Computer Simulation Study of Mechanical Properties of Nanoscale Materials by Molecular Dynamics and Lattice Green's Function Methods

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ABSTRACT

The mechanical properties of nanoscale materials are studied using the molecular dynamics and lattice Green's function methods. The initial atomic structures of the dislocations and cracks are determined both from the elastic solutions as well as from those by lattice Green's function method for the infinite systems. Firstly, we calculate the Green function for the defective lattice, with dislocation and crack, by solving the Dyson equation, appropriate for absolute zero temperature. The thermal expansion and the temperature dependence of the interatomic force constants are determined by using the statistical moment method and they are taken into account in the lattice Green's functions. The strength and fracture properties are then investigated for the nanocrystalline materials like semiconductor quantum wire and carbon related materials like graphenes and nanotubes. The O(N) tight-binding molecular dynamics (TBMD) method is used to analyze the reconstruction of atomic bonding near the crack tip as well as the cleaved surface. We compare the mechanical properties of nanoscale materials with those of corresponding bulk-size materials.

keywords: molecular dynamics method, O(N) TBMD, lattice Green's function method, nanoscale materials, fracture behavior

1. INTRODUCTION

Fracture behaviors of materials depend sensitively on the temperature as well as the microscopic materials parameters, like elastic constants, surface tension, and interatomic force laws at the cohesive region near the crack tip [1-3]. Recently, there has been a great interest in the study of fracture of brittle materials such as semiconductors and ceramic materials [3-5]. One of the reasons is the engineering need to improve the fracture toughness of the ceramic materials. Furthermore, in these materials the plastic deformation associated with crack extension is effectively absent and does not play a significant role.

It is the purpose of the present paper to investigate the crack extension process of nanoscale materials with the use of the atomistic theoretical scheme, with particular emphasis on their size and temperature dependence. There exists at present two basic models for the atomistic calculation of the crack properties. The model more widely used employs a molecular dynamics approach [5,6]. The possible problems arising from this model are that (i) it tends to predict atomic configurations of local energy minimum condition and (ii) it uses the artificial imposition of an elastic continuum displacement field at a fixed distance from the defect (crack) center. An alternative model based on the lattice statistics approach has been used less extensively. This method was developed by Matsubara and Kanzaki [7,8]. It has been applied to cracks by Thomson *et al*. [9], Esterling [10] and Thomson and coworkers [11-14]. The difficulty in applying this approach to crack calculation is the introduction of an anharmonic region wherein the atoms must be treated by taking the details of the interatomic chemical bonding into consideration.

In the present paper , we shall use the lattice Green's function method taking into account the temperature dependences of lattice spacing and the resulting changes in the interatomic force constants. The full atomic relaxation calculations have been performed by using the O(N) tight-binding molecular dynamics (TBMD) methods. We shall show that the essential fracture behavior of the nanoscale materials can be analyzed within the framework of the present atomistic and electronic theories.

2. PRINCIPLE OF CALCULATIONS

2.1 Cracked-lattice Green's function

We introduce a crack in the lattice, where the atomic bonding between the atom pair facing one another across the cleavage plane is annihilated. Then the force constant matrix Φ^* of the cracked lattice is obtained from that of the perfect crystal by introducing the force terms on the cleavage surface that annihilate the bonds there. Thus Φ^* can be written formally as [11-14]

$$\Phi^* = \Phi - \delta\,\Phi, \qquad (1a)$$

$$\delta\Phi = [\Phi]_{\text{crack faces}}. \qquad (1b)$$

The formal solution of the problem is given by the Dyson equation [11]

$$\mathbf{G}^* = \mathbf{G} + \mathbf{G}\delta\Phi\mathbf{G}^*, \qquad (2)$$

together with the "master equation" $\boldsymbol{u}=\mathbf{G}^*\boldsymbol{F}$ for the Green's function, where $\boldsymbol{u}$ and $\boldsymbol{F}$ represent the displacement and external force vectors, respectively.

More precisely, the lattice Green's functions are defined as the inverse of the force constant operator Φ^* defined by the equations of equilibrium for the lattice:

$$\sum_{l'}\Phi^*(l,l')\boldsymbol{u}(l') = \boldsymbol{F}(l) \qquad (3)$$

and

$$\mathbf{G}^*(l,l') = [\Phi^*(l,l')]^{-1}. \qquad (4)$$

The constant elements in the tensor Φ are just the spring constants connecting a reference atom at position l to its neighbors l'. In deriving the cracked-lattice Green's function, our starting point is always the perfect-lattice Green's function. We use quantities with asterisks to denote the cracked lattice and quantities without asterisks to denote the perfect lattice as in the above eqs.(1) and (2). Because of the translational symmetry of the perfect lattice, $\Phi(l,l')=\Phi(l-l')$, Φ becomes a function of only one lattice variable $\mathbf{l}-\mathbf{l'}$, the position relative to a reference atom. Thus in the Fourier representation the transform of the force constant matrix of cubic crystal is given as

$$\Phi(l-l') = \frac{1}{8\pi^3}\int\int_{-\pi}^{\pi}\int\phi(\boldsymbol{q})\exp\{i\boldsymbol{q}\cdot(l-l')\}d^3\boldsymbol{q} \qquad (5)$$

and

$$\Phi(l-l') = \sum_{l'}\phi(l-l')\exp\{-iq\cdot(l-l')\}. \qquad (6)$$

In the above eqn. (6) the sum is over the neighbors of the reference atom $\boldsymbol{l}$. It is therefore a finite sum over the neighbor shell of the reference atom and can be written in a straightforward manner. Thus the Green's function for the perfect lattice is also obtained in Fourier space;

$$\mathbf{G}(\boldsymbol{q}) = \phi^{-1}(\boldsymbol{q}). \qquad (7)$$

In this equation, Φ is a tensor quantity which can be written as a matrix by proper numbering of its elements, and the inverse is the inverse of the matrix.

We use the constraint that the sum of all the forces acting on each atom must vanish, *i.e.* from eqn.(3)

$$F + f + \Phi^*u = 0. \qquad (8)$$

Here f denote forces which are exerted by atoms whose bonds have been stretched into their non-linear regimes. The atomic displacements $\mathbf{u}$ are given by solutions of the coupled equation

$$u = G^*F + G^*f\{u\}. \qquad (9)$$

After the appropriate Green functions have been determined, the relaxation problem for the reconstituted bonds in the cohesive zone, eqn. (9) above, is solved with force laws appropriate to the problem. The force laws used in the present calculations are obtained by TB electronic theory.

The calculated atomistic results of the fracture properties of the nanoscale materials are compared with those of the elasticity criterion [15,16]. The results of the present atomistic simulations are given in terms of stress intensity factors.

2.2 Treatment at finite temperature

The present theory includes the temperature effects on the crack extension events by explicitly taking into account the changes in the lattice spacing and interatomic force constants, which are important ingredients in the lattice Green' function approach. To derive the temperature dependent lattice constants and interatomic force constants, we use the moment method in the statistical mechanics [17,18]. This method allows us to take into account explicitly the anharmonicity effects of lattice vibration within the fourth order moment approximation.

2.3 O(N) TBMD method

For performing the molecular dynamics simulations, we use the total energy calculation procedure based on the TB electronic theory. The total energy of the system is assumed to be given by a sum of two terms [19,20]:

$$U = U_{el} + U_{rep} = \sum_{k}\varepsilon_k + (1/2)\sum_{ij}\phi(r_{ij}), \qquad (13)$$

where U_{el} is the band structure energies ε_k for the occupied states, and U_{rep} represents the remaining repulsive energy contribution. Here r_{ij} is the separation of atoms i and j. The repulsive potential $\phi(r)$ is taken to be short ranged and varies exponentially with the interatomic distance. For treating the nanoscale semiconductor crystallites, we will use the minimal parameter generalized tight-binding molecular dynamics (GTBMD) scheme of non-orthogonal basis [19,20]. For the GTB scheme, the characteristic equation to be solved is written in matrix form as

$$(\mathbf{H}-E_n\mathbf{S})C^n=0, \qquad (14)$$

where **H** and **S** are the Hamiltonian and overlap matrixes, respectively. C^n is the column vector of LCAO coefficients.

For treating the large-scale systems containing atoms more than 1,000 atoms, we will use the nonorthogonal density matrix (DM) scheme [21]. The DM in a nonorthogonal basis is introduced by defining the two quantities

$$\overline{X} = S^{-1}\overline{X}S^{-1}, \; \overline{\rho} = 3\overline{X}S\overline{X} - 2\overline{X}S\overline{X}S\overline{X} , \qquad (15)$$

as alternative representation for the trial and physical DM, respectively. In terms of $\overline{X}$ and $\overline{\rho}$ the energy functional is written as

$$\Omega = tr[(3\overline{X}S\overline{X} - 2\overline{X}S\overline{X}S\overline{X})H'] . \qquad (16)$$

In order to achieve linear scaling, a cutoff radius (R_c) is postulated beyond which all elements of the trial density matrix are set to zero. This leads to a sparse density matrix.

3. RESULTS AND DISCUSSIONS

Firstly, we calculate the atomistic structures and strength properties of the carbon nanowires, which are cut in a shape of "belt", the small nanographite ribbon, from graphene sheets. The carbon nanowires without containing defects show the sufficient elongation, i.e., "superplasticity" associated with the structural phase transformation like the Peierls transition of one-dimensional (1D) system. In contrast, the carbon nanowires including surface defects like cracks show very brittle fracture.

The tensile tests are also performed for larger quasi-1D systems of $(Si_m)_n$ and $(C_m)_n$, m=6,24, ...For instance, the structure of $(Si_6)_n$ is composed of six-memberd Si rings, while those of $(C_{24})_n$ are the large structures composed of 7 six-membered rings. Under the tensile stress, this type of nanowire exhibits the non-uniform deformation, and certain necking occurs near the center region of the nanowire. The appearance and location of the necking depends sensitively on the size of the wire, and we have found the necking occurs near the edge of wires and cracking in the central region. In general, this type of nanowire fails at the notch tip when it has been stretched by about a few percents. The imposed strain rate was set to zero at the onset of crack motion. As in the case of $(Si_6)_n$ nanowires, the $(C_{24})_n$ nanographites do not show the uniform deformation. Even when the crack-like surface defects are absent in the initial structure, the cleavage fracture occurs from the certain surface sites between the two graphene layers.

We have also studied cracks and dislocation in carbon nanotube (CNT) and extended graphene sheets. The core structure of the c-axis edge dislocation is characterized by the five- and seven-membered rings in the 2D graphene sheets. The core structure of the pair of the edge dislocations is also characterized by a pair of pentagon-heptagons. We have found that the pair of edge dislocations are most stable in the configuration of "nearest-neighbour position", and excess energies of the dislocations are further reduced for this configuration. We have found that there are no marked differences in the stability between the small size graphenes with and without edge dislocations. This indicates that the self-energy of the edge dislocation is very small and may become even negative for the certain clusters. Here, it is noted that the quite high energy barriers, 5.4eV for the related Stone-Wales transformation in C_{60} (which have closed surface) and 10.4eV barrier for bond rotation in flat graphite, are reported in the literature. Then, we come to the conclusion that the dislocation can be generated spontaneously without sizeable activation energy in the small semiconductor clusters.

We now describe the results of the nanoplasticity, uniaxial compression tests, of single wall CNT [19]. The axial compression of a CNT is achieved by keeping the edge atoms of the tube transparent to the forces generated in the GTBMD method. The positions of the edge atoms are moved axially inward at a fixed rate to compress the nanotube. As external stress is applied to nanotubes, initial linear elastic deformations are observed up to a certain critical strain beyond which nonlinear responses set in. In the nonlinear response regime, locally deformed structures such as pinches, kinks, and buckles have been observed [19]. Under the compressive stress, the nanotube exhibits the drastic change of the bonding geometry, from a graphite (sp^2) to a localized diamond like (sp^3) reconstruction, at the critical stress ($\approx$ 153GPa). In a recent experiment, large compressive strains were applied to CNT dispersed in composite polymeric films. It has been observed that there are two distinct deformation modes, sideways buckling of thick tubes and collapse/fracture of thin tubes without any buckling. The compressive strain in the experiment is estimated to be larger than 5%, and critical stress for inward collapse or fracture is expected to be 100-150GPa for thin tubes. Furthermore, it is worth noting that the simulations by the GTBMD method are significantly different from the previously reported results. For instance, the classical MD simulations employing Tersoff-Brenner potential [26] for the nanotube never plastically deform, even at larger compression. Classical molecular dynamics (MD) simulations, performed for single and multiwalled CNT under tensile and compressive stresses show them to be elastic.

We have also investigated the plasticity of the single-wall carbon nanotube containing dislocations. Upon the tensile test, the CNT containing edge dislocation shows a stepwise change of diameter near the core of the dislocations. We have found that the CNT containing the edge dislocation exhibits the critical stress far below (~80Gpa) than that (153Gpa) of the CNT without dislocation. The c-axis edge dislocation provides the efficient center for stress concentration and gives rise to the failure of the CNT. The details of the plastic flow and failure depend on the symmetry of CNT and will be presented elsewhere.

We have also studied the crack properties of the extended graphene sheets. It has been found that the temperature

dependence of the force constants in the lattice is larger than that of the unstable stacking energy. We have found that the lattice trapping and stress intensity factors for dislocation emission K_{IIe} depend sensitively on the temperature T, and they are decreasing function of T (for bulk-size materials). The important factor for controlling the dislocation emission is the temperature dependent unstable stacking energy, in agreement with the results of the absolute zero temperature [9].

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