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The nanoindentation of a copper substrate by single-walled carbon nanocone tips: a molecular dynamics study

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Abstract

This study dealt with deep nanoindentation of a copper substrate with single-walled carbon nanocones (SWCNCs) as the proximal probe tip, using molecular dynamics (MD) simulations. As an important feature, during the indentation the end part of the SWCNC tip will suffer a narrowing effect due to the radial component of resistant compression from the substrate and then forms into a somewhat flat arrowhead-like shape. The effective cross-sectional area of the SWCNC tip inside the substrate that the resistant force is acting on therefore is reduced to lower the normal resistant force on the tip. The narrowing effect is more significant for longer SWCNC tips. Two categories of SWCNCs are therefore classified according to whether the SWCNC tip buckles at its part inside or outside the substrate. SWCNCs of the first category defined in this paper are found able to indent into the substrate up to a desired depth. Further analyses demonstrate that a longer SWCNC tip of the first category will encounter smaller repulsive force during the indentation and thus require less net work to accomplish the indentation process. Raising temperatures will weaken the narrowing effect, so an SWCNC tip of the first category also encounters greater repulsive force and larger net work in the indentation process performed at a higher temperature. Notably, a permanent hollow hole with high aspect ratio will be produced on the copper substrate, while copper atoms in close proximity to the hole are only slightly disordered, especially when the indentation is manipulated at a lower temperature by using a longer SWCNC tip.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Knowledge of nanoscale surface contact mechanics required in the advancement and application of nanotechnologies such as nanoimprint lithography [1, 2] and high-density data storage technology [3–7] can be provided by the investigation of nanoindentation on solid surfaces. Instead of traditional

pyramid-like tips made of silicon or silicon nitride, Smalley and colleagues [8] proposed the utilization of carbon nanotubes (CNTs) as proximal probe tips in scanning probe microscopy (SPM) to offer high resolution imaging. It is also suggested that, in high resolution nanolithography, CNTs, with their ability to buckle elastically can replace conventional probe tips, which often break or wear off during direct contact

with the solid surface. Due to their high aspect ratios, small tip radii of curvature and high stiffness, using CNTs as the indenters to improve the spatial resolution has become popular in both nanoindentation experiments [9–14] and molecular dynamics (MD) simulations [15–21]. If applied in deep nanoindentations, however, the CNT tip is only allowed to indent a specimen uniaxially due to its lateral elastic compliance. In particular, shorter CNTs are required to perform a deep indentation without buckling at higher temperatures [22].

Carbon nanocones (CNCs), another form of nanostructure that also have high aspect ratios and high stiffness, were also suggested to be used as proximal probe tips due to their ability to retain several metastable shapes [23]. Recently, Chen *et al* [24] used CNCs as proximal probe tips in magnetic force microscopy (MFM) to obtain high resolution magnetic force imaging. CNCs were predicted by Ge and Sattler [25] and verified by Krishnan *et al* [26] and they can be distinguished by five conical angle values, namely 19.2°, 38.9°, 60.0°, 83.6° and 112.9°. Wei and Srivastava [27], by employing continuum elastic theory and MD simulation, found the structural stiffness of a single-walled CNC (SWCNC), which is derived via the equivalent continuum formula to the Young's modulus of a bulk material, to be $\cos^4 \theta$ of that of an equivalent single-walled CNT (SWCNT). Although SWCNCs with a smaller conical angle have a higher structural stiffness, SWCNCs with a large conical angle, however, are predicted to have greater structural stability [28]. The elastic and plastic properties of opened SWCNCs under tension were investigated by Wei *et al* [29] using MD simulation. Wei *et al* found that SWCNCs with a larger apex angle present larger failure strength but smaller maximum strain under tension.

Hsieh *et al* [22] have reported that the mechanical processing using SWCNTs as proximal probe tips can be manipulated on soft substrates since some SWCNT tips are able to penetrate the substrate. Like SWCNT tips, in this work, following the suggestion of Shenderova *et al* [23], SWCNCs were used as proximal probe tips to penetrate soft specimens in manipulating the mechanical processing. Our simulations show that, in the indentation of soft substrates, the SWCNC tips can penetrate into the material surfaces more efficiently than SWCNT tips. The analysis presented in this study thus attempts to investigate the deep nanoindentations on a copper substrate with SWCNC tips that have a conical angle 19.2° by performing classical MD simulations at a variety of temperatures. The reason for the utilization of the conical angle of 19.2° is simply that the SWCNC tips with such an angle will have the largest structural stiffness, as compared with those with conical angles larger than 19.2°, and can then be used to penetrate the copper specimen more effectively. Moreover, Zhang *et al* [30] have explained the experimentally observed preference of 19.2° for the conical angle of SWCNC by using the continuum model. Meanwhile, as compared with SWCNTs, the SWCNC tips are supposed to be more stable in deeply indenting into the substrate to a desired depth, especially at high temperatures [28].

The effects of the indenter length on the indentation of the copper surface are first examined in this study by varying the

length of the SWCNC indenters in the MD simulations at a specified temperature. To simplify the investigation, a desired indentation depth and a fixed indenting rate are designated in all simulations. Two categories of SWCNC mode have been analyzed and compared. In the first category, an SWCNC tip, with its length shorter than a certain critical length, is expected to penetrate the copper surface all the way until it reaches the intended depth. In the second category, an SWCNC with a length longer than the critical length is expected to penetrate the surface but will only indent to a depth shallower than the desired depth. It is reasonable to suggest that in the second category a longer SWCNC will buckle at a shallower depth. At each specified temperature the critical length that separates the two categories of SWCNC is to be determined, and subsequently the temperature variations of the critical length can then be determined. The indentation using the first category of SWCNCs will be studied further. Additionally, the temperature effects on both the repulsive force of SWCNCs of the first category and the net work required by the SWCNCs to complete the indentation process will also be investigated. Finally, the material structure in the deformed zone around the permanent hole produced by the indentation will be analyzed.

