

*Ab initio* molecular dynamics simulations on structure change of liquid Te from normal- to supercooled-state

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 335102

(<http://iopscience.iop.org/0953-8984/20/33/335102>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:54

Please note that [terms and conditions apply](#).

# *Ab initio* molecular dynamics simulations on structure change of liquid Te from normal- to supercooled-state

G Zhao<sup>1,3</sup>, C S Liu<sup>2</sup> and Z G Zhu<sup>2</sup>

<sup>1</sup> Department of Physics and Electronic Engineering, Ludong University, Yantai 264025, People's Republic of China

<sup>2</sup> Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, PO Box 1129, Hefei 230031, People's Republic of China

E-mail: [gzhao19800209@126.com](mailto:gzhao19800209@126.com)

Received 6 April 2008, in final form 8 June 2008

Published 8 July 2008

Online at [stacks.iop.org/JPhysCM/20/335102](http://stacks.iop.org/JPhysCM/20/335102)

## Abstract

Using *ab initio* molecular dynamics simulations and inherent structure formalism, the local atomic structures and electronic properties of liquid Te from the normal- to supercooled-state were studied. The calculated structure factors agree acceptably with available experimental data. There is a noticeable maximum at around 723 K in the curve of first-peak-height of  $S(Q)$  versus temperature. With increasing temperature, in the low-temperature region from 573 to 673 K, the average coordination number increases gradually in contrast to the behavior of a classical isotropic fluid; but in the high-temperature region from 843 to 1073 K, it remains nearly constant. Our calculated angular limited bond–bond correlation functions first show that there are two types of Peierls distorted local atomic structures in liquid Te: the lengths of short and long bonds in the first type are similar to those in crystalline Te, while the lengths of short and long bonds in the second one are very different from those in crystalline Te. With decreasing temperature, the lengths of the two short intrachain bonds are unchanged, but those of the two long interchain bonds become longer, indicating that the interchain correlation reduces with decreasing temperature. Our results suggest that the change of the Peierls-type distorted local atomic structures with temperature may be responsible for the striking anomalies of many thermophysical properties of liquid Te. The calculated DOS and LDOS shows that there is an obvious dip in DOS at  $E_F$ , but the dip at 1073 K is shallower than that at 573 K. The variation of the dip in DOS mainly results from the change of Te p orbital.

## 1. Introduction

Tellurium (Te) is a chalcogen element. In the periodic table of elements, it follows selenium (Se) in the VI group. At normal conditions of pressure and temperature, crystalline Te is the semiconducting trigonal phase, with helical chains of atoms running along the axes of the hexagonal cell and a coordination number of 2 [1]. This structure may be considered as resulting from a distortion of close-packed layers stacked in an ABC sequence. Alternatively, the lattice may be derived from a simple cubic structure via a ‘bond breaking’ distortion [1]. After melting at 723 K, this structure is disrupted. Over the

past three decades, liquid Te has remained an object of interest for many researchers, mainly due to two reasons. One is that it comprises two features which are usually considered to be incompatible with each other: covalently bound atoms and metallic-like behavior upon melting [2]. The other is that many thermophysical properties of liquid Te show striking anomalies ranging from the equilibrium liquid above the melting point down to the supercooled-state [4]. For example, liquid Te exhibits a minimum volume at about 733 K, and on decreasing the temperature from the melting point (723 K) to 573 K, supercooled liquid Te undergoes an abnormal volume expansion, which is accompanied by a very sharp extrema at about 623 K in the thermal expansion coefficient, adiabatic compressibility, and the constant pressure heat capacity [4].

<sup>3</sup> Author to whom any correspondence should be addressed.

These anomalies indicate the occurrence of a rapid structural change in liquid Te from 733 to 573 K. But the corresponding atomic structure of liquid Te and the driving mechanism for the structural change are still controversial.

The liquid structure is usually understood with reference to its crystal structure. As is well known, the trigonal crystal structure of Te mentioned above is usually discussed in terms of a Peierls distortion of the simple cubic lattice: the s bands are completely filled and nonbonding and the p bands directed along three orthogonal axes lead to a simple cubic structure [5]. However, for Te, the p bands is two-thirds filled, so that the lattice is unstable against a Peierls distortion dividing the six nearest-neighbor bonds into two short intrachain bonds ( $d_1 = 0.284$  nm) and four long interchain bonds ( $d_2 = 0.349$  nm) [3]. The ratio of the nearest- and next-nearest-neighbor distances is a direct measure for the strength of the Peierls distortion. For Te, the ratio is 1.23 [3]. Although the concept of Peierls distortion was established in the context of low dimensional and periodic structures, recently it has been generalized for aperiodic systems using the direct space method [3].

