Preparation of long monatomic carbon chains: Molecular dynamics studies

Yin Wang, Xi-Jing Ning,* Zheng-Zhe Lin, and Peng Li
Institute of Modern Physics, Fudan University, Shanghai 200433, China
and Key Laboratory of Applied Ion Beam Physics, Ministry of Education, China

Jun Zhuang
Department of Optic Science and Engineering, Fudan University, Shanghai 200433, China
(Received 27 June 2007; revised manuscript received 10 September 2007; published 18 October 2007)

Molecular dynamics simulations based on the Brenner potential, a tight-binding method, and the Car-Parrinello algorithm were performed to explore the conditions for pulling out long monatomic chains from a graphite layer. The results show that the method of pulling, the ambient temperature, and the pulling speed are important factors. The simulations indicate that free monatomic carbon chains with macro length can be obtained at about 1000 K if the pulling speed is much lower than 30 m/s.

DOI: 10.1103/PhysRevB.76.165423 PACS number(s): 71.15.Pd, 36.20.Fz, 31.15.Qg

I. INTRODUCTION

Preparation of free monatomic chains with macro length (FMCMLs) is of great importance for both scientific and technical research. Calculations of condensed material properties based on first principles, as is well known, have to take various approximations to many-body problems, and thus it is highly desirable to judge experimentally which approximate algorithms are more reliable. FMCMLs are ideal models for such studies because they have high symmetry, and the boundary effects at the ends become unimportant for both theoretical treatments and experimental measurements. For example, the interaction potential obtained theoretically for atoms in an atomic chain can be examined by simply measuring the force acting on the ends of the chain. Moreover, such long chains can be expected to show quantum features and may be used to weave bulk materials with desired structures.

Although single atoms can be controlled by modern microprobe techniques to form desired patterns on surfaces, it is still difficult to prepare FMCMLs up to date. An acetylenic compound with a chain of tens of carbon atoms was synthesized in 1995,[1] followed by similar compounds produced by different chemical methods.[2,3] After a single atomic chain of several carbon atoms was pulled out at the end of a carbon nanotube,[4] a free monatomic gold chain of several atoms was obtained in 1998 by pulling Au atoms on Cu substrates.[5,6] These discoveries led to a series of theoretical and experimental investigations on monatomic chains[7–12] although chains are not yet available experimentally for other elements.

In recent classical molecular dynamics (MD) simulations aimed at studying the mechanical properties of C_{60} dimers,[13] we surprisingly obtained a long monatomic chain when several atoms at each end of the dimer were pulled in opposite directions at speeds slower than 200 m/s. This result together with the MD simulations of stretching carbon nanotubes by Yakobson *et al.*[14] gives us a hint to pull out free monatomic chains from single graphite layers with macro sizes; these can be controlled more easily than nanotubes and clusters, and may contain enough atoms to form macro length chains. In this paper the feasibility of obtaining FMCMLs of carbon atoms is explored by MD simulations based on the Brenner potential, a tight-binding method, and the Car-Parrinello algorithm.

II. CLASSICAL MD SIMULATIONS

In our classical MD model with the Brenner potential,[15] a rectangular graphite layer with its left side fixed was allowed to relax at an initial temperature T_i first, and then the right side was pulled away from the fixed side, during which the motion of the atoms was integrated by the standard Verlet method with a fixed time step of 0.2 fs. Considering a realistic experimental system, where the fixed side of a graphite layer is assumed to be in contact with a macro object at temperature T_i, we used a thermal bath in our dynamical model, i.e., one atom was randomly selected from the three columns (columns 2 to 4 from the left side) next to the fixed side every 1 fs and was reset to a new velocity v_i^{new} instead of its old velocity v_i^{old} by the equation[16]

$$v_i^{new} = (1-\theta)^{1/2} v_i^{old} + \theta^{1/2} v_i^T(\xi), \tag{1}$$

where $v_i^T(\xi)$ is a velocity selected randomly from the Maxwell velocity distribution at T_i, while the value of θ was adjusted to be 0.5 to make the temperature of the next three columns (columns 5 to 7 from the left side) stay at T_i.

Our simulations show that the method of pulling, the pulling speed, and the temperature are important factors for the pulling processes. When we pulled all the atoms of the right side, the graphite layer first got longer and then ruptured as the pulling proceeded, which can be illustrated via the example shown in Fig. 1(a). However, when the pulling started from the corner of the right side under the same conditions, a monatomic chain was formed with the atoms coming off the graphite layer one by one, just like unraveling a knitted scarf [Fig. 1(b)]. Many simulations performed in different conditions give the same conclusion. So five atoms at a corner of the right side were pulled in the subsequent classical MD simulations.

For testing the effects of speed, five atoms at the right corner of a layer of 16×25 atoms were pulled with different

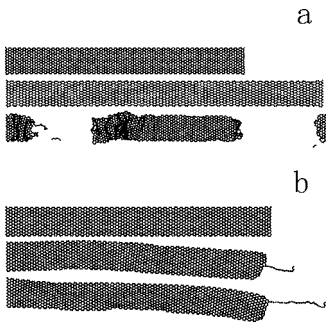

FIG. 1. Snapshots for pulling (a) all the atoms of the right side and (b) five corner atoms of the right side.

speeds v, with the thermal bath at 300 K. On decreasing speed from 300 to 70 m/s, the system tended to form longer tails attached to the five forced corner atoms, but it was hard to produce a chain of more than 40 atoms, and in some cases none except for the five forced corner atoms come off the layer. When v gets below 50 m/s, the entire layer can be "unraveled" to form a monatomic chain.

For testing the effects of temperature, a similar pulling process was simulated except that the layer consists of 16×50 atoms, the pulling speed is 30 m/s, and, especially, the system is isolated from the thermal bath, i.e., the procedure for resetting the velocity [Eq. (1)] was no longer performed. In these processes, a monatomic chain, shown in Fig. 2(a), formed at the early stage and its transverse vibration became more and more violent as the pulling proceeded, accompanied by rising temperature [Fig. 2(c)]. When the temperature climbed to about 3000 K, the chain broke off due to the violent vibrations, as shown in Fig. 2(b). Notably, the break occurred in the body of the chain but not at the joint between the chain and the layer. In order to determine if the monatomic chain can exist at lower temperatures, we performed a

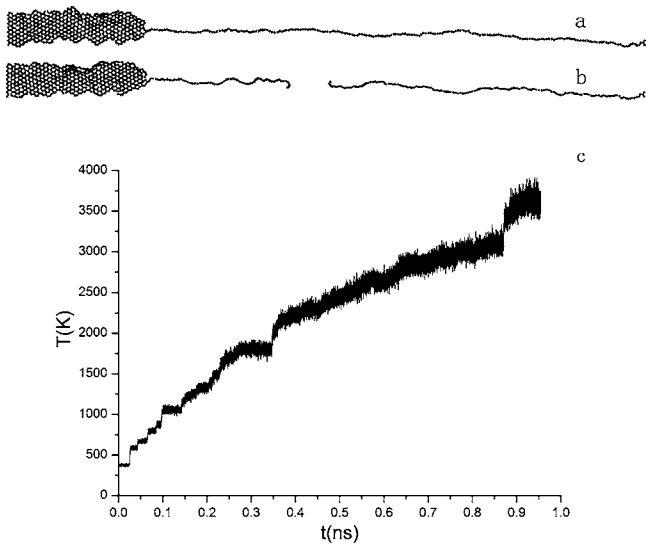

FIG. 2. Snapshots of (a) a chain of nearly 200 carbon atoms formed in an adiabatically pulling process and (b) the break of the chain in the body, corresponding to rising temperature with time as shown in (c).

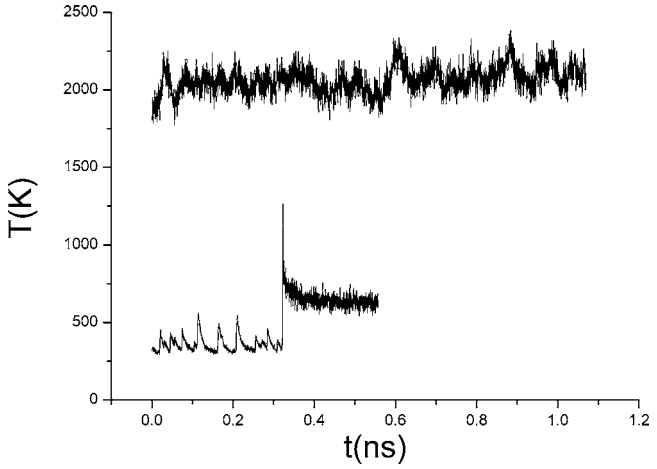

FIG. 3. Temperature curves for 300 (lower) and 2000 K (upper) systems, respectively. The peaks of the lower curve correspond to avalanche processes of graphite bond breaking.

simulation starting from a monatomic line consisting of 100 atoms, sampled from the above simulation when the graphite layer of 700 atoms was at about 2000 K. Without moving the five forced atoms, the system was allowed to relax adiabatically for 5 ns and the chain stayed unbroken.

The simulations mentioned above indicate that a FMCML may be obtained by pulling some corner atoms of a rectangular graphite layer with macro size at speeds lower than 50 m/s as long as the temperature is controlled at a moderate level. This proposal was tested by the following simulations. A graphite layer of 16×50 atoms was pulled with a speed of 30 m/s and the left side was assigned temperatures of 100, 300, 1000, 1500, and 2000 K, respectively, corresponding to liquid nitrogen temperature, room temperature, and high temperatures. The temperature curves for the 100 and 300 K systems consist of alternating peaks and slopes on a platform; they are remarkably different from those for the 1000, 1500, and 2000 K systems (Fig. 3). Visualizing the trajectories of all the atoms, we see that each peak and slope corresponds, respectively, to shrinking and stretching of the graphite layer. During the stretching process, a single atom comes off the layer occasionally and joins the chain. The layer shrinking takes place just after an avalanche process of graphite bond breaking with several graphite atoms joining the chain within about 1 ps. Clearly, the cause of the shrinking is that the strain from the chain becomes weak with lengthening of the chain. The shrinking proceeds in the direction opposite to the pulling, and actually increases the pulling speed, which is harmful to formation of a long chain according to our simulations mentioned above. For example, the last peak for the 300 K system corresponds to a severe shrinking and the chain breaks at the joint (Fig. 4). A higher-temperature peak indicates a more violent avalanche process followed by a more severe shrinking. Obviously, Fig. 3 shows that the avalanche process is more violent at lower temperatures but seldom occurs in the high-temperature system, coinciding with the fact that escape of single atoms from the graphite bonds can be enhanced by thermal motion. Actually, the pulling in the 1000, 1500, and 2000 K systems

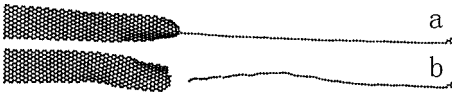

FIG. 4. Chain breaking at the joint due to an avalanche process.

produced a monatomic chain of more than 400 atoms in our simulations, and this can be continued until the entire layer is unraveled to form a monatomic chain, provided the temperature of the system is controlled at about 1000 K, which can be easily implemented in practice. For instance, if the pulling is slowed down to a speed of about 0.01 m/s, which is suitable for general experimental conditions and three orders of magnitude slower than our simulations, then the system will have enough time to arrive at the ambient temperature, which can be set exactly at 1000 K.

Obviously, as the pulling speed gets close to practical ones, such as 1 m/s or much slower, thermal fluctuations may cause the chain to break. In order to test this effect, we performed a simulation pulling a graphite layer of 16×50 atoms with a speed of 1 m/s at 1500 K, and obtained a short chain of more than 20 atoms in 4 ns. In the pulling process, the graphite layer and the pulled chain behaved much more stably, but we had to stop the simulation because it lasted about 50 days. In addition, a much slower speed, 0.05 m/s, was also adopted in our simulations to pull only one atom at the corner of a smaller graphite layer of 42 atoms arranged in the configuration shown in Fig. 5(a). As expected, all the atoms except for the ones fixed at the left side were pulled out to form a carbon line. These simulations indicate that much lower pulling speeds are beneficial to prevent the chain from breaking at the joint, as will be discussed later in detail.

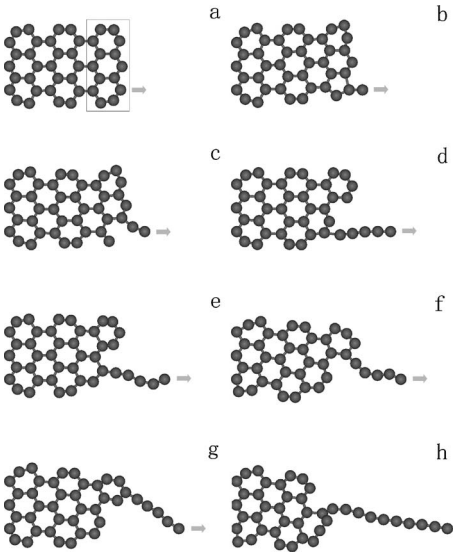

FIG. 5. Snapshots for pulling chain from a system of 42 atoms: (a) initial configuration, (b), (c) bond breaking process, (d)–(g) bond drifting process and (h) final structure in our Car-Parinello MD simulation.

III. TIGHT-BINDING AND CAR-PARRINELLO MD SIMULATIONS

In order to confirm the main conclusions of our classical simulations, we performed tight-binding MD simulations[17] of similar processes. Considering the calculation costs, we chose a smaller graphite layer of 42 atoms arranged in the configuration shown in Fig. 5(a) and pulled one atom at the corner of the right side, while the system evolved adiabatically. The integration step size was set as 0.2 fs. We tried to pull out carbon chains at speeds of 60, 50, and 40 m/s but could not obtain chains with more than five atoms. When the pulling speed got down to 30 m/s, the graphite layer was unraveled in the same way as shown in our classical simulations [Fig. 1(b)], and a long monatomic chain was pulled out. In this process the temperature of the system fluctuated at about 1900 K, and the avalanche process of graphite bond breaking was not observed. This is in agreement with our simulations described in the preceding section. After the 14 atoms of the three hexagons at the right side [indicated by a rectangle in Fig. 5(a)] were pulled out, we terminated the simulation, considering the fact that similar processes of unraveling hexagons will repeat if the simulation is continued.

The above pulling process starting from the graphite layer of 42 atoms [Fig. 5(a)] was further investigated by Car-Parrinello MD simulations[18,19] with blyp (Becke-Lee-Yang-Parr) function and Troullier-Martins pseudopotential.[20] The integration step size was set as 0.12 fs. Similarly to the results of the tight-binding simulations, a long monatomic chain was also obtained [Fig. 5(h)] with a pulling speed of 30 m/s. In this process, the graphite bonds near the joint may break (bond breaking) with release of one or more atoms to joint the chain [Figs. 5(b) and 5(c)], or the left end of the chain may drift from one graphite atom to another nearby (bond drifting) without lengthening the chain [Figs. 5(d)–5(g)]. These two different mechanisms were also observed in our other two kinds of simulations. In the bond breaking process, breaking of the chain body will be unlikely because the energy of the *sp* hybrid bond in a monatomic chain[7] is larger than that of the sp^2 hybrid bond in a graphite layer. However, the joining bond that connects an *sp* hybrid atom in the chain to an sp^2 hybrid atom of the layer should be weaker than the *sp* hybrid bond in the chain body, so the former is also easy to break, and it is the main obstacle to continuation of the pulling process. In the case of severe shrinking of the graphite layer observed in our classical simulations at lower temperatures, if the joining bond breaks, there exists little chance for the chain to be bonded to the layer again. In the present case without shrinking, the joining bond may break but recovers immediately. Obviously, if the temperature of the graphite is high enough that the avalanche process of bond breaking is hindered, just as in the situations without shrinking shown in Fig. 3 for the 1000 K system, the pulling can be continued indefinitely to produce a FMCML, as long as the pulling is much slower than 30 m/s.