2. Simulation methodology

This study simulated the nanoindentation on a {1, 0, 0} FCC crystalline copper specimen with SWCNC tips. Positions and velocities of both the SWCNC tip and the substrate atoms were calculated as functions of time using MD methodology. The heat generated in the indentation process was assumed to dissipate at a high rate that is much faster than the indenting speed. Therefore, in each of the present simulations, the indentation was considered as an isothermal process, that both the tip and the substrate were controlled at a common temperature. The effect of the nanocone length was first investigated as the whole system was kept at a certain temperature. As the indentation systems controlled at several distinct temperatures were simulated, the temperature dependence of the cone-length effect was then determined. Figure 1 shows the configuration of the indentation system considered herein. The SWCNC was composed of 447–4491 carbon atoms, depending on its length, which correspondingly ranges between 40.0 and 140.0 Å. The SWCNC atoms with centers located in the uppermost layer of 2 Å thickness were simulated as rigid, and next to them is the thermal control layer of 3.5 Å thickness, which was used to maintain the constant temperature throughout the indentation process. The remaining part of the cone was simulated as in free motion, which thus has flexible characteristics. The relatively soft substrate consists of 32 000 FCC copper atoms in a finite slab with a lateral area of 72.200 Å × 72.200 Å and thickness of 70.395 Å. The two lowest layers of the substrate are simulated as rigid layers to prevent the substrate from moving along the direction of the indenting force caused by the tip. Two thermal control layers above and next to the rigid layers were employed to impose the substrate temperature. The remaining part of the substrate consists of free motion atoms designed to allow dislocation motions in the deformed substrate.

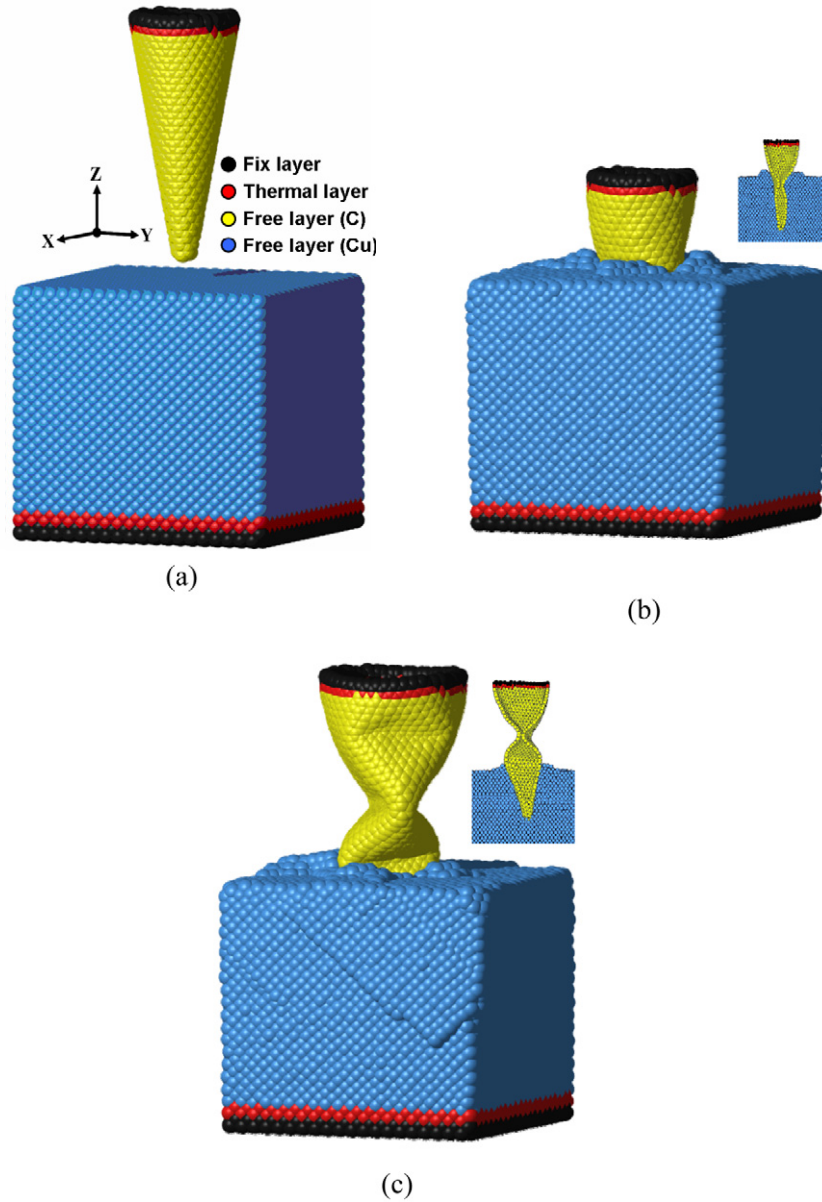


Figure 1. Configuration of the indentation system and SWCNTs of the two categories. The black and red particles are the rigid atoms and the thermal control atoms for both SWCNT tip and substrate, while the yellow and blue particles are the carbon atoms and the copper atoms in free motion, respectively. (a) Before the simulation takes place, the apex of the SWCNT is arranged 10 Å ahead above the substrate surface; (b) the SWCNT of category (I) buckles at its part inside the substrate; (c) the SWCNT of category (II) buckles at its part outside the substrate. The side views of the arrowhead-like end of the SWCNTs are demonstrated in (b) and (c).

A constant incremental time increment $\Delta t = 0.1$ fs for integrating the equations of motion for all non-rigid atoms was employed in the current computations. Such a time increment is a compromised choice since it is less than the thermal motion periods of both the tip and substrate atoms, but not too large to avoid a large round-off error. The nanoindentation processes simulated herein comprised pre-equilibrium, indentation and post-equilibrium stages. The pre-equilibrium stage consumed a computation time of 5 ps, which is sufficiently long for the relaxation of the whole system. During this stage, the apex of the nanocone tip was positioned 10 Å above the substrate surface such that the effect of the long-range attractive force between the tip

and substrate can be avoided. The initial positions of the tip and substrate atoms were arranged in accordance with their crystalline structures, respectively, and the initial velocities were randomized according to the specific temperature using numbers uniformly distributed in an interval. The indentation stage then started when both the tip and substrate have been relaxed to their equilibrium atomic configurations. During the indentation stage, the indentation was modeled by moving the rigid layer of the nanocone tip 50.0 Å downwards at a constant speed $v = 10^{-3}$ Å fs⁻¹, halting it for 10 ps, and then retracting it back to its original position at the same speed. Finally, the whole indentation system was allowed to relax for 5 ps in the post-equilibrium stage. Consequently, the prescribed

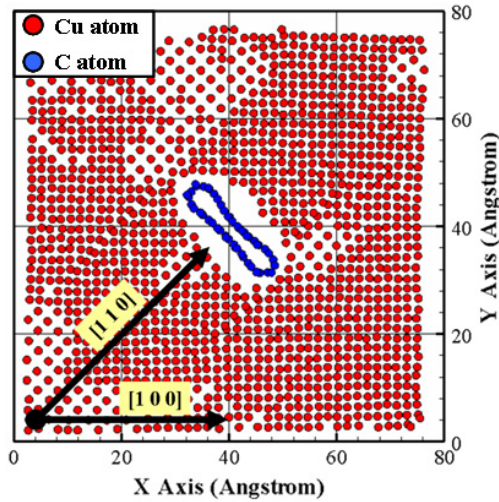


Figure 2. Top view of the substrate surface and the cross section of the SWCNC tip taken during the indentation. The red particles are the copper atoms and the blue ones are the carbon atoms. As clearly displayed, the cross section of the tip is significantly narrowed in the $[1, 1, 0]$ direction and is forced to be widened in the $[-1, 1, 0]$ direction; the copper substrate has the largest density in both directions. The cross-sectional area is smaller than its original circular area. The effective area of the tip that the normal resistant force is acting on within the substrate can be simply evaluated by calculating the cross-sectional area surrounded by the carbon atoms, as shown in this figure.

indentation depth is $d_{\max} = 40.0 \text{ \AA}$, as if a rigid SWCNC were used in the indentation. Since the desired depth is $40 \text{ \AA}$, the length of all simulated SWCNCs was then given to be greater than $40 \text{ \AA}$. In all stages of the MD simulation, the temperatures of the thermal control layers of both nanocone and substrate were held at a desired value using the rescaling method [31, 32]. The leap-frog algorithm was implemented to derive new position and velocity vectors of the nanocone and the substrate atoms from the corresponding data obtained in the previous step. The motion of each atom in the system was governed by Newton's law of motion in which the resulting force acting on the atom was deduced from energy potentials relevant to the interactions with the neighboring atoms within a cutoff radius.

Three kinds of bonding should be considered in the present indentation system, similar to the situation encountered in the works of Hsieh *et al* [22, 33], which dealt with nanoindentations on copper substrates using single-walled CNTs and diamond-like tips, respectively. The carbon-carbon bonding in the nanocone was simulated using the Tersoff many-body empirical inter-atomic potential [34], which was chosen because it needs less computing time during the present simulations. The Tersoff potential can be appropriately used to derive the inter-atomic forces among the carbon atoms of the nanocone because it provides rapid insights into the mechanical behavior of the nanocone without considering chemical reactions that account for bond making and breaking. The copper-copper bonding was derived from the calculation of the total energy of the metallic bonding in the copper substrate using the tight-binding potential [35]. The carbon-

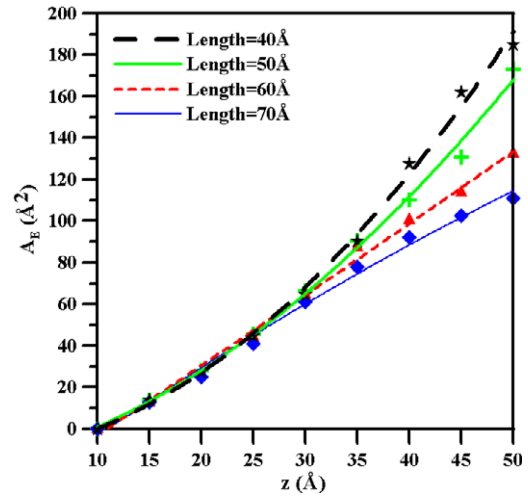


Figure 3. Variations of the effective area (A_E) with the displacement of the rigid atoms (z) for the SWCNC tips of lengths $40 \text{ \AA}$, $50 \text{ \AA}$, $60 \text{ \AA}$ and $70 \text{ \AA}$ at 300 K , respectively. The least squares fitting curves shown here demonstrate that A_E approximately varies with $(z - 10)^{1.41}$, $(z - 10)^{1.23}$, $(z - 10)^{1.04}$ and $(z - 10)^{0.93}$ for the SWCNC tips of lengths $40 \text{ \AA}$, $50 \text{ \AA}$, $60 \text{ \AA}$ and $70 \text{ \AA}$, respectively.

copper bonding occurring between the nanocone tip and the substrate was simulated by implementing an applicable Morse-type pair potential [36].

3. Results and discussion

As a proximal probe tip, when the SWCNC is indenting into the copper substrate, it suffers from compression due to the resistant interaction with the copper atoms in thermal vibration motion. In particular, the radial (lateral) component of the resistant compression plays an important role in the nanomechanics of the indentation. As shown in figure 2, the radial compression will cause the end part of the SWCNC tip to be significantly narrower than its original size in the $[1, 1, 0]$ direction, along which the copper atoms are most close-packed. However, the end part of the SWCNC tip was forced to be slightly widened in the direction perpendicular to the $[1, 1, 0]$, along which the copper atoms are also close-packed. As a result, the end part of the tip is formed into a somewhat flat arrowhead-like shape. Such a phenomenon resulted from the narrowing effect, which is so named herein as it will reduce the effective area of the SWCNC tip that the normal resistant force is acting on within the substrate. Consequently, the narrowing effect will cause the arrowhead-like SWCNC tip to penetrate the substrate more easily since it in turn lowers the normal resistant force acting on the tip. As the tip is indenting into the substrate, the effective area of the tip that the normal force is acting on can be simply evaluated by measuring the maximal normal cross-sectional area of the tip within the substrate, as also depicted in figure 2. Figure 3 shows the variations of the effective area with the displacement of the rigid atoms for the SWCNC tips of lengths $40 \text{ \AA}$, $50 \text{ \AA}$, $60 \text{ \AA}$ and $70 \text{ \AA}$ at 300 K , respectively. It is clearly shown in this figure that a longer SWCNC undergoes a more significant narrowing effect than a shorter one does. Theoretically, if the

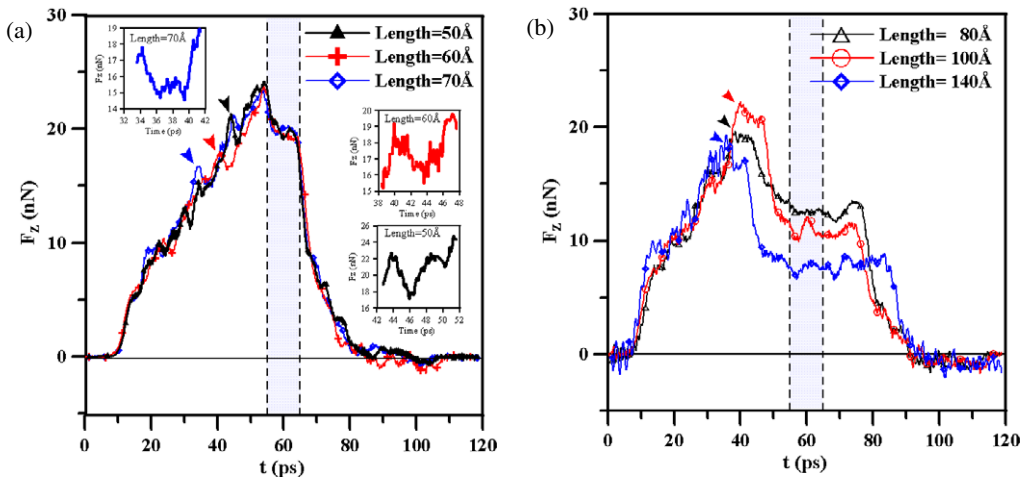


Figure 4. Variations of the normal force (F_z) on the uppermost rigid atoms of the SWCNCs as a function of the indentation time (t) at 300 K. In (a), the marked slight force drops indicate the occurrence of the buckling for the category (I) SWCNCs of lengths 50 Å, 60 Å and 70 Å, respectively. The insets display the detailed force variations around the occurrence of buckling. In (b), the obvious force discontinuities indicate the occurrence of the buckling for the category (II) SWCNCs of lengths 80 Å, 100 Å and 140 Å, respectively. The buckling of a longer SWCNC of both categories occurs earlier than that of a shorter one.

nanocone tip is entirely rigid, then the effective area should vary proportionally with $(z - 10)^2$, where z , in Å, represents the indentation displacement of the tip and thus $z - 10$ the indentation depth. In realistic situations, however, $z - 10$ can only represent an approximate indentation depth for the, in fact, flexible SWCNC if z is the indentation displacement of the uppermost rigid atoms of the tip and, in this case, the effective area varies with $(z - 10)^{1.41}$, $(z - 10)^{1.23}$, $(z - 10)^{1.04}$ and $(z - 10)^{0.93}$ for the flexible SWCNC tips of lengths 40 Å, 50 Å, 60 Å and 70 Å, respectively. While the part of the tip inside the substrate is arrowhead-like, the part of the tip outside of the substrate remains almost the same size as its original geometry. As a result from the narrowing effect, due to the instability arising from the intrinsic thermal vibration motion of both the carbon and copper atoms, an SWCNC will buckle at some point during the indentation stage. The simulation results show that, while the indenter is penetrating the substrate, the buckling may occur at either the part of the SWCNC that is inside or outside the substrate, depending on the SWCNC's length. Then, two categories of SWCNC can be defined according to whether the buckling occurs inside or outside the substrate as the SWCNC is indenting into the copper substrate at a certain temperature. Figures 1(b) and (c) show the morphologies of these categories of SWCNC when the buckling has taken place in the indentation stage. In this study, a particular critical length was used for classifying the SWCNC. The simulation results show that, if an SWCNC has length shorter than the critical length, denoted by L_C , then it will mostly buckle while indenting into the substrate, with the buckling occurring at its part inside the substrate. Such an SWCNC then belongs to the first category (I) defined herein, as shown in figure 1(b). In fact, some SWCNCs, which have lengths very close to the desired depth of 40 Å, did not buckle at all while penetrating the substrate. This kind of SWCNC is also classified as category (I). On the other hand, if an SWCNC has length longer than L_C , it will buckle at its part outside the

substrate. Meanwhile, the apex of such an SWCNC, like that of a long SWCNT, tends to tilt from the direction of the Z axis. This kind of SWCNC is classified as the second category (II), as shown in figure 1(c). The SWCNC of category (I) is able to bore into the substrate to the desired depth. In contrast, the SWCNCs of category (II) are unsuitable as tools for boring the substrate since they are unable to reach the desired depth. The critical length L_C can be determined at each designated temperature. During the indentation process, the normal resultant force acting on the uppermost rigid atoms of the SWCNCs were monitored and then expressed as a function of the indentation time. Figure 4 demonstrates the diagram of the force functions of some typical SWCNCs that belong to each of the two categories. As clearly shown in figure 4(a), the buckling behavior of the category (I) SWCNC is indicated by the relatively slight force jump, while as shown in figure 4(b), the buckling of the category (II) SWCNC is revealed by the obvious force discontinuities. It is noticeable that, for the category (I) SWCNC, the normal resistant force continues to climb as the tip keeps penetrating the substrate, demonstrating the ability for further penetration after the occurrence of the buckling. Meanwhile, figure 4 also shows the buckling of a longer SWCNC, of both categories, occurs earlier than that of a shorter one.

The MD simulations of a variety of temperatures were performed to establish the temperature dependences of the critical length L_C and, as a result, the temperature dependence of L_C is shown in figure 5. It is found from this figure that the critical length increases with increasing temperature. Such a trend totally differs from what happens in the indentation on a copper substrate performed by using (5, 5) SWCNT tips, in which the two critical lengths of the SWCNT decrease with increasing temperature [22]. In the latter case, the thermal motion of the copper atoms interacts with the SWCNT more intensively at a higher temperature and thus causes the tube to tilt further from the perpendicular and, as a consequence,

