\},\{\mathbf{x}^{\mathrm{LC}}\}) \tag{14}$$

where C_{SH} denotes the aggregate of atoms in handshaking region, and $A_{i\mathrm{atom}}^{\mathrm{SH}}$ is the free energy of the ith atom in the region.

In the handshaking region, some atoms are constrained by the nodes in local region. Hence, the coordinates of these atoms can be calculated by interpolating those of the nodes. And, some atoms are themselves nonlocal nodes. Therefore, the free energy in the handshaking region can be rewritten as a function of the coordinates of local and nonlocal nodes as:

$$A^{\mathrm{SH}}(\{\mathbf{X}^{\mathrm{LC}}\},\{\mathbf{X}^{\mathrm{NL}}\}) = \sum_{i=1}^{N_{\mathrm{node}}^{\mathrm{SH}}} A_i^{\mathrm{SH}}(\{\mathbf{X}^{\mathrm{NL}}\},\{\mathbf{X}^{\mathrm{LC}}\}) \tag{15}$$

where A_i^{SH} is the free energy of the ith node in the region. Notably, in Eq. (14), the summation is over all atoms in the region, while in Eq. (15), the summation is over all nodes in it. Hence, in these equations, the free energy are functions of coordinates of atoms and nodes, respectively. And, the A_i^{SH} in Eq. (15) can be expressed as

$$A_i^{\mathrm{SH}} = \Phi_i^{\mathrm{SH}} + 2kT\ln\frac{\hbar\mid D_i^{\mathrm{SH}}\mid^{1/4}}{kT} \tag{16}$$

where Φ_i^{SH} and D_i^{SH} are the potential energy and the determinant of the local dynamic matrix of the ith nonlocal node. Φ_i^{SH} and D_i^{SH} are both functions of the coordinates of its adjacent nodes in local and nonlocal regions.

Till now, we have established the HMCST method. The method, by treating atoms as oscillators and particles simultaneously, as well as clusters, comprises different spatial and temporal scales. In fact, in order to overcome the shortcomings of molecular dynamics, Tadmor et al. (1998), Shenoy et al. (1998, 1999) and Dupuy et al. (2005) reported the QC method for molecular simulation. The QC method is implemented via two main steps: kinematically by introducing representative atoms (repatoms) to reduce the number of degrees of freedom in regions where the atomic displacement is smooth; energetically by introducing the simplified simulation rule based on the so-called Cauchy-Born (CB) hypothesis and the concept of a potential of mean force (PMF) to approximately compute the total energy of the system. Although some equations of both methods are similar, they differ from each other in three aspects. Firstly, the starting point is the particle–oscillator duality of atoms in the HMCST method, while it is the concept of PMF in the QC method. Secondly, the local mean field approximation in HMCST and the Cauchy-Born (CB) hypothesis in QC method are employed to reduce the degrees of freedoms of the system, respectively. Thirdly, besides local and nonlocal regions, the handshaking regions in HMCST are treated separately, which leads to a more accurate energy function of the system and hence a reduction in ghost force.

3. Validation of MST, CST and HMCST methods

In this section, we will validate the formulas and schemes presented in the previous section, by comparing the results obtained using MST, CST, HMCST with conventional MD simulations. For a two-dimensional hexagonally packed lattice of Lennard-Jones particles, we implement a uniaxial quasi-static compressive loading at 300 K. As shown in Fig. 3, the compression direction is horizontal (x_1) with a fixed left end and the two vertical (x_2) boundaries are traction free for all simulations. The initial dimensions of the sample is 683 Å × 169 Å. The total of atoms is 20,549 and the number of fixed boundary atoms is 400. Figs. 4 and 5 show the cluster partition in CST and HMCST simulation, respectively. In the HMCST and CST simulations, the clusters are equilateral triangles with 12 atoms on each side. In all simulations, the right end of the sample moves 6.83×10^{-2} Å in each loading step.

We assume that the potential energy between two atoms with distance r_{ij} is $\varphi(r_{ij}) = 4\varepsilon_\mathrm{p}\left[\left(\frac{r_0}{r_{ij}}\right)^{12} - \left(\frac{r_0}{r_{ij}}\right)^{6}\right] - 4\varepsilon_\mathrm{p}\left[\left(\frac{r_0}{r_\mathrm{c}}\right)^{12} - \left(\frac{r_0}{r_\mathrm{c}}\right)^{6}\right]$, where the parameters $r_0 = 2.3276$ Å, $\varepsilon_\mathrm{p} = 0.4912$ev (Najafabadi and Srolovitz, 1995) and the truncated distance $r_\mathrm{c} = 5.4865$ Å. The mass of an atom is assumed to be

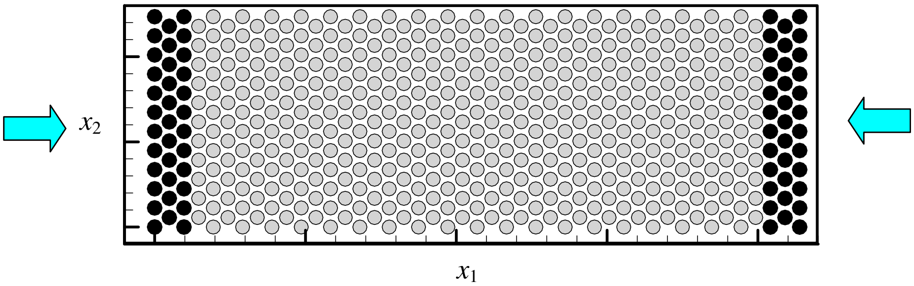

Fig. 3. Schematic of initial atomic configuration of a two-dimensional hexagonally packed lattice under uniaxial compression. The black circles represent boundary atoms in the compression direction (x_1). For all simulations, the boundary atoms on the right end move while those on the left are fixed, and the two vertical (x_2) boundaries are traction free.

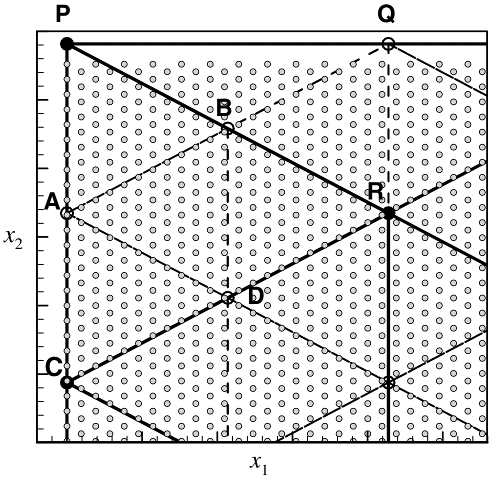

Fig. 4. Partition of clusters in CST simulation.

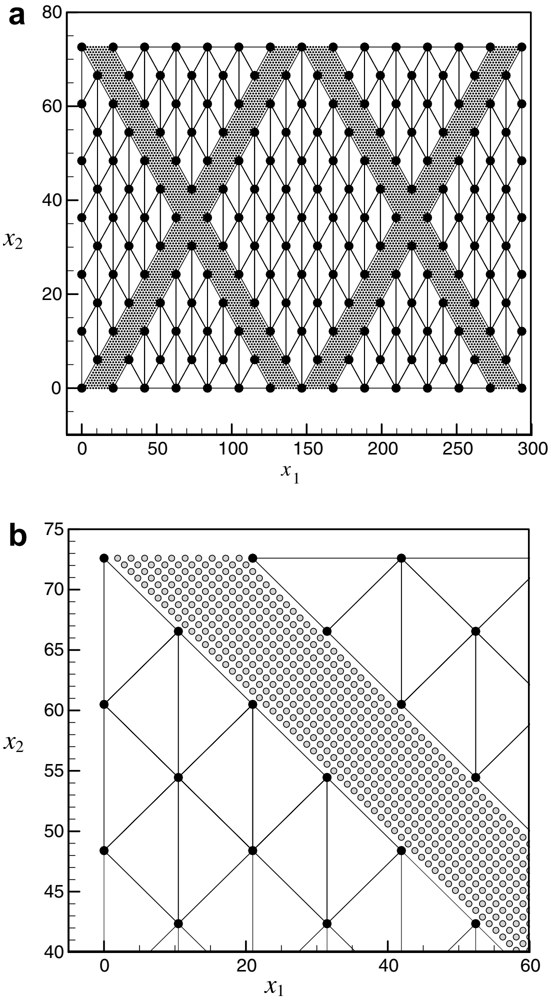

Fig. 5. Partition of local and nonlocal regions in the HMCST simulation of uniaxial compression of the lattice shown as Fig. 3. The black and grey circles are local and nonlocal nodes, respectively. The regions consisting of only nonlocal nodes or local nodes are correspondingly nonlocal or local regions, while those of both local and nonlocal nodes are handshaking regions. (a) Global view and (b) enlarged local view.

$m = 1.062 \times 10^{-25}$ kg and the Debye temperature is $\theta_D = 343$ K. In the simulations, all variables are nondimensionalized and normalized with r_0, m and θ_D.

For each loading step, MD computations was conducted over a relaxation time of about 40 ps with a time step of 2 fs using the standard Verlet algorithm (Leach, 1996). Fig. 6 shows the variation of the mean of the total potential energy during the relaxation process in the MD simulation. Obviously, the mean value reaches a constant after relaxation of about 20 ps. Therefore, the relaxation of 40 ps contains two parts: the first 20 ps are used to search the thermo-equilibrium state and the remainder for statistical calculation of time-average positions of atoms $\{\mathbf{x}_{eq}\}$.

In MST, CST and HMCST simulations, all the atoms reach their equilibrium positions at each loading state by minimizing the total Helmholtz free energy of the whole system with respect to the atoms or nodes positions using the conjugate gradient method (Press et al., 1992).

In order to facilitate the comparison of the results, we adopt the same stress definition, i.e. stress being the derivative of Helmholtz free energy with respect to the displacement of the moving boundary,

$$\sigma = -\frac{1}{L_{x2_0}} \frac{\partial A}{\partial L_{x1}} \tag{17}$$

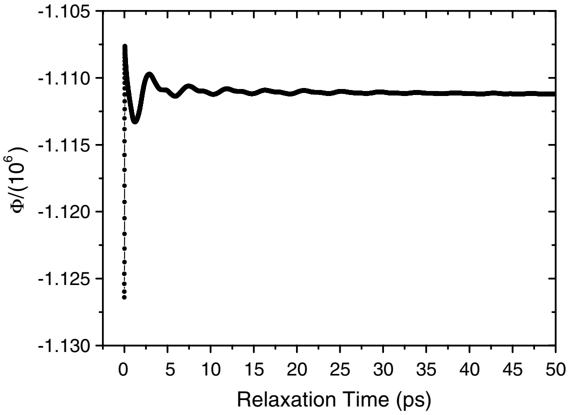

Fig. 6. Variation of the mean of the total potential energy during the relaxation process in MD simulation. The mean value reaches a constant after relaxation for about 20 ps.

where L_{x2_0} is the initial width in x_2 direction and L_{x1} is the length in x_1 direction.

Fig. 7 shows the stress–strain curves obtained from different simulations. Obviously, the initial phase of these curves almost coincide with each other, indicating that all these methods can accurately simulate elastic deformation at finite temperature.

More importantly, Fig. 7 shows that the yielding obtained from these methods varies. The CST method does not reproduce yielding at all, since yielding generally happens locally while CST method suppresses such local deformations. The yielding from MST and HMCST imulations are a little higher than that from MD. Perhaps, without random velocity, MST and HMCST methods most likely search for the solution in a potential well.