IV. SUMMARY

Our simulations show that a long monatomic chain can be obtained by pulling the corner atoms of a rectangular graph-

ite layer at about 1000 K with speeds lower than 30 m/s, indicating that a FMCML can be pulled out from graphite if the pulling speed is decreased to a general experimental level, such as 0.01 m/s. These theoretical results coincide qualitatively with an experiment by Rinzler *et al.*[4] who supposed that a monatomic chain of 10–100 atoms was pulled out from the open edges of a nanotube. The temperatures for producing the chains were estimated to be 1300–1800 K, which is in the temperature range of our simulations for long chains. It is surprising that the authors of Ref. 4 guessed that the chain was produced in a way similar to unraveling the sleeve of a sweater, as is observed in our MD simulations. In addition, our MD simulations show that the main bodies of the graphite layers do not scroll during the pulling processes, implying that graphene sheets may exist in vacuum. This conclusion is in agreement with recent experimental observations.[21]

ACKNOWLEDGMENTS

This work was supported by the National Nature Science Foundation of China under Grant No. 10574030. Some of the calculations are performed on the Shanghai Supercomputer Center and National High Performance Computing Center of Fudan University.

*Corresponding author. xjning@fudan.edu.cn

[1] R. J. Lagow, J. J. Kampa, H. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw, and E. Munson, Science **267**, 362 (1995).
[2] K. H. Xue, F. F. Tao, W. Shen, C. J. He, Q. L. Chem, L. J. Wu, and Y. M. Zhu, Chem. Phys. Lett. **385**, 477 (2004).
[3] N. P. Bowling, R. J. Halter, J. A. Hodges, R. A. Seburg, P. S. Thomas, C. S. Simmons, J. F. Stanton, and R. J. McMahon, J. Am. Chem. Soc. **128**, 3291 (2006).
[4] A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, Science **269**, 1550 (1995).
[5] H. Ohnishi, Y. Kondo, and K. Takayanagi, Nature (London) **395**, 780 (1998).
[6] A. I. Yanson, G. R. Bollinger, H. E. Brom, N. Agrait, and J. M. Ruitenbeek, Nature (London) **395**, 783 (1998).
[7] A. V. Orden and R. J. Saykally, Chem. Rev. (Washington, D.C.) **98**, 2313 (1998).
[8] D. R. Bowler, J. Phys.: Condens. Matter **16**, R721 (2004).
[9] S. Szafert and J. A. Gladysz, Chem. Rev. (Washington, D.C.) **106**, PR1 (2006).
[10] S. R. Bahn and K. W. Jacobsen, Phys. Rev. Lett. **87**, 266101 (2001).
[11] D. Krüger, H. Fuchs, R. Rousseau, D. Marx, and M. Parrinello, Phys. Rev. Lett. **89**, 186402 (2002).
[12] X. Zhao, Y. Ando, Y. Liu, M. Jinno, and T. Suzuki, Phys. Rev. Lett. **90**, 187401 (2003).
[13] Y. Wang, J. Zhuang, M. Z. Ma, and X. J. Ning, J. Mol. Struct.: THEOCHEM **807**, 201 (2007).
[14] B. I. Yakobson, M. P. Campbell, C. J. Brabec, and J. Bernholc, Comput. Mater. Sci. **8**, 341 (1997).
[15] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[16] M. E. Riley and M. E. Coltrin, J. Chem. Phys. **88**, 5934 (1988).
[17] M. Menon, E. Richter, and K. R. Subbaswamy, J. Chem. Phys. **104**, 5875 (1996).
[18] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[19] CPMD Computer code (IBM, 1990–2006/MPI für Festkörperforschung Stuttgart, 1997–2001).
[20] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoseov, T. J. Booth, and S. Roth, Nature (London) **446**, 60 (2007).