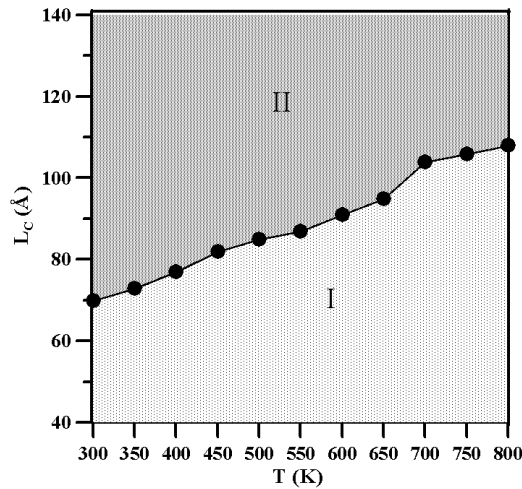


Figure 5. Variations of the critical length L_C as a function of temperature (T). The critical length increases with increasing temperature.

shorter SWCNTs may buckle at a higher temperature during the indentation, but may not at a lower temperature. In the present case, however, the buckling of the category (I) SWCNT is induced, not by the tilting from the perpendicular, but mainly by the elastic compliance to the narrowing effect by the resistant compression that the SWCNT suffers during the indentation. At higher temperatures, although both the SWCNT and the copper substrate are softer, the narrowing effect on the part of the tip inside the substrate becomes even less significant, as shown in figure 6 for example. Figure 6 shows that, for the SWCNT of length 70 Å, the effective area varies with $(z - 10)^{1.06}$, $(z - 10)^{1.00}$ and $(z - 10)^{0.96}$ at temperatures 700 K, 500 K and 300 K, respectively, implying that the increasing temperature enlarges the effective area of an SWCNT tip due to the less significant narrowing effect. Consequently, the buckling of an SWCNT occurring outside the substrate at a lower temperature will in turn be likely to be postponed to taking place inside the substrate at a higher temperature.

As tools for boring the substrate, the category (I) SWCNT was further investigated. Figure 7 shows the variation of the resultant normal force on the uppermost rigid atoms of an SWCNT as a function of the displacement of the rigid atoms for the indentation performed at 300 K. The force–displacement variations for a rigid SWCNT and a solid, diamond-structured nanocone of the same size of this flexible SWCNT are also shown in figure 7 for comparison. As can be observed from this figure, all the tips experienced proportionally increasing repulsive forces as they were indenting into the substrate. The increasing repulsive forces clearly are attributed to the increasing effective area of the tip during the penetration because of the tips' cone shape. It is also found from figure 7 that the force–displacement variations for both the hollow tips exhibit approximately the same trend and significantly differ from that for the solid tip. The repulsive force acting on the flexible SWCNT tip is somewhat greater than that on the rigid tip at the temperature

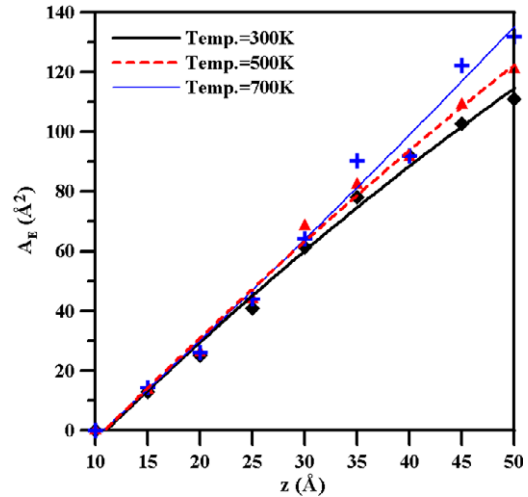


Figure 6. Variations of the effective area (A_E) with the displacement of the rigid atoms (z) for the SWCNT tip of length 70 Å at 300 K, 500 K and 700 K, respectively. As shown, A_E varies with $(z - 10)^{0.96}$, $(z - 10)^{1.00}$ and $(z - 10)^{1.06}$ at these temperatures, respectively. Increasing temperature clearly weakens the narrowing effect on the SWCNT tip to increase the contact area.

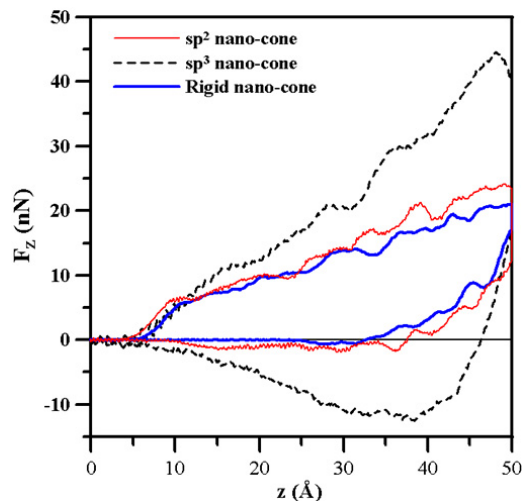


Figure 7. Variations of the normal force on the uppermost rigid atoms of the nanocone tips of length 50 Å at 300 K as a function of the displacement of these atoms. The tips considered here are the flexible SWCNT (red curve), the rigid SWCNT (blue curve) and the solid, diamond-structured nanocone (broken curve in black).

of 300 K simply because both the flexible SWCNT tip and the substrate are deformable. When the rigid tip indents into the soft substrate, it will naturally undergo a smaller resistance than that suffered by the flexible tip. At higher temperatures, the more deformable flexible SWCNT tip and substrate plus the weakened narrowing effect on the flexible tip will make a greater difference between the repulsive forces acting on the flexible and the rigid SWCNT tips (as can be seen in figure 9). However, the repulsive force acting on the solid tip is rather greater than those on the two hollow tips since the solid tip not only is almost as rigid as the rigid tip but also has inner atoms for contributing the excess interactions with the copper

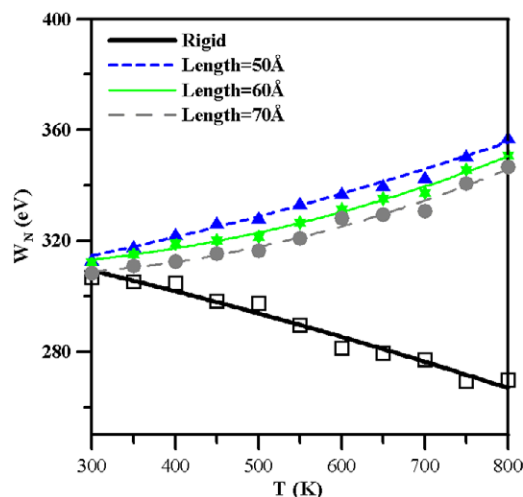


Figure 8. Temperature dependences of the net work (W_N) required by the SWCNC tips of lengths 50 Å, 60 Å and 70 Å for accomplishing the indentation process. As shown, the net work increases with increasing temperature. Meanwhile, a shorter SWCNC requires larger net work to complete the indentation cycle.

atoms outside the tip's shell. As long as the nanocone tips have reached the maximum indentation depth, they were halted for 10 ps and then retracted from the substrate at the same rate as designated in the indentation phase. The interval of 10 ps for halting the tip allows the deformed copper atoms around the tip to relax and thus reconstruct their new positions with only a minority of elastic potential still remaining in the deformed zone of the substrate. From figure 7, it is observed that, at the beginning of the retraction phase, all the tips of the present simulations experienced repulsive forces, from large to small, due to the rebounding response of the remaining elastic potential in the substrate. However, it is interesting to observe that, in the rest of the retraction phase, both the hollow tips experienced approximately zero forces, though actually negligible attractive forces, implying the formation of a plastically deformed zone around the tip. In contrast, the solid tip experienced an attractive force after encountering the repulsive force. Such a phenomenon can be attributed to the excess attractive interactions between the inner carbon atoms of the solid tip and the copper atoms outside the tip's shell during the corresponding period. It should be mentioned that, in an MD simulation not shown here, as long as the rigid SWCNC reached the maximum indentation depth, if without a halting manipulation, it will automatically be extruded out of the substrate at an average rate of 1150 m s^{-1} , which is far beyond the retraction rate of 100 m s^{-1} assigned in the present simulations. Therefore, the rigid SWCNC is expected to encounter a repulsive force during all the retraction phase retracting speed constraint if no halting is manipulated to relax the deformed substrate in between the indentation and retraction phases.

The net work required by the SWCNCs to accomplish the complete cycle of the indentation process can be calculated by measuring the area enclosed by the normal force hysteresis like those shown in figure 7. As a result, the temperature dependences of the net work required by the SWCNCs of

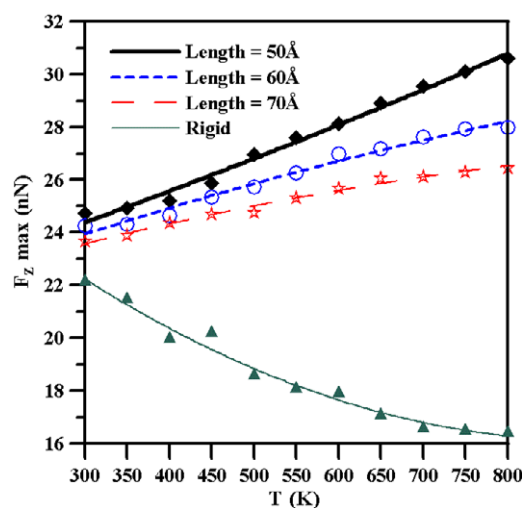


Figure 9. Temperature dependences of the maximal repulsive force ($F_{Z\text{max}}$) experienced by the SWCNC tips of lengths 50 Å, 60 Å and 70 Å and by the rigid tip during the indentation process. As shown, the maximal repulsive force on the flexible tip increases with increasing temperature, and a shorter SWCNC experiences a greater maximal repulsive force, both consistent with the trends demonstrated in figure 8. The maximal repulsive force on the rigid tip, however, decreases with increasing temperature.

lengths 50 Å, 60 Å and 70 Å to complete the indentation are shown in figure 8, respectively. Since the net work required by the solid nanocone tip to complete the indentation is apparently greater than that required by the flexible SWCNC tip, it is therefore excluded from the consideration in what follows. The temperature dependence of the net work required by the rigid SWCNCs to complete the whole cycle of indentation process, which apparently is length-independent, is also shown in figure 8 for comparison. The net work required by the rigid SWCNCs to complete the indentation decreases with increasing temperature. Clearly, as shown in the figure, the net work functions corresponding to the flexible SWCNCs have a trend opposite to that of the rigid one; they increase with increasing temperature. Similar trends to such a finding have also been reported in the indentations by a (5, 5) SWCNT and a diamond-like tip [22, 33]. It is obvious that, for the rigid SWCNC tip, the required net work becomes less at a higher temperature simply because the substrate becomes softer. On the other hand, however, the net work required by the flexible SWCNCs to accomplish the indentation process increases with increasing temperature. For the indentation performed by flexible SWCNCs, though both the tip and the substrate become softer at a higher temperature, the narrowing effect on the SWCNCs inside the substrate becomes even weaker, as mentioned. Therefore at a higher temperature the SWCNC tip with a larger effective area requires a larger force to indent into the substrate, which in turn results in the larger net work required to complete the indentation process. At a common temperature, a longer SWCNC requires less net work to complete an indentation cycle since it encounters a smaller repulsive force during the penetration due to a more significant narrowing effect. In figure 9, the temperature dependences of the maximal repulsive force experienced by the SWCNC tips

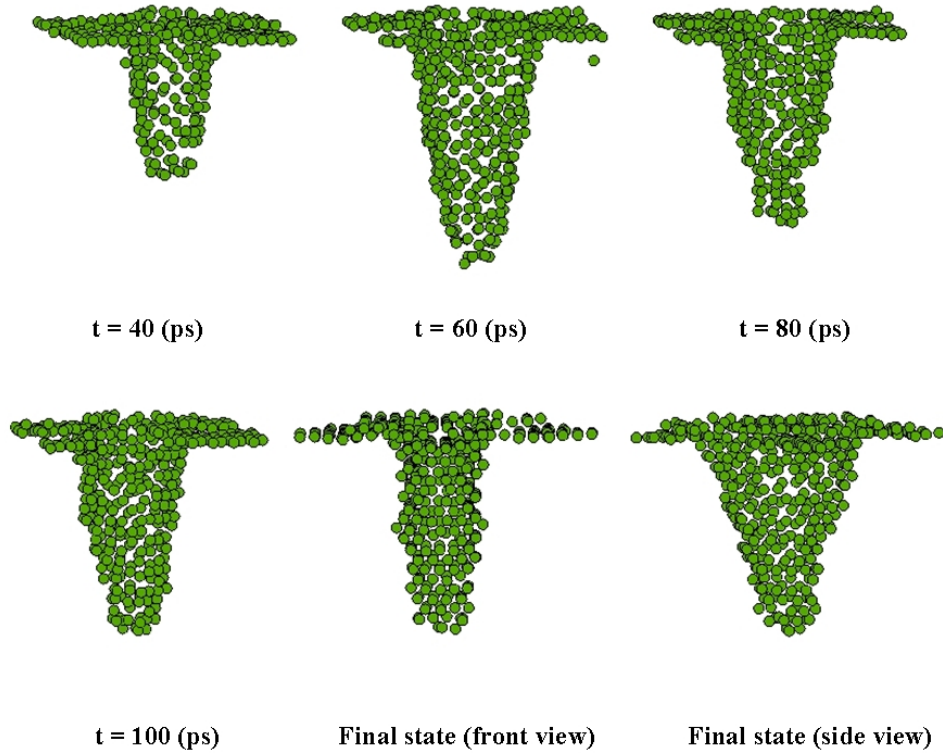


Figure 10. Snapshot of the copper atoms around the SWCNC indenter at several time steps during the entire indentation process.

of lengths 50 Å, 60 Å and 70 Å, respectively, show trends consistent with those revealed in figure 8. The trend that a longer SWCNC tip undergoes smaller repulsive force and thus requires less net work to accomplish an indentation cycle is opposite to that found in the indentation performed by using (5, 5) SWCNTs as the tip [22].

As a mechanical processing technology, deep indentation using SWCNTs of category (I) as the proximal tip can promisingly produce nanometer-scale hollow holes of high aspect ratio on a copper substrate. Only a small amount of disordered copper atoms during the indentation stage can be found in the deformation zone affected by the tip, as shown in figure 10, in which snapshots of only the disordered copper atoms around the proximal tip are displayed. In this work, the complex analysis of the variation of the substrate lattice structure in the zone around the tip, when the substrate underwent the indentation cycle, was simplified by examining the evolution of the structure factor for that zone defined by Rapaport [31]:

$$\rho(\vec{k}) = \frac{1}{N_a} \sum_{j=1}^{N_a} \exp(i\vec{k} \cdot \vec{r}_j), \quad \vec{k} = \frac{2\pi}{a}(1, -1, 1). \quad (1)$$

In equation (1), N_a is the number of the selected atoms in the deformation zone around the tip, $\vec{r}_j$ represents the position vector of atom j and a is the length of the unit FCC lattice in the copper substrate. In the analysis of lattice structure, a higher absolute value of the structure factor represents a more perfect lattice structure in the solid substrate. The maximal absolute value of the structure factor is 1, which corresponds

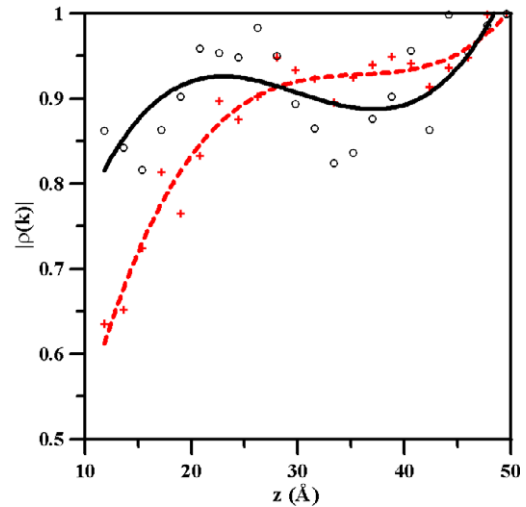


Figure 11. Variations of the structure factor in absolute value within the deformation zone around the tip as a function of the indentation displacement for the SWCNC tips of lengths 50 Å (red broken curve) and 70 Å (black solid curve) at 300 K, respectively. Both the curves are the least squares fitting of the corresponding data marked in the figure.

to the perfect FCC lattice structure. This study only shows the final value of the structure factor calculated after the post-equilibrium stage. Figure 11 shows the variations of the structure factor in absolute value within the deformation zone around the tip as a function of the indentation displacement for the SWCNC tips of lengths 50 Å and 70 Å at 300 K,

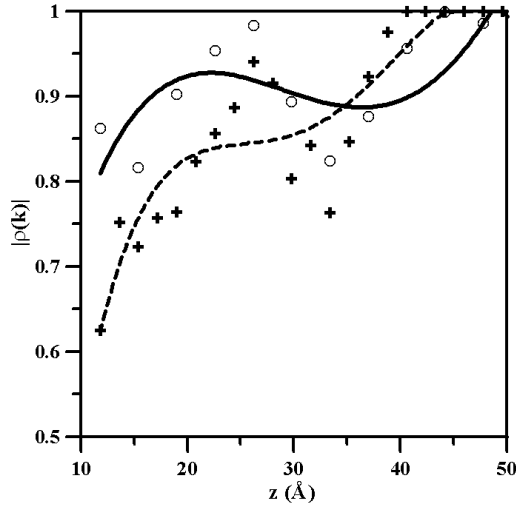


Figure 12. Variations of the structure factor in absolute value as a function of the indentation displacement for the 70 Å long SWCNC at temperatures of 300 K (solid curve) and 600 K (broken curve).

respectively. It is found that, as a whole, for both tips, the deformation zone around the tip is significantly disordered only in the shallow part near the substrate surface. Relatively large differences between the two distributions of the structure factor can be found in the proximity of the substrate surface. Meanwhile, the structure factor distributions for the holes produced by the SWCNC of length 70 Å at 300 and 600 K are displayed in figure 12. As observed, significantly disordered lattice structure can be found even at deeper positions inside the hole produced at a higher temperature. The excellence for using the SWCNC to produce high aspect ratio holes can also be revealed by calculating the recovery rate of the hole after the indentation. Suppose the volumes of the empty space in the hole at the beginning and at the end of the post-equilibrium stage are V_I and V_F , respectively, then the recovery ratio (RR) of the hole is defined by

$$RR = (V_I - V_F) / V_I. \quad (2)$$

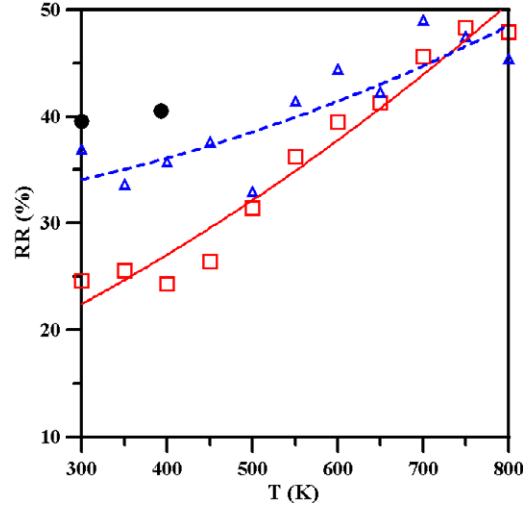


Figure 14. Temperature dependences of the recovery ratio (RR) of the holes produced by using the SWCNC tips of lengths 50 Å (red solid curve) and 70 Å (blue broken curve). The solid circles in the diagram represent the RR of the holes produced by using the solid nanocone tip of length 50 Å at 300 K and 400 K, respectively. Apparently, the holes produced by the solid nanocone tip have RRs much greater than those produced by the SWCNC tip.

Therefore a lower RR measures a more permanently disordered structure around the hole after the retraction of the tip. Figure 13 shows the perpendicular cross sections of the hollow holes produced by using the SWCNC tips of lengths 50 Å and 70 Å, respectively. In this figure, the substrate atoms at the beginning of the post-equilibrium stage are displayed in black, while the volume difference $V_I - V_F$ is shown in yellow. The temperature dependences of the recovery ratio of the holes produced by using the SWCNC tips of lengths 50 and 70 Å are shown in figure 14. The RRs of the holes produced by using the solid nanocone tip of length 50 Å at 300 and 400 K are shown in this figure for comparison, too. These temperature dependences imply that, as the copper substrate undergoes an indentation process either performed by a shorter SWCNC tip

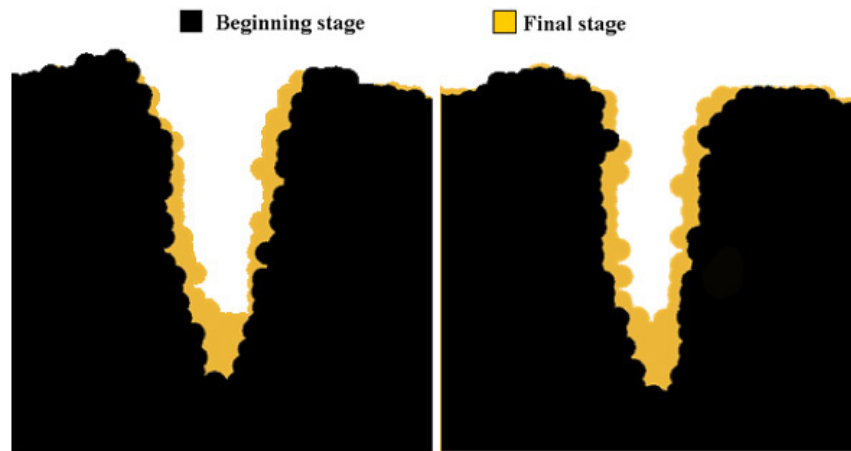


Figure 13. Perpendicular cross sections of the hollow holes produced by using the SWCNC tips of lengths 50 Å (a) and 70 Å (b), respectively. The black configurations represent the holes formed right after the retraction of the tip, while the yellow configurations are the final holes after the post-equilibrium stage.

or at a lower temperature, a permanent hollow hole with a lower recovery ratio will be produced.

4. Conclusion

This study performed MD simulations to investigate the deep indentation of the {1, 0, 0} copper substrate by using SWCNCs as the proximal probe tip. A unique feature of the utilization of the SWCNC to perform the indentation is the narrowing effect on the SWCNC tip during the indentation. The narrowing effect can reduce the effective area of the category (I) SWCNCs to help penetrating the substrate up to the desired depth, despite that the SWCNC tip may buckle at its part inside the substrate. The narrowing effect is more significant for a longer SWCNC, and therefore a longer SWCNC of category (I) will encounter a smaller repulsive force in the indentation and thus requires less net work to complete the indentation process at a certain temperature. This finding differs from that reported by Hsieh *et al* [22], in which a longer (5, 5) SWCNT, when used as the tip to perform the indentation on a copper substrate, was found to experience greater repulsive force during the indentation and thus required a larger net work to complete the indentation cycle. When the SWCNC has a length greater than L_C , the narrow effect can cause it to buckle at the part outside the substrate. Such an SWCNC is classified in category (II) and was found unable to indent the substrate to the desired depth. Increasing temperature can weaken the narrow effect. The simulation results of this study have shown that an SWCNC will undergo greater repulsive force during the indentation and then require a larger net work to accomplish the indentation cycle at a higher temperature. Since the proximal probe tip will more likely break or wear off as it suffers greater force and larger net work in an indentation cycle, a longer SWCNC of category (I), according to the present findings, therefore is recommended to be applied in the indentation process manipulated at a lower temperature. Meanwhile, a permanent hollow hole of high aspect ratio was promisingly produced on the copper substrate after the SWCNC of category (I) has been used as the tip to complete the indentation process. When the indentation is manipulated at a higher temperature, the copper atoms around the hollow hole are found significantly disordered even at deeper positions. Nevertheless, the hole produced at a higher temperature will have a permanent size rather less than that obtained right after the tip has been retracted from the substrate because the disordered copper atoms around the hole will recover in a higher percentage ratio during the post-equilibrium stage. When the hole is produced by using a shorter SWCNC tip, the deformed zone around it has a lower recovery ratio, but with a more disordered lattice structure near the substrate surface. If the SWCNC is considered as a tool for boring a hole on the copper substrate, then from the viewpoint of reusability of the tip and the effectiveness of producing the hole, the processing is recommended to be manipulated at low temperatures, according to the present findings.

What is obtained in this paper as a whole is a theoretical prediction, which should be verified by future related experiments. The present results, however, should be

a promising prediction because the force fields and physical parameters involved used to simulate the carbon-carbon, carbon-copper and copper-copper interactions are the same as those used in our previous papers [22, 33, 37]. Reported in [37], the structural stiffness (1.86 MPa) of the (5, 5) SWCNT obtained using MD simulations is in between the *ab initio* result (1.54 TPa) obtained by van Lier *et al* [38] and the density functional result (2.05 TPa) calculated by Peralta-Inga *et al* [39].

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