Interestingly, both MST and HMCST demonstrate the slipping of atoms along the most closely packed direction as MD does. Fig. 8 shows the atomic configurations from MST, HMCST and MD after their first slips, corresponding to points A, B and C in Fig. 7, respectively. The sparse atomic region is the slip zone and the slip direction makes an angle of 60 degrees with the x_1 axis, exactly the most closely packed direction for the lattice shown in Fig. 3. The slip zones predicted by MST and HMCST are symmetrical in both x_1 and x_2 directions, while MD loses the symmetry because of the effect of the random velocity.

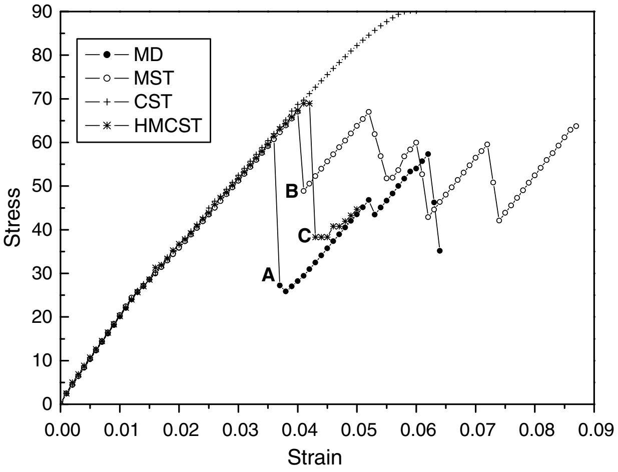

Fig. 7. Stress–strain curves obtained from MD (●), MST (○), CST (+) and HMCST (∗) simulations of the two-dimensional uniaxial compression at 300 K. The stress σ is calculated by $\sigma = -\frac{1}{L_{x2_0}}\frac{\partial A}{\partial L_{x1}}$. The unit of stress is $k\Theta/r_0^2$, where $\Theta = 343$ K is Debye temperature.

