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Molecular Dynamics Simulation of Coarse-Grain Model of Silicon Functionalized Graphene

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Abstract. The electronic transport, the storage capacity and the service life of the anode material for lithium ion batteries will be reduced seriously in the event of the material layering or cracking, so the anode material must have strong mechanical reliability. Firstly, in view of the traditional molecular dynamics (MD) limited by the geometric scales of the model of Silicon functionalized graphenen (SFG) as lithium ion batteries anode material, some full atomic models of SFG were established using Tersoff potential and Lennard-Jones potential, and used to calculate the modulus and the adhesion properties. What's more, the assertion of mechanical equilibrium condition and energy conservation between full atomic and coarse-grain models through elastic strain energy were enforced to arrive at model parameters. The model of SFG coarse-grain bead-spring elements and its system energy function were obtained via full atomic simulations. Finally, the validity of the SFG coarse-grain model was verified by comparing the tensile property of coarse-grain model with full atoms model.

1 Introduction

SFG [1] is an anode material for lithium ion batteries, which was prepared via ultrasonication by American scientist Zhao and his team in 2011. It was found that the configuration of SFG could accommodate large volume variations effectively during charge/discharge cycle, meanwhile it also increase and enhance the anode metarial reversible capacity, the cycle life and charge/discharge rates. The focal point of this paper is to establish a multi-scale coarse-grain model that can replicate the mechanical behavior of SFG. In the paper, a series of full atoms models of SFG were established to calculate the mechanical test cases such as tensile, shear and adsorption via classical molecular dynamics (MD). The assertion of energy conservation between full atomic and coarse-grain models was enforced in the paper to arrive at model parameters needed. The MD simulations are performed using the code large-scale atomic molecular massively parallel simulator (LAMMPS) [2].

2 The full atomic model of SFG and its mechanical properties

A series of full atomic models of SFG was established using Tersoff [3] potential given by

$$E = \frac{1}{2}\sum_i \sum_{i \neq j} V_{ij} , \tag{1}$$

$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + f_{ij} f_A(r_{ij})], \tag{2}$$

$$f_C(r_{ij}) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2}\sin(\frac{\pi}{2}\frac{r-D}{D}) & \text{R - D} < r < R + D \\ 0 & r > R + D, \end{cases} \tag{3}$$

$$f_R(r_{ij}) = A\exp(-\lambda_1 r) , \tag{4}$$

$$f_A(r_{ij}) = -B\exp(-\lambda_2 r) , \tag{5}$$

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}} , \tag{6}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk} \exp[\lambda_3^m (r_{ij} - r_{ik})]) , \tag{7}$$

$$g(\theta) = \gamma_{ijk}(1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (\cos\theta - \cos\theta_0)^2]}) . \tag{8}$$

and Lennard-Jones [4]potential given by

$$V(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] , \tag{9}$$

with σ as the distance parameter and ε describing the energy well depth at equilibrium. The velocity Verlet

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time stepping algorithm [5], a style of time integrator used in the present molecular dynamics simulations, are given as:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + a(t)\Delta t^2/2, \quad (10)$$

$$v(t+\Delta t/2) = v(t) + a(t)\Delta t/2, \quad (11)$$

$$a(t+\Delta t) = -\Delta E(r(t+\Delta t))/m, \quad (12)$$

$$v(t+\Delta t) = v(t+\Delta t/2) + a(t+\Delta t)\Delta t/2. \quad (13)$$

The simulation test suite includes 4 cases: (1) Uniaxial tensile loading to calculate and determine the Young's modulus E; (2) Shear loading to calculate and determine the shear modulus G; (3) An relaxation of two graphene sheets to calculate and determine the graphene's surface adhesion energy $E_{C\text{-}C}$; (4) An relaxation of silicon functionalized monolayer graphene to calculate and determine the silicon nanopartical and graphene sheet surface adhesion energy $E_{Si\text{-}C}$. The box of full atomic garaphene model in our simulation was a block with a side length of 100Å and 100Å along the x-axis and y-axis, and contained 3854 carbon atoms. The mechanical properties of tensile and shear loading for graphene was shown in Fig. 1 and Fig. 2. As can be seen from Fig. 1 that at the early stage of a tensile and shear loading silulation showed obvious linear relationship between stress and strain, linear fit to small strain to derive Young's modulus, E≈1.04 TPa, and shear molulus, G≈212.85GPa. The results show good agreement with previous investigations [5].

To obtain the weak interaction energy between graphene sheets, between monolayer graphene and silicon nano-particle, models of monolayer graphene sheet (100Å×100Å) , bilayer graphene sheet, a silicon nano-particle with diameter of 20 Å, monolayer silicon functionalized graphene with only a silicon partile were all relaxed on the NVT ensemble and the minimum potential energy of each system inclined to a constant, as shown in Fig. 3 and Fig. 4. Minimum potential energy of monolayer graphene expanded to 2 times is -56276eV, which minus the minimum potential energy of bilayer graphene -27880eV is 516eV. We can get the unit area adoption energy of $E_{C\text{-}C}$=-413.3 mJm-2 for monolayer graphene sheet. Similarly, the unit area adoption energy of silicon particle and graphene sheet is $E_{Si\text{-}C}$=-42.72eV. all the parameters about the full atomic models were determined and are listed in Tab. 1 and Tab. 2.

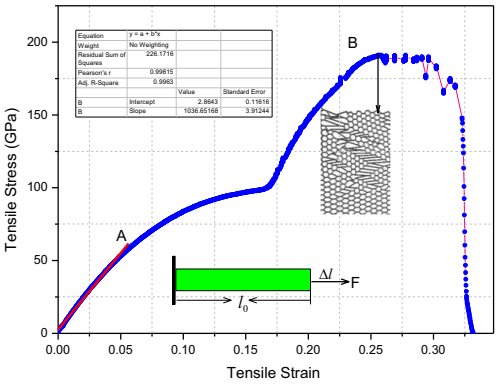

Figure 1. The tensile curves of graphene full atomic model

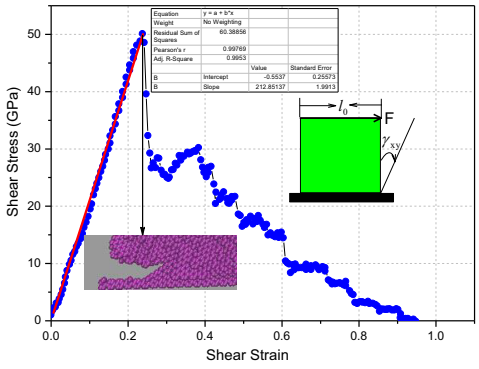

Figure 2. The shear curves of graphene full atomic model

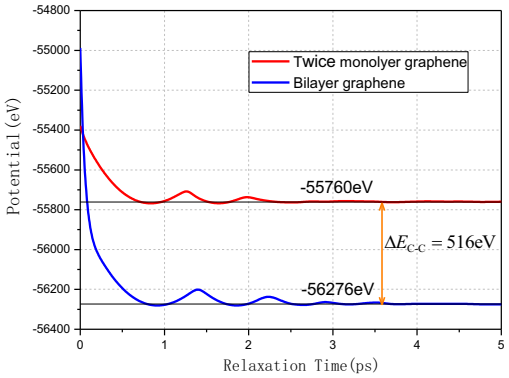

Figure 3. The adsorption energy of graphene sheets

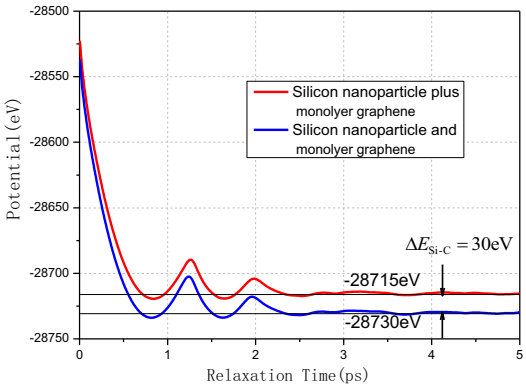

Figure 4. The adsorption energy of SFG

3 The coarse-grain model of SFG

The Lennard-Jones potential is used to simulate. σ_{C-C} and ε_{C-C} denote collision diameter between carbon particles and well depth of carbon particles interaction respectively, Correspondingly, σ_{Si-C} and ε_{Si-C} denote collision diameter between carbon and silicon particles and well depth of carbon and silicon particles interaction respectively. The mass of each carbon particle is determined from the mass distribution of graphene sheet

and depend on the unit area mass of graphene. The mass of each silicon coarse-grain equals to the mass silicon nano-particle. For the monolayer garphene sheet with two with side length of 100 Å contains 3854 carbon atoms, so the carbon coarse-grain particle mass is 2892.90875 gmol-1 which equal to the all mass of graphene sheent with area of 25Å×25Å. The silicon coarse-grain particle mass equals to 5926.146 $gmol^{-1}$. The value is the all mass of a silicon nano-particle with 211 silicon atoms. Monolayer graphene coarse-grain model was establish us LAMMPS code and was shown in Fig.3. Schematic diagram of the graphene coarse-grain was shown in Fig. 4 (a). (b) is shown the partial Magnification of the model. (c) is the Scale comparison between graphene coarse-grain model and full atomic model. The simulation box contains 341 particles which is just 0.47% of the atoms' number of the full atomic model with the same size box.

In order to verify the effectiveness of the graphene coarse-grain model, the tensile simulation was performed along the model length. The spring scaling energy was used to denote the bond energy between two carbon particles and the L-J potential was used to simulate the no-bonding atoms interaction in the simulation. The model is then subject to equilibration at 10K for 0.1 ns and minimization with time-step of 1fs. The simulation was subject to a microcanonical (NVE) ensemble, carried out at a low temperature of 10K to prevent large thermal vibrations. Temperature control was achieved using a Berendsen thermostat [6]. The tensile stress-strain curve was shown in Fig. 6. Obvious linear relationship was fitted to gain the Young modulus $E \approx 981.5GPa$ which shown good agreement with previous investigations.

Table 1. Parameters of full atomic models

Parameter	Value	Units
Young's modulus, E	1.04	TPa
Maximum stress, σ_{max}	189.94	GPa
Ultimate strain, ε_{ult}	29	%
Shear modulus, G	212.85	GPa
Maximum Shear Stress, τ_{max}	50.11	GPa
Ultimate shear strain, γ_{ult}	0.24	rad
surface adsorption, $E_{C\text{-}C}$	413.3	mJm-2
surface adsorption, $E_{Si\text{-}C}$	42.72	mJm-2

Table 2. Parameters used in coarse-grained molecular dynamics simulation

Parameter	Value	Units
Molar mass of carbon coarse-grain particle , mC	2892.909	gmol-1
Molar mass of silicon coarse-grain particle, mSi	5926.146	gmol-1
Bond balance distance of carbon particles, r0	25	Á
Bond balance angle of carbon particles, φ_0	900	\
Tensile elastic constant, kT	21.748	eV Á-2
Shear elastic constant, k_φ	695.439	eVrad-2
Collision diameter between carbon particles, σ_{C-C}	16.0273	Á
Well depth of carbon particles interaction, ε_{C-C}	3.8834	eV
Collision diameter between carbon and silicon particles, σ_{Si-C}	19.4929	Á
Well depth of carbon and silicon particles interaction, ε_{Si-C}	0.3843	eV

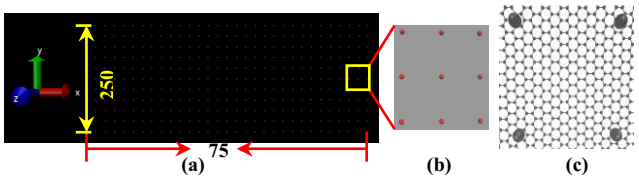

Figure 5. The coarse-grain model of grapheme

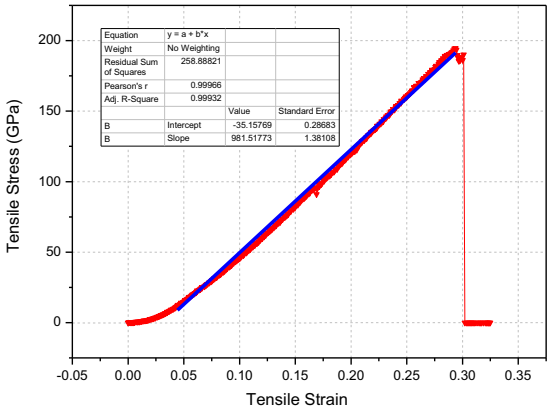

Figure 6. Tensile stress-strain curves of the coarse-grain model of graphene

4 Conclusions

The tensile properties of graphene established using coarse-grain bead-spring model was studied using molecular dynamics simulation with the Tersoff potential, the Lennard–Jones potential and the velocity Verlet time-stepping algorithm. The tensile result showed that the Young's modulus *E*=981.5Gpa was good agreement with the result of the graphene full atomic model.

Acknowledgements

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