Over the past three decades, there has been considerable data concerning the structural properties and their temperature-dependence in liquid Te, not only from experimental but also from theoretical points of view. Most of the results from x-ray or neutron scattering experiments showed that the coordination number in liquid Te is about 3 at higher temperature and 2.5 at the melting point, which is larger than that in crystalline Te [6–9], indicating that it is not a pure chain structure in liquid Te. Indeed, a molecular dynamics simulation of the structure of liquid Te based on effective interatomic forces derived from pseudopotential theory described the structure in terms of ‘entangled broken chains’ [10]. Analyzing the structure factors of liquid Te based on a short-chain model, Misawa suggested that the anomalous volume contraction and the semiconductor–metal (SC–M) transition may be related to the shortening of the chains of atoms [11]. A recent study on liquid  $\text{Ge}_{15}\text{Te}_{85}$  indicated that the density anomaly is not related to a tetrahedral bonding as in the case of water and silica, and it is considered that the density anomaly of other p-bonded elements may also not be related to a tetrahedral bonding [12]. By a tight-binding Monte Carlo simulation, Bichara [13] showed that on melting, the chain structure of the crystalline Te is preserved and a short–long alternation (0.280 and 0.290 nm) of the bonds takes place within the chains. The local environment of each atom changes from two short and four long neighbor distances to two short, one medium, and three long neighbor distances. And the third bond is responsible for the SC–M transition. According to the analysis from the EXAFS data of Tsuzuki *et al* [14–16], the first coordination shell can be thought of as the superposition of two Gaussians centered at a short and long bond length (0.278 and 0.295 nm at 643 K) inside the first peak of the pair-correlation function  $g(r)$ , and there is a strong interchain correlation between the chains at the melting point. As the temperature decreases from the melting point, the number of long bonds is reduced and the local structure changes substantially accompanied by the reduction of the interchain correlation. Moreover, they argued that the long bonds and the strong interchain correlation are

associated with the metallic nature of liquid Te. Analyzing the EXAFS data for supercooled liquid Te by adopting a ‘model-independent’ method, Kawakita *et al* [17] found that the short chains in liquid Te with a metallic nature are composed of short (0.280 nm) and long (0.295 nm) covalent bonds. However, Molina and Lomba [18] demonstrated that the opinion about short and long bond length inside the first peak of  $g(r)$  may be a rather naive view of the nearest-neighbor structure, and it might actually be the case that the continuous distribution, even if it can be represented by the superposition of two Gaussians, is the only true physical representation of the microscopic structure. They also pointed out that a clearer picture about whether there is a short bond and a long one inside the first peak of  $g(r)$ , i.e. a short–long alternation of the bonds within the chains, can be obtained if the inherent structure is derived. The ‘inherent structure’ formalism [19, 20], introduced by Stillinger and Weber, is an insightful approach to study the local atomic structure of liquid and amorphous states. It is a way to partition the configuration space for the vibrations of a  $n$ -body system into various regions. Within each region, there is one local minimum of the potential energy surface that can be reached by a minimization algorithm, and the structure at the local minimum is the inherent structure of the corresponding region.

The experimental and theoretical results quoted above indicate that the structure of liquid Te is complex. In this work, to investigate further the microscopic atomic structure and electronic properties of liquid Te and attempt to obtain some information on the above anomalous temperature-dependence of the physical properties, using *ab initio* molecular dynamics simulations and ‘inherent structure’ formalism, we studied the general and inherent structures of liquid Te from 1073 to 573 K, including the normal- and supercooled-state. The paper is organized as follows: in section 2, we describe the method of our simulations; the results of our simulations and the corresponding discussion are reported in section 3; a short summary is given in section 4.

## 2. Computational methods

Our simulations were performed within the framework of the density function theory (DFT) [21]. We used the Vienna *ab initio* simulation package (VASP) [22], and employed the projector augmented wave (PAW) potential [23], with the generalized gradient approximation (GGA) formulated by Perdew and Wang (PW91) to the exchange–correlation energy [24]. The system (80 Te atoms) was put in a simple cubic box with periodic boundary conditions. The  $\Gamma$  point was used to sample the Brillouin zone of the supercell. The electronic wavefunctions were expanded in the plane wave basis set, with an energy cutoff of 175 eV. Our canonical ensemble simulations were performed at 573, 623, 673, 843, and 1073 K with a Nosé thermostat for temperature control [25]. The experimental densities at different temperatures were used [4]. The Verlet algorithm was used to integrate Newton’s equations of motion and the time step of ion motion was 4 fs. The Kohn–Sham energy

functional was minimized by the preconditioned conjugate gradient method.

The initial atomic configuration adopted was a random distribution of 80 atoms on the grid, which was constructed by dividing the supercell into  $5 \times 5 \times 5$  square segments. Then, the system was heated up to 1073 K by rescaling the ionic velocities. After a run of 20 ps at this temperature, the system arrived at an equilibrium liquid state. Another run of 16 ps was performed to obtain 4000 configurations (called general structure configurations) and analyze the physical quantities of interest, then the temperature gradually reduced to 843 K. At this temperature, the physical quantities of interest were obtained by averaging over 16 ps after an equilibration taking 8 ps. For other temperatures, we only repeated this procedure and changed the final temperature to 673, 623, and 573 K, respectively. At 1073 and 573 K, we obtained 20 configurations during the run of 16 ps and relaxed them to their closest local minima (the corresponding configurations are called inherent structure configurations) by a conjugate gradient energy minimization algorithm [19, 20], and then analyzed the inherent structure by averaging the 20 inherent structure configurations.

### 3. Results and discussions

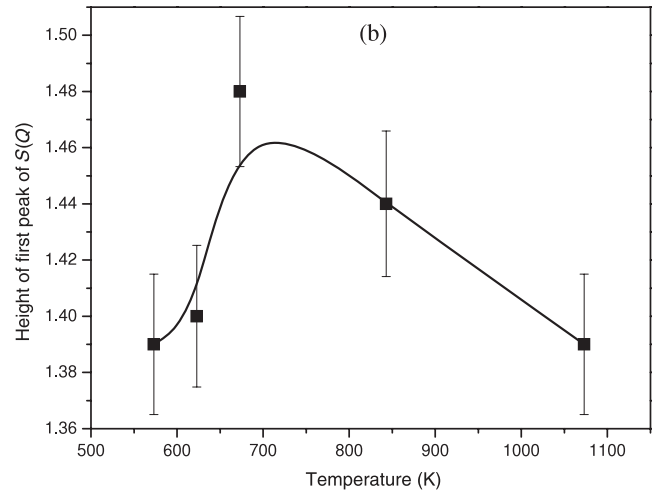
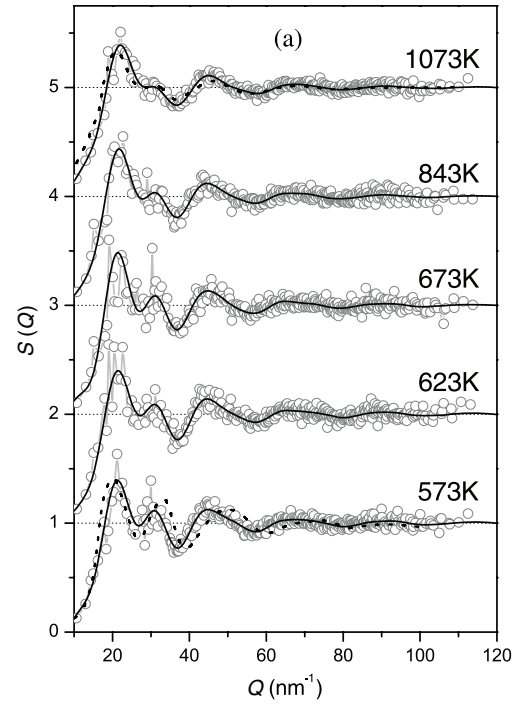
In a molecular dynamics simulation of liquid state, the structure factor  $S(Q)$  is an important physical quantity, which serves as a connection with experimental results. In one-element liquids,  $S(Q)$  can be obtained by Fourier transformation of the pair-correlation function  $g(r)$ ,

$$S(Q) = 1 + 4\pi\rho_0 \int [g(r) - 1] \frac{\sin Qr}{Qr} r^2 dr, \quad (1)$$

where  $\rho_0$  is the average number density of atoms. Considering that the calculation of  $S(Q)$  by equation (1) on a small simulation box may lead to significant errors, a direct calculation from the atomic coordinates in the simulations was also performed,

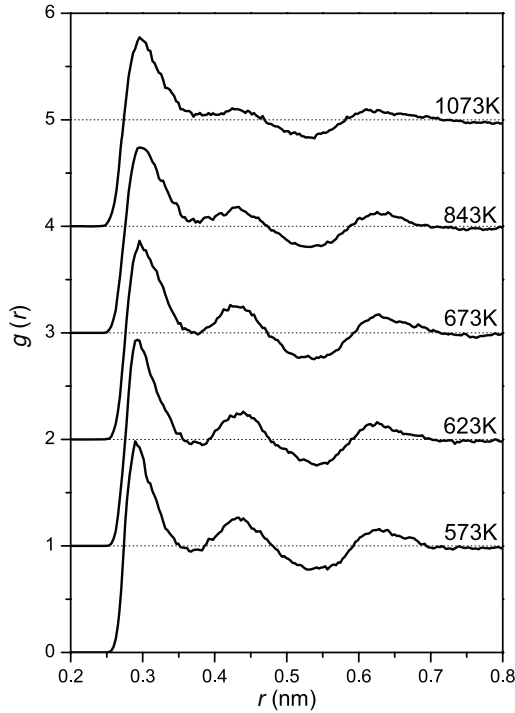
$$S(Q) = \frac{1}{N} \left\langle \sum_i \sum_{j \neq i} \exp(-i\vec{Q} \cdot \vec{r}_{ij}) \right\rangle - N\delta_{Q,0}, \quad (2)$$

where  $N$  is the total number of atoms,  $r_{ij}$  is the interatomic distance between atom  $i$  and  $j$ . The calculated results at five different temperatures from 573 to 1073 K are shown in figure 1(a). The experimental results obtained from neutron diffraction at 603 and 1073 K are also shown in figure 1(a). It can be easily found that the calculated structure factors by the two methods are in good agreement with each other, which indicates that the errors in the calculation of  $S(Q)$  by equation (1) on our simulation box are negligible. As can also be seen from figure 1(a), at a higher temperature 1073 K, the calculated  $S(Q)$  is in good agreement with the experimental result [11], especially the shoulder on the right-hand side of the first peak. As demonstrated in [26], its presence is a signature of local order resulting from covalent bonding, implying a nonsimple local structure in liquid Te. At a lower temperature 573 K, compared to the experimental data at 603 K [8, 9],



**Figure 1.** (a) Structure factors of liquid Te calculated by Fourier transform (solid line) and direct calculation (gray line and circle) at five different temperatures, compared with experimental data (dash line) at 1073 K from [11] and 603 K from [8, 9]; (b) temperature-dependent height of the first peak in  $S(Q)$  of the simulated liquid Te. The error bars correspond to the root-mean-square fluctuations.

although the second and the third peaks are slightly shifted to larger  $q$  values, the overall agreement between them is acceptable. Compared to the experimental results [8, 9], we can also find that our calculated results reproduce the evolution of structure factor with temperature: (i) the positions of the first peak and the second one seem insensitive to temperature; (ii) with increasing temperature, the height of the second peak decreases monotonically in the whole temperature region from 573 to 1073 K, however, the height of the first peak shows a non-monotonic temperature-dependence. Figure 1(b) plots the first peak height of  $S(Q)$  as a function of temperature. It can be



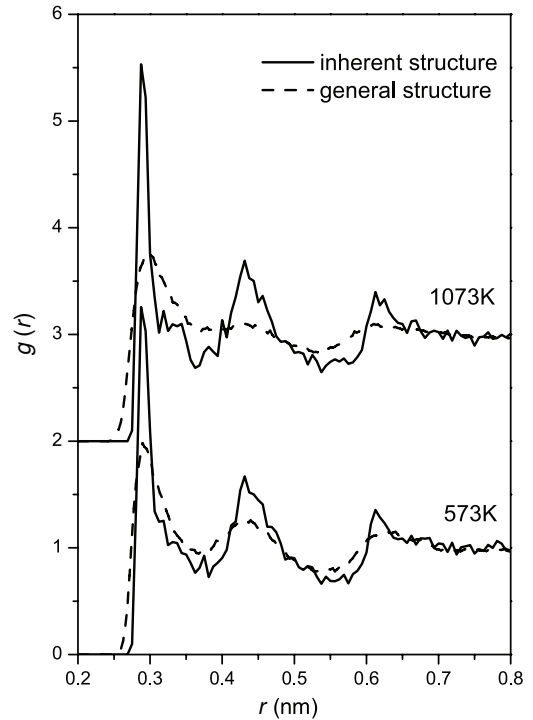
**Figure 2.** Pair-correlation functions of liquid Te from the general structures at five different temperatures.

seen that, with an increase of temperature, the first peak height increases in the low-temperature region from 573 to 673 K and decreases in the high-temperature region from 843 to 1073 K. In other words, there is an obvious extrema at around 723 K in the curve of peak height versus temperature. These results are in good agreement with experimental observation [4], indicating that a rapid structural change occurs in liquid Te with decreasing temperature from 723 to 573 K.

In the physics of liquids, the pair-correlation function  $g(r)$  is also an important physical quantity because, in principle, various properties of liquid materials can be estimated from the pair-correlation function when coupled with an appropriate theory. In the molecular dynamics simulations, the pair-correlation function can be calculated from the atomic coordinates according to equation (3),

$$g(r) = \frac{1}{\rho_0 N} \left\langle \sum_i \sum_{j \neq i} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle, \quad (3)$$

where  $N$  is the total number of atoms,  $\rho_0$  is the average number density of atoms,  $r_{ij}$  is the interatomic distance between atom  $i$  and  $j$ . Using the atomic coordinates in the molecular dynamics simulations, the pair-correlation functions of liquid Te, shown in figure 2, were calculated at five different temperatures ranging from 573 to 1073 K. As can be seen from figure 2, there are three peaks located at about 0.290, 0.430, and 0.620 nm respectively. It should also be noticed that the first peak is asymmetric and there is a shallow trough between the first peak and the second one, which indicate a nonsimple local structure in liquid Te. With increasing temperature, the position of the first peak presents a little shift towards large

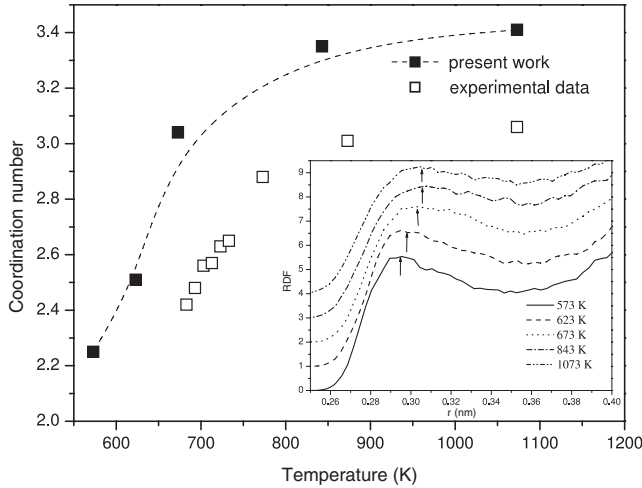


**Figure 3.** Pair-correlation functions of liquid Te from the inherent structures (solid line), compared with that from the general structures (dash line) at 1073 and 573 K.

$r$  value, however, the positions of the second peak and the third one are almost unchanged. The heights of the three peaks decrease with increasing temperature. In particular, the second peak becomes almost a shoulder at 1073 K. Moreover, the trough between the first peak and the second one becomes shallower with increasing temperature, and almost disappears at 1073 K. The evolution of these features is in good agreement with experimental results [8, 9]. We also calculated the pair-correlation functions from the inherent structures of liquid Te at 573 and 1073 K. The calculated results are shown in figure 3. We find that the first peak in  $g(r)$  from inherent structures, located at 0.287 nm, is sharper than that in  $g(r)$ , from the general structures, as are the second peak and the third one. As introduced in section 1, many results not only from simulation but also from experiment showed that the chain structure is preserved in liquid Te and a short-long alternation (about 0.280 and 0.290 nm in [13], about 0.280 and 0.295 nm in [17]) of the bonds takes place within the chains. Here, the splitting of the first peak between 0.280 and 0.295 nm does not occur; this may be due to the lengths of the two bonds being too close. It should also be noticed that an obvious shoulder appears in the right side of the first peak about 0.340 nm. The positions of the first peak and the shoulder are very close to the two characteristic bond lengths of Peierls distortion in trigonal Te (0.284 and 0.349 nm [3]). This implies that the Peierls-type distorted local atomic structure similar to that in crystalline Te can be still preserved in liquid Te in both supercooled- and normal-state.

Given the pair-correlation function, the average coordination number (CN) can be estimated according to equation (4)





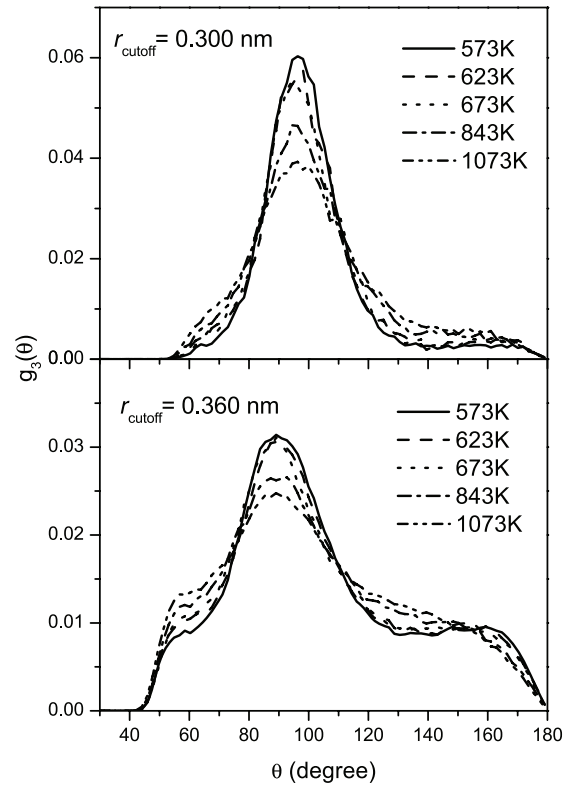
**Figure 4.** Temperature-dependence of the average coordination number. The inset displays radial distribution functions at five different temperatures and the arrow indicates the position of the first peak.

as in [27],

$$N = 2 \int_0^{r_{\max}} 4\pi r^2 \rho_0 g(r) dr, \quad (4)$$

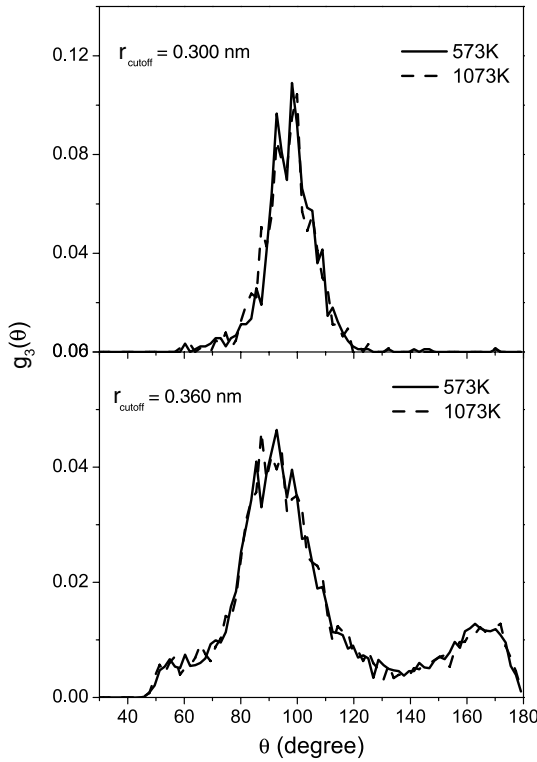
where  $r_{\max}$  is the position of the first peak in radial distribution function (RDF)  $4\pi r^2 \rho_0 g(r)$ ,  $\rho_0$  is the average number density of atoms. The RDF,  $r_{\max}$ , and CN from our simulations are all shown in figure 4. As can be seen that, in the low-temperature region from 573 to 673 K,  $r_{\max}$  increases gradually with increasing temperature; however, it hardly depends on temperature in the high-temperature region from 843 to 1073 K. Correspondingly, in the low-temperature region from 573 to 673 K, the coordination number increases steadily with an increase of temperature, which is in contrast to the behavior of a classical isotropic fluid. This suggests that, with decreasing temperature from 673 to 573 K, the volume expands and hence a negative thermal expansion coefficient is observed. However, in the high-temperature region from 843 to 1073 K, the coordination number seems almost unchanged with temperature. In order to draw a comparison between calculated and experimental results, the experimental coordination numbers at different temperatures are also given in figure 4. As demonstrated in [28], the overestimation of the width of the first neighbor peak leads to an overestimation of the number of first neighbors, however, the evolution of the coordination number with temperature is in good accordance with the experimental results.

To obtain more microscopic atomic structure information, we have also calculated the bond-angle distribution function  $g_3(\theta)$ , which is one type of three body distribution functions. The angle noted in  $g_3(\theta)$  is formed by a pair of vectors drawn from a reference atom to any other two atoms within a sphere of cutoff radius  $r_{\text{cutoff}}$ . Figure 5 gives the calculated bond-angle distribution functions of liquid Te from the general structures at five different temperatures. When  $r_{\text{cutoff}}$  is taken to be 0.360 nm, including the first peak and the shoulder on its right side in  $g(r)$  from inherent structures, the  $g_3(\theta)$



**Figure 5.** Bond-angle distribution functions from general structures at five different temperatures for  $r_{\text{cutoff}} = 0.300$  nm (upper) and  $r_{\text{cutoff}} = 0.360$  nm (lower).

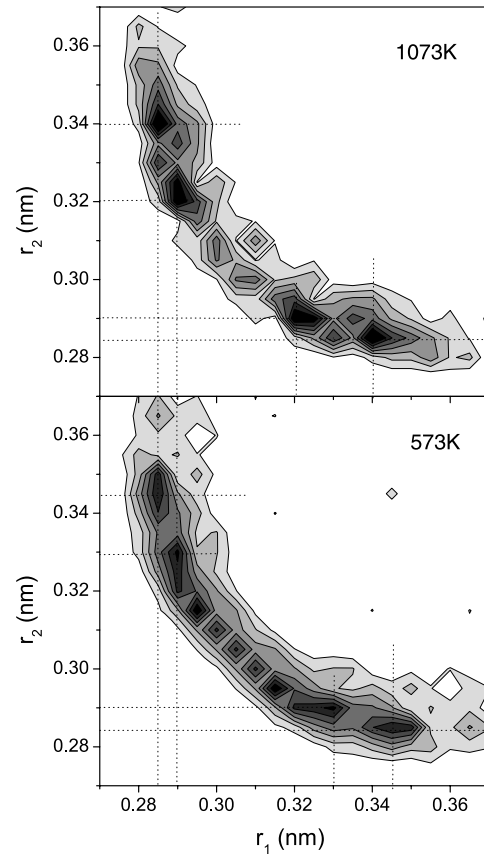
shows three peaks. For the first peak, its position is around  $60^\circ$  invariant with a change of temperature; but its height increases with increasing temperature. This indicates that the close-packed structure of atoms in liquid Te becomes more close-packed with increasing temperature. The second peak is located at  $\theta \sim 90^\circ$ , which is slightly less than that in trigonal Te ( $\theta \sim 103^\circ$  [3]). Its height increases with a decrease in temperature. Additionally, the third peak is located at around  $\theta \sim 160^\circ$ . It shifts slightly to the left side and its height is almost unchanged with increasing temperature. In the case of  $r_{\text{cutoff}} = 0.300$  nm, not including the shoulder in the right side of the first peak in  $g(r)$  from inherent structures, the  $60^\circ$  and the  $160^\circ$  peaks almost disappear, however, the second peak moves to about  $96^\circ$ , and obviously becomes higher. We have also calculated the bond-angle distribution function from the inherent structures at 573 and 1073 K. The results are shown in figure 6. When  $r_{\text{cutoff}}$  is taken to be 0.360 nm, compared to  $g_3(\theta)$  from general structures, the first peak is lower, while the second and the third peaks become more pronounced and of greater height. Moreover, the third peak appears at about  $167^\circ$ . The second and the third peaks seem to indicate that a Peierls-like distorted local atomic structure similar to that in crystalline Te is still preserved in liquid Te in both supercooled- and normal-state. This is consistent with that found in  $g(r)$  from the inherent structures (as shown in figure 3). In the case of  $r_{\text{cutoff}} = 0.300$  nm, the first and the third peaks disappear completely, indicating that at least one of the two bonds which form the  $167^\circ$  angle is included in the shoulder of the first peak



**Figure 6.** Bond-angle distribution functions from inherent structures at 573 and 1073 K for  $r_{\text{cutoff}} = 0.300$  nm (upper) and  $r_{\text{cutoff}} = 0.360$  nm (lower).

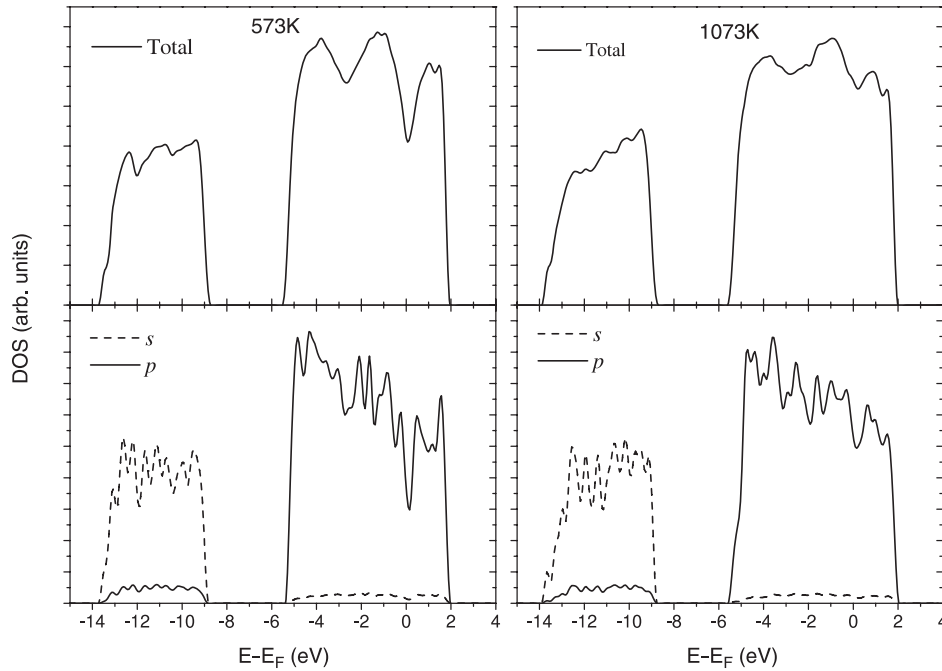
in  $g(r)$  from inherent structures. The second peak moves to  $100^\circ$ , which is very close to that in crystalline Te ( $\theta \sim 103^\circ$ , formed by two adjacent bonds within the chain of atoms), implying the chain structure of the crystalline Te is still present in liquid Te in both supercooled- and normal-state. This is consistent with the results of simulations by Bichara [13] and experimental observation by Kawakita and co-workers [17].

To gain further insight into the structural change in liquid Te, we have also calculated the angular limited bond–bond correlation function from the inherent structures as introduced in [29]. This function  $P(r_1, r_2)$  is defined as the probability of finding an atom C at a distance  $r_2$  from an atom B, which is at a distance  $r_1$  from the reference atom A. A constraint is placed on the position of atom C. Namely, the angle  $\theta$  formed by vectors  $\vec{BA}$  and  $\vec{BC}$  is constrained in a small range. Here, in order to investigate the correlation of two bonds which form the angle around  $167^\circ$  (i.e., the third peak in  $g_3(\theta)$  from inherent structures),  $\theta$  is chosen between  $160^\circ$  and  $170^\circ$ . The results at 573 and 1073 K are shown in figure 7. At a higher temperature 1073 K, the maxima of  $P(r_1, r_2)$  are mainly centered in four regions (0.285, 0.340 nm), (0.340, 0.285 nm) and (0.290, 0.320 nm), (0.320, 0.290 nm). This indicates that a short bond of length  $r_1$  (0.285 or 0.290 nm) is most probably followed by a longer bond of length  $r_2$  (0.340 or 0.320 nm), and vice versa. The values that  $r_1 = 0.285$  nm and  $r_2 = 0.340$  nm are very close to the lengths of two characteristic bonds of Peierls distortion in trigonal Te (two strong and short interchain covalent bonds 0.284 nm and four longer and weaker interchain bonds 0.349 nm [1, 3]). This indicates that the



**Figure 7.** Comparison of the angular limited bond–bond correlation function ( $\theta \sim 167^\circ$ ) at  $T = 1073$  K (upper) and  $T = 573$  K (lower).

Peierls-type distorted local atomic structure similar to that in crystalline Te is still preserved in normal liquid Te at 1073 K. The values of  $r_1 = 0.290$  nm and  $r_2 = 0.320$  nm indicate the occurrence of two new characteristic bonds in liquid Te. The bond length 0.290 nm is inside the first peak of  $g(r)$ , and the bonding is clearly covalent. The occurrence of the third bond with bond length 0.320 nm is in accordance with experimental observations by different researchers [9, 12, 14], although 0.320 nm is slightly larger than the experimental and theoretical results 0.310 nm. Moreover, from our results, it can be found that the two bonds  $r_1 = 0.290$  nm and  $r_2 = 0.320$  nm also form a Peierls-type distorted local structure, i.e., the short–long alternation of bonds, although the lengths of the two bonds are very different from those in crystalline Te. The characteristic bond lengths 0.285 and 0.290 nm are both inside the first peak of  $g(r)$ , suggesting a short–long alternation of the bonds within the chains of atoms in liquid Te. This is in agreement with the recent experimental results (0.282 and 0.299 nm) [14, 15] and theoretical results (0.280 and 0.290 nm) [13]. The existence of the characteristic bonds with bond length  $r_2 = 0.340$  nm and  $r_2 = 0.320$  nm also shows that an interchain correlation exists between the chains of atoms in liquid Te. However it should be noticed that the two bonds, especially  $r_2 = 0.320$  nm, are both shorter than the interchain bond length in crystalline Te 0.349 nm, indicating that the interchain correlation in liquid Te at 1073 K is stronger than that in crystalline Te. At a lower temperature 573 K, the



**Figure 8.** The total and local electronic density of states for liquid Te at 573 K (left panel) and 1073 K (right panel).

maxima of  $P(r_1, r_2)$  are also mainly centered in four regions (0.285, 0.345 nm), (0.345, 0.285 nm) and (0.290, 0.330 nm), (0.330, 0.290 nm). This also indicates that a short bond of length  $r_1$  (0.285 or 0.290 nm) is most probably followed by a longer bond of length  $r_2$  (0.345 or 0.330 nm), and vice versa. The short–long alternation of bonds  $r_1 = 0.285$  nm and  $r_2 = 0.345$  nm also indicate that the Peierls-type distorted local atomic structure similar to that in crystalline Te is still preserved in the supercooled liquid Te at 573 K. Similarly, the two bonds  $r_1 = 0.290$  nm and  $r_2 = 0.330$  nm also form a Peierls-type distorted local atomic structure, different from that in crystalline Te.

Comparing the results at 573 and 1073 K, it can be found that the two shorter bonds 0.285 and 0.290 nm are unchanged with temperature, but the two longer bonds change from 0.320 and 0.340 nm at 1073 K to 0.330 and 0.345 nm at 573 K, respectively. This indicates that the interchain correlation reduces when decreasing the temperature from 1073 to 573 K. Obviously, the Peierls-type distorted local atomic structures at 573 K correspond to a larger atomic volume than that at 1073 K. It can be expected that, with decreasing temperature, the lengths of the two short intrachain bonds are unchanged, but that of the two long interchain bonds become longer and longer, so that the Peierls-type distorted local atomic structures occupy larger and larger volume, resulting in the experimentally observed abnormal volume expansion from 723 to 573 K. So our results suggest that the change of the Peierls-type distorted local atomic structure with temperature may be responsible for the striking anomalies of many thermophysical properties of liquid Te. This novel mechanism of density anomaly for liquid Te is different from that of liquid water, in which tetrahedrally bonded local atomic structure plays an important role [30]. It is the first time that our work suggests a Peierls distorted

local atomic structure plays an important role for the density anomaly of liquid Te.

The microscopic atomic structure is correlated with the electronic structure. Here we also studied the electronic density of state (DOS) and the local density of states (LDOS), i.e., the DOS is decomposed into angular-momentum-resolved contributions. By projecting all the wavefunctions in a sphere of radius  $R$  around atom  $i$  onto the spherical harmonic  $(l, m)$ , we obtained the  $(l, m)$  angular momentum component of the atom  $i$ . The calculated DOS and LDOS of liquid Te are represented in figure 8. We can see that the major contribution to the density of states at the Fermi level  $E_F$  is mainly due to Te p orbital. Besides the feature of bond-angle distribution function mentioned above, this feature of DOS is indeed another condition that has to be fulfilled to allow a Peierls distortion of the local atomic environment as explained in [3]. It can also be found that there is an obvious dip in DOS at  $E_F$ , but it should also be noticed that the dip at 1073 K is shallower than that at 573 K. From LDOS, we can also conclude that the variation of the dip in DOS mainly results from the change of Te p orbital.

#### 4. Conclusions

In summary, the local atomic structures and electronic properties of liquid p-bonded element Te from normal- to supercooled-state were studied using *ab initio* molecular dynamics simulations and inherent structure formalism. The structure factor, pair-correlation function, average coordination number, bond-angle distribution function, angular limited bond–bond correlation function, and DOS were calculated. The calculated structure factors agree acceptably with available experimental data. There is an obvious maximum at around 723 K in the curve of first-peak-height of  $S(Q)$  versus temperature. This is in good agreement with experimental



observation, indicating that a rapid structural change occurs in liquid Te with a decrease in temperature from 723 to 573 K. With increasing temperature, in the low-temperature region from 573 to 673 K, the average coordination number increases gradually; but in the high-temperature region from 843 to 1073 K, it remains almost constant, indicating a rapid structural change of liquid Te in the temperature region from 573 to 673 K. The evolution of the coordination number with temperature is in good accordance with the experimental results. Our calculated results for the angular limited bond–bond correlation functions first show that there are two types of Peierls distorted local atomic structures in liquid Te: the lengths of short and long bonds in the first type are similar to that in crystalline Te, while the lengths of short and long bonds in the second type are very different from that in crystalline Te. With decreasing temperature, the lengths of the two short intrachain bonds are unchanged, but those of the two long interchain bonds become longer, indicating that the interchain correlation reduces when decreasing the temperature from 1073 to 573 K. Our results suggest that the change of the Peierls-type distorted local atomic structures with temperature may be responsible for the striking anomalies of many thermophysical properties of liquid Te. The calculated DOS and LDOS shows that there is an obvious dip in DOS at  $E_F$ , but the dip at 1073 K is shallower than that at 573 K. The variation of the dip in DOS mainly results from the change of Te p orbital.

### Acknowledgment

This work was supported by the School Scientific Research Foundation of Ludong University.

### References

- [1] Pearson W B 1972 *The Physics and Chemistry of Metals and Alloys* (New York: Wiley)
- [2] Perron J C 1967 *Adv. Phys.* **16** 657
- [3] Gaspard J P, Pellegatti A, Marinelli F and Bichara C 1998 *Phil. Mag. B* **77** 727
- [4] Tsuchiya Y 1991 *J. Phys. Soc. Japan* **60** 227
- [5] Kresse G, Furthmüller J and Hafner J 1994 *Phys. Rev. B* **50** 13181
- [6] Enderby J E and Gay M 1980 *J. Non-Cryst. Solids* **35/36** 1269
- [7] Takeda S, Tamaki S and Waseda Y 1984 *J. Phys. Soc. Japan* **53** 3830
- [8] Menelle A, Bellisent R and Flank A M 1989 *Physica B* **156/157** 174
- [9] Menelle A, Bellisent R and Flank A M 1987 *Europhys. Lett.* **4** 705
- [10] Hafner J 1990 *J. Phys.: Condens. Matter* **2** 1271
- [11] Misawa M 1992 *J. Phys.: Condens. Matter* **4** 9491
- [12] Bichara C, Johnson M and Raty J Y 2005 *Phys. Rev. Lett.* **95** 267801
- [13] Bichara C, Raty J Y and Gaspard J P 1996 *Phys. Rev. B* **53** 206
- [14] Tsuzuki T, Yao M and Endo H 1995 *J. Phys. Soc. Japan* **64** 485
- [15] Tsuzuki T, Sano A, Kawakita Y, Ohmasa Y, Yao M, Endo H, Inui M and Misawa M 1993 *J. Non-Cryst. Solids* **156–158** 695
- [16] Endo H 1993 *J. Non-Cryst. Solids* **156–158** 667
- [17] Kawakita Y, Yao M and Endo H 1999 *J. Non-Cryst. Solids* **250–252** 447
- [18] Molina D and Lomba E 2003 *Phys. Rev. B* **67** 094208
- [19] Stillinger F H 1995 *Science* **267** 1935
- [20] Sastry S, Debenedetti P G and Stillinger F H 1998 *Nature* **393** 554
- [21] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [22] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [23] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [24] Wang Y and Perdew J P 1991 *Phys. Rev. B* **44** 13298
- [25] Nosé S 1984 *J. Chem. Phys.* **81** 511
- [26] Gu T, Bian X, Qin J and Xu C 2005 *Phys. Rev. B* **71** 104206
- [27] Mizuki J, Kakimoto K, Misawa M, Fukunaga T and Watanabe N 1993 *J. Phys.: Condens. Matter* **5** 3391
- [28] Stadler R and Gillan M J 2000 *J. Phys.: Condens. Matter* **12** 6053
- [29] Bichara C, Pellegatti A and Gaspard J P 1993 *Phys. Rev. B* **47** 5002
- [30] Debenedetti P G 2003 *J. Phys.: Condens. Matter* **15** R1669