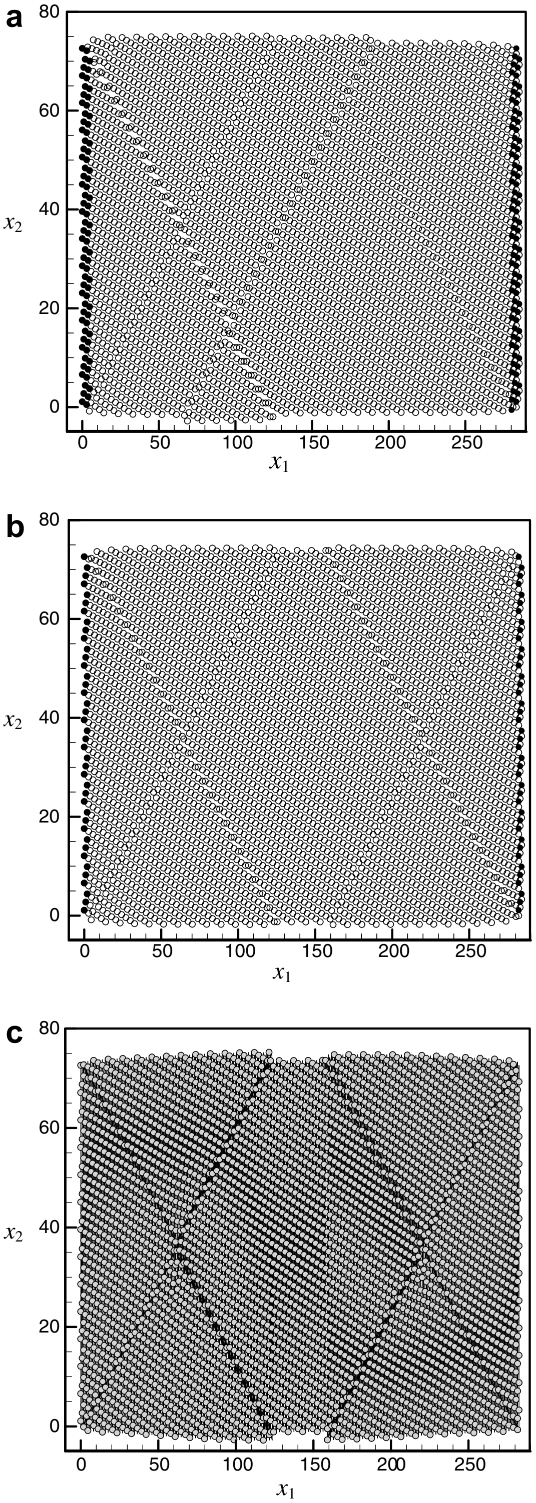

Fig. 8. Atomic configurations of MD (a), MST (b), and HCMST (c) simulations after the first slip, corresponding to point A, B, and C in Fig. 7, respectively.

One major pitfall of many multiscale methods is the spurious or "ghost" force in the handshaking regions. Generally, the existence of ghost force is a manifestation of the incompatibility between different physical descriptions at the interface. In the QC method, due to the inherent mismatch in the summation rules used in the local and nonlocal regions, the ghost force appears at the interface between the local region and nonlocal region, identified with nonphysical displacement of atoms near the interface (Shenoy et al., 1999). Will the HMCST scheme proposed in this paper generate ghost force? Fig. 9 shows the displacement in x_1 direction of atoms (or nodes) in the middle layer of the sample. Obviously, the atoms deform smoothly in both cluster and fully atomistic regions, especially the interface between the regions, which is physically accessible. Hence, the smoothness of deformation demonstrates that the ghost force can be avoided in the HMCST simulation. As a matter of fact, this smoothness may due to the unified formulation of Helmholtz free energy in the HMCST method.

The comparison between the results of MST, CST, HMCST and MD proves that MST and HMCST can accurately simulate the quasi-static deformation of materials, including plastic behavior. Besides, the efficiency of these methods is very encouraging. As Fig. 10 shows, with the same PC, the calculations for each loading state took about 0.1 min for CST, 10 min for MST and HMCST, but 120 min for MD. Thus compared with

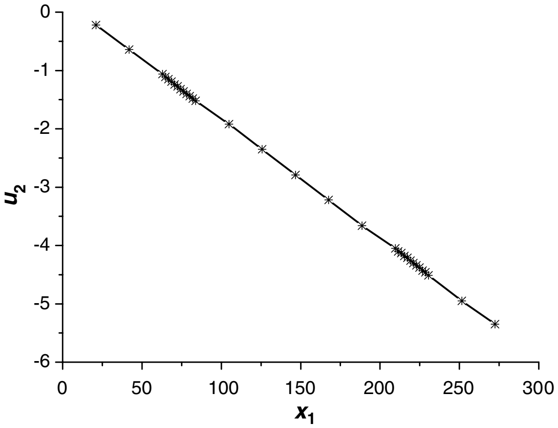

Fig. 9. Displacements of atoms (or nodes) in the middle layer of the sample. The atoms deform smoothly in both cluster and fully atomistic regions, as well as the interface between the regions, which demonstrates that the ghost force can be avoided in the HMCST simulation.

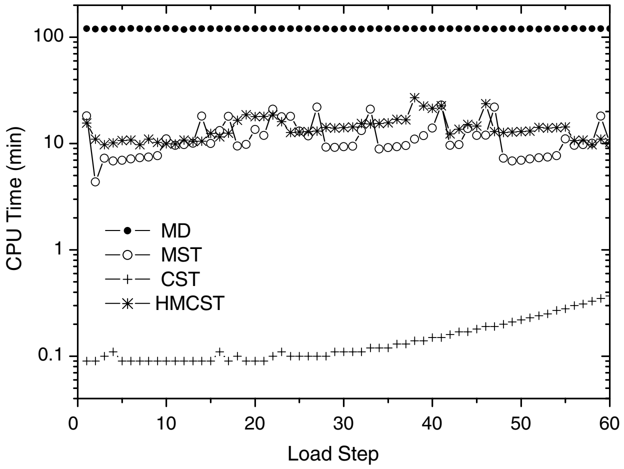

Fig. 10. CPU time consumed in the simulations of uniaxial quasi-static compression with MD (●), MST (○), CST (+) and HCMST (∗) method, respectively.

MD simulation, MST and HMCST are 12 times faster without sacrificing computational accuracy. For the case studied in this section, the efficiency of HMCST is not higher than MST because the system is too small and it takes a lot of computational resources to calculate the quantities in the handshaking region in HMCST scheme. For larger scale systems requiring huge storage, like nanoindentation shown in next section, the advantages of HMCST over MST will be much pronounced. The validation proves that the new methods are very efficient and promising approaches to numerical simulations of solid deformations under quasi-static loadings at finite temperature, based on molecular potentials.

4. Application of HMCST simulation to nanoindentation

Since the proposed HMCST method distinguishes uniform deformation from severe distortion, it can efficiently cope with larger scale system and long processes. To demonstrate the capability and efficiency of the HMCST method, in this section, we employ the method to simulate a more complex process, the quasi-static nanoindentation test, and compare the results with those from MD simulation.

Nanoindentation is a powerful tool to investigate nano- and micro-scale mechanical properties of materials and has been widely used in bio-, materials and mechanical engineering (Oliver and Pharr, 1992; Wang et al., 2002). Previous atomistic simulations of the process have mostly been limited to zero temperature, small system or short loading time (Dupuy et al., 2005; Kelchner et al., 1998; Li et al., 2002). The use of HMCST method is compelling for its high efficiency and accuracy, especially in future direct simulation of realistic experimental processes at finite temperature.

In the simulation, a single crystal of Cu with dimensions of 28.2 nm × 28.2 nm × 14.1 nm, containing 973,636 atoms, is indented by a spherical diamond tip with radius 2 nm at 300 K (Fig. 11). The top surface of the sample is (0 0 1) crystal plane and the other two side surface are (1 0 0) and (0 1 0) planes, respectively. The top surface is traction free, and the bottom layer and the side surfaces of the sample are fixed. In the HMCST simulation, the nonlocal region of the sample has a size of 19 nm × 19 nm × 9.4 nm, containing 275,834 atoms; and there are 380 clusters with 196 nodes in the rest of it (the clusters are tetrahedrons with 22 atoms on each side). Obviously, with the introduction of cluster, the degree of freedoms in the HMCST

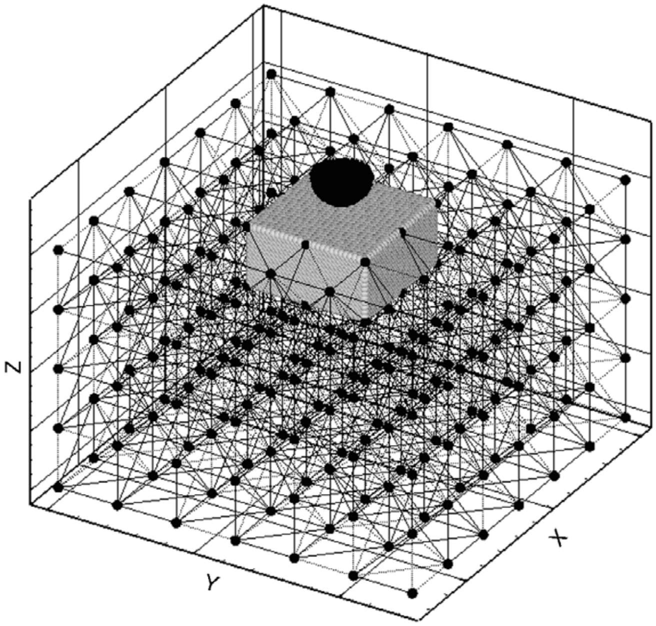

Fig. 11. Schematic diagram of the simulation set-up for indentation on the Cu(0 0 1) surface. The x axis is along a $\langle 1,0,0\rangle$ direction, the z axis is oriented in the $\langle 0,0,1\rangle$ direction, and y axis forms a right-hand coordinate system along a $\langle 0,1,0\rangle$ direction. Periodic boundaries are held in the x and y directions. The nodes in the bottom layer are fixed.

simulation is reduced by 72%. As a comparison, only 275,834 atoms, equivalent to those in the nonlocal region in HMCST simulation, is simulated with traditional MD method.

To simplify the comparison of different method, in both simulations, the potential for Cu–Cu atomic interaction was as the same as that used in the above compression case and for C–Cu interaction, the simple L–J potential $e_{\text{C–Cu}}(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$ is adopted with parameters $C_6 = 41.548$ eV Å^6, $C_{12} = 2989.1$ eV Å^{12} (Ellis et al., 2000). In each loading step, the indenter was lowered by 0.05 Å and the tip atoms were held fixed while the sample atoms were maintained at 300 K in both HMCST and MD simulation. In order to model the quasi-static process as far as possible, the MD simulation was conducted over 2 ps for equilibrium and 8 ps for statistical calculation, corresponding to a loading speed of 0.5 ms^{-1}.

The force vs. displacement curves of nanoindentation and retraction obtained from the two methods are shown in Fig. 12. In both simulations, the tip forces were calculated by directly adding all the interaction acting on the tip atoms along the indenting direction. The point where the tip-sample force transited from attractive to repulsive is chosen as the zero point of indented depth. As expected, the two curves coincides each other very well, verifying the algorithm of HMCST method.

Noticeably, the HMCST method clearly reproduces the evolution of dislocations in the process of indentation. In order to characterize the evolution of dislocation, the centrosymmetry parameter is employed. The centrosymmetry parameter is defined as (Kelchner et al., 1998)

$$P = \sum_{i=1}^{6} \mid \mathbf{R}_i + \mathbf{R}_{i+6} \mid^2 \tag{18}$$

where $\mathbf{R}_i$ and $\mathbf{R}_{i+6}$ are the vectors corresponding to the six pairs of opposite nearest neighbors in the fcc lattice. For reference, the centrosymmetry parameter takes the value of zero for an atom in the perfect Cu lattice, 4.8 (with dimension r_0^2) for a surface atom, 1.6 for a stacking faulte, and 0.4 for a partial dislocation.

The computed dislocation structures at the maximum depth are shown in Fig. 13. The atoms in Fig. 13 are colored according to the value of the centrosymmetry parameter, with grey for surfaces atoms with $P \geqslant 4.8$, white for stacking faults with $1.6 \leqslant P \leqslant 4.8$), and black for partial dislocations($0.4 \leqslant P \leqslant 1.6$). As expected, slip occurs predominantly on (1 1 1) planes, the dominant slip planes in fcc crystals. This is in good agreement with earlier results (Liang et al., 2003). In particular, slip is observed on four sets of (1 1 1) slip planes and terminates at the (0 0 1) surface. The maximum depth the slips can reach increases during the indentation and decreases during the retraction. In addition, after the sample is unloaded, there exist significant residual slips in the sample, representing the permanent plastic deformation produced by indentation, as Fig. 14 shows.

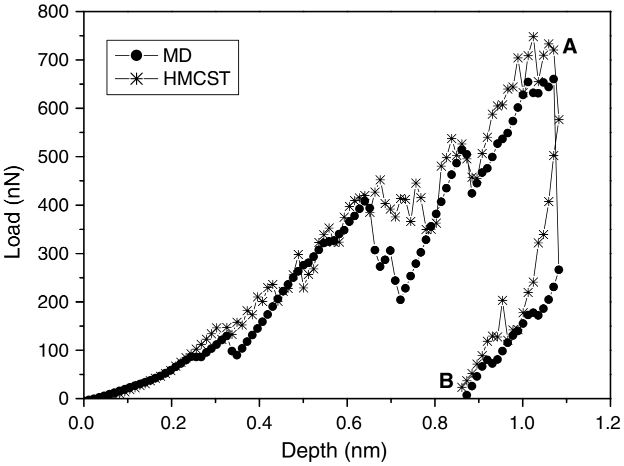

Fig. 12. The force vs. displacement curves for Cu(0 0 1) during indentation and retraction obtained by HMCST (∗) and MD (●), respectively.

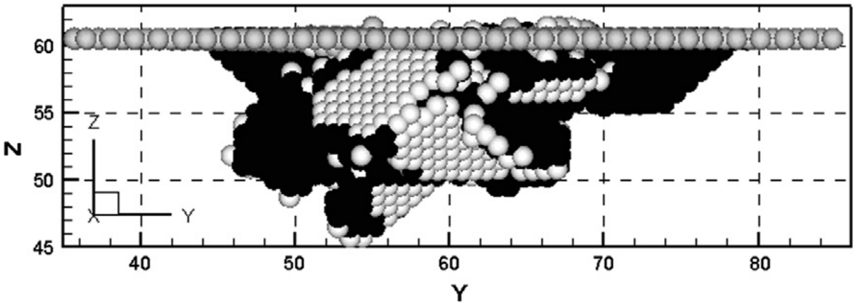

Fig. 13. Dislocation structure at the maximum indentation depth (about 1 nm, corresponding to point A in Fig. 12), from HMCST simulation. The colors indicate defect types as follows: grey for surface atoms ($P \geqslant 4.8$), white for stacking faults ($1.6 \leqslant P \leqslant 4.8$), and black for partial dislocations ($0.4 \leqslant P \leqslant 1.6$). Only atoms with $P \geqslant 0.4$ are shown.

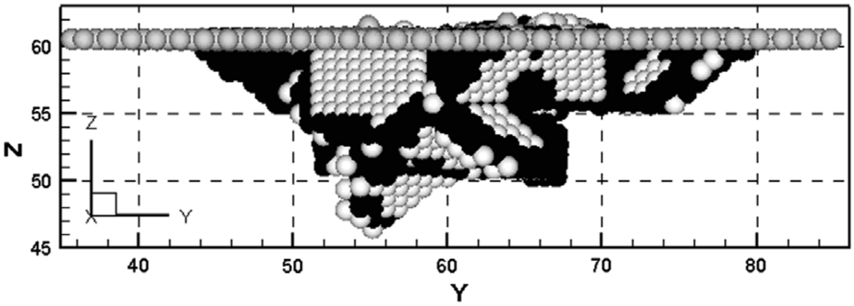

Fig. 14. Dislocation structure after unloading (corresponding to point B in Fig. 12), from HMCST simulation. The color scale is the same as Fig. 13.

More importantly, let us compare the computation time for the nanoindentation case by HMCST and MD methods. All the calculations for the nanoindentation were performed on the parallel computing resources LSSC-II of the State Key Laboratory of Scientific and Engineering Computing, Chinese Academy of Sciences. The calculations for each loading step took about 130 min for HMCST but 1300 min for MD. Considering that the scale of HMCST simulation is three times larger than MD, this example clearly demonstrates that the efficiency of HMCST is much higher than that of MD simulation without sacrificing computational accuracy, and HMCST appears to be a potential resource for simulations of practical larger systems.

5. Summary

The rapid evolution of nanotechnology necessitates novel, sophisticated, and physically based approaches to bridge the gaps between different length and time scales. In this paper, we propose a group of statistical thermodynamics methods to simulate quasi-static deformation at finite temperature, that is, molecular statistical thermodynamics (MST) method, cluster statistical thermodynamics (CST) method, and the hybrid molecular/cluster statistical thermodynamics (HMCST) method. These multiscale methods bridge different length scales with the introduction of clusters, and link different temporal scales by treating atoms as oscillators and particles simultaneously. One attractive feature of these methods is their “seamlessness” or consistency, in which the same underlying atomistic model is used in the energy calculation in both the cluster and fully atomistic regions, regardless of additional constitutive relations, and hence avoid the ghost force in the simulation. In addition, compared with conventional MD simulations, their high computational efficiency appears to be very desirable. The simulations of uniaxial compression and nanoindentation prove that the MST and HMCST methods are very promising approaches for the simulations of quasi-static deformation at finite temperature, based on inter-atomic potentials.

Acknowledgements

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