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# Molecular-dynamics simulation of structural and thermodynamic properties of boron nitride

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**Abstract.** Structural and thermodynamic properties of cubic boron nitride (c-BN) under pressure and for varying temperature are studied by molecular-dynamics (MD) simulation with the use of a well-tested Tersoff potential. Various physical quantities including the thermal expansion coefficient and heat capacity are predicted. Our simulation is extended to study liquid boron nitride at various densities.

## 1. Introduction

With the many exciting developments, the zinc-blende structure nitrides have been arousing increasing interest because of their potential inherent advantages [1–5]. Indeed, they have excellent physical hardness, extremely large heterojunction offsets, high thermal conductivity and high melting temperature. One promising candidate, boron nitride, has many applications in tool coating and packaging for operation in adverse environments. Boron nitride is unique among the III–V materials in its ability to form strong covalent bonds. Recently, there has been great progress in the enhancement of crystal quality, p-type control and the growth method of c-BN [6–10]. Moreover, electrically active, moderately shallow n(Si)- and p(Be)-type dopants exist for c-BN ( $E_g \approx 6.4$  eV), and considerable interest in this material as regards microelectronics applications has been stimulated by the recent creation of a p–n junction diode having a portion of its emission spectrum in the ultraviolet [11]. Boron nitride is similar to carbon in having three crystalline structures: a layered hexagonal structure (h-BN) which is similar to that of graphite, the cubic zinc-blende structure (c-BN), analogous to that of diamond, and a rare hexagonal wurtzite structure (w-BN) corresponding to lonsdaleite. Despite extensive studies, some interesting problems remain unresolved, including those of a high-pressure and high-temperature phase of c-BN. This has prompted us to explore its structural and thermodynamic properties. There have been many first-principles theoretical studies [3, 12] of the structural properties of BN. While these methods generally give the most accurate results, they cannot be applied to problems which require much larger system sizes or longer simulations. On the other hand, empirical interatomic potentials while simple in nature, have proven to be efficient for calculations of physical properties of semiconductors. They are used for investigating many aspects, such as microcluster formation [13, 14], amorphous structure formation [15, 16], epitaxial growth

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[17, 18] and surface reconstructions [19]. One of them, the three-body Tersoff potential [20–22], has been used for the treatment of both elemental and complex covalent systems.

In our calculation, we use the original formulation of Tersoff's potential [20] which is adapted for one-component systems, since we treat BN as equivalent to a one-component system. Using this empirical model, we describe in the present study the results of classical molecular-dynamics simulation used to simulate structural and thermodynamic properties of boron nitride. This method has been extensively used for investigations of equilibrium and nonequilibrium properties [23]. Such diverse studies as those of the properties of fluids [24, 25], the crystal–amorphous transition [26], melting [27], growth mechanisms [28] and radiation damage [29] have all employed molecular-dynamics simulations. In our work, this method is used to predict different properties of BN under pressure and for varying temperature. This study can be a first step towards simulating nonequilibrium properties of BN using Tersoff's potential.

The remainder of this paper is organized as follows. Section 2 describes our calculation model and numerical method. Our results are presented in section 3, followed by a conclusion in section 4.

## 2. Simulation details

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been the most successful in that it reproduces many of the properties of the semiconductors. The form of the energy  $E$ , between two neighbouring atoms  $i$  and  $j$ , is taken to be [20]

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (1)$$

with

$$V_{ij} = f_C(r_{ij}) [a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \quad (2)$$

where

$$\begin{aligned} f_R(r) &= A \exp(-\lambda_1 r) \\ f_A(r) &= -B \exp(-\lambda_2 r) \\ f_C(r) &= \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi}{2} \frac{(r - R)}{D} \right] & R - D < r < R + D \\ 0 & r > R + D. \end{cases} \end{aligned}$$

$b_{ij}$  is the many-body order parameter describing how the bond-formation energy is affected by the local atomic arrangement due to the presence of other neighbouring atoms (the  $k$  atoms). It is a many-body function of the positions of atoms  $i$ ,  $j$ , and  $k$ . It has the form

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/(2n)} \quad (3)$$

with

$$\begin{aligned} \zeta_{ij} &= \sum_{k (\neq i, j)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \\ g(\theta) &= 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2} \end{aligned}$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/(2n)}$$

$$\eta_{ij} = \sum_{k (\neq i, j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3].$$

$\zeta$  is called the effective coordination number and  $g(\theta)$  is a function of the angle between  $r_{ij}$  and  $r_{ik}$  that has been fitted to stabilize the tetrahedral structure. We note that  $\lambda_3$  and  $\alpha$  are set equal to zero [20].

**Table 1.** The adjusted Tersoff parameters for BN in the zinc-blende structure.

$A$ (eV)	1393.6
$B$ (eV)	346.7
$\lambda_1$ ( $\text{\AA}^{-1}$ )	3.468
$\lambda_2$ ( $\text{\AA}^{-1}$ )	2.220
$n$	0.72751
$h$	-0.57058
$\beta$	$1.5724 \times 10^{-7}$
$c$	38049
$d$	4.384
$R$ ( $\text{\AA}$ )	1.95
$D$ ( $\text{\AA}$ )	0.20

Boron nitride and carbon have important physical characteristics in common. They share a number of similar physical properties including high melting temperatures ( $>3000$  K), large bulk moduli, high thermal conductivities and chemical inertness [30–32]. In addition, the phase diagrams of c-BN and carbon are very similar. This has prompted us to use carbon's parameters as a starting point for fitting the potential parameters to structural properties of BN. To our knowledge, no parameters have been found for the Tersoff potential which fit crystalline BN. Our fitted potential parameters are summarized in table 1. They differ slightly from carbon's parameters listed in reference [21].

We carry out our MD simulations within the canonical  $NVT$ -ensemble. We simulate 216 atoms in a simple cubic simulation cell with periodic boundary conditions. To integrate the Newtonian equations of motion, we use the fifth-order predictor–corrector algorithm with a time step of  $1.52 \times 10^{-15}$  s. After 20 000 iterations ( $\approx 30$  ps), different average properties are calculated.

**Table 2.** Peak distances and numbers of pairs for cubic BN in the zinc-blende structure.

Peak	Distance ( $\text{\AA}$ )	Number of pairs
First	1.569 <sup>a</sup> , 1.565 <sup>b</sup>	4.00 <sup>a</sup>
Second	2.560 <sup>a</sup> , 2.556 <sup>b</sup>	12.04 <sup>a</sup>
Third	3.007 <sup>a</sup> , 2.997 <sup>b</sup>	12.05 <sup>a</sup>
Fourth	3.628 <sup>a</sup> , 3.615 <sup>b</sup>	6.00 <sup>a</sup>

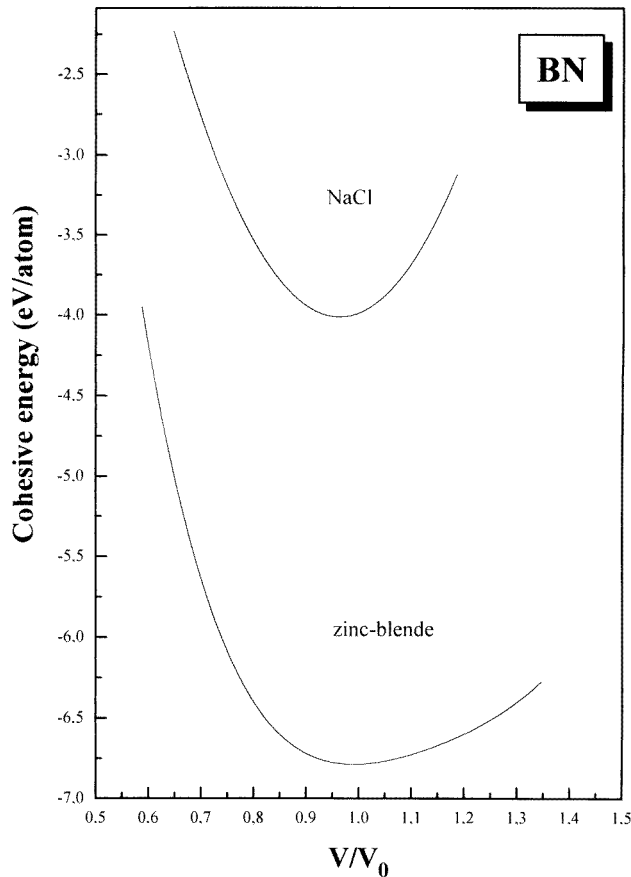
<sup>a</sup> Present work.

<sup>b</sup> Calculated from the experimental value of the lattice parameter taken from reference [12].

### 3. Numerical results

#### 3.1. Structural properties

The first step of our study is that of examining the structural properties of cubic BN at  $T = 300$  K in order to test the accuracy of our potential. We calculate the pair distribution function  $g(r)$  for cubic BN in the zinc-blende structure. The fourth peaks appear at 1.569, 2.560, 3.007 and 3.628 Å in good agreement with the experimental values of reference [12]. These results are summarized in table 2.



**Figure 1.** The cohesive energy as a function of the relative volume  $V/V_0$  ( $V_0$  is the equilibrium volume of the zinc-blende structure) for two phases of BN.

Figure 1 displays the cohesive energy versus the relative volume for BN in the zinc-blende structure. The curve is fitted to the equation of state of Murnaghan [33] from which we obtain the equilibrium lattice parameter, the bulk modulus, its derivative and the cohesive energy. The results are given in table 3 along with the experimental measurements [12, 34–37] and the recent *ab initio* calculations [3, 32, 38–41]. The overall agreement confirms the validity of our adjusted potential parameters. We notice that the lattice parameter for the zinc-blende structure of BN is 3.623 Å in excellent agreement with the experimental value of 3.615 Å [12] (with an accuracy of 0.22%). For the bulk modulus and the cohesive energy, the

**Table 3.** Equilibrium properties of BN in the zinc-blende and rock-salt phases compared with the results from the first-principles calculations and experiments. The experimental carbon data are listed for comparison.

	BN					Carbon
	Zinc-blende			Rock-salt		Diamond
	Present	Calculation	Experiment	Present	Calculation	Experiment
Lattice constant ( $\text{\AA}$ )	3.623	3.56–3.77 <sup>a</sup>	3.615 <sup>b</sup>	3.580	3.500 <sup>e</sup> 3.493 <sup>f</sup>	3.567 <sup>g</sup>
$B$ (Mbar)	3.653	3.53–4.12 <sup>a</sup>	3.69–3.82 <sup>c</sup>	4.80	4.06 <sup>e</sup> 4.25 <sup>f</sup>	4.42 <sup>g</sup>
$B'$	3.94	3.1–3.6 <sup>a</sup>	4.0–4.5 <sup>c</sup>	4.59	3.70 <sup>e</sup>	4 <sup>g</sup>
Cohesive energy (eV/atom)	6.7117		6.6800 <sup>d</sup>	4.0088		7.37 <sup>g</sup>

<sup>a</sup> From references [3, 32, 38–41].

<sup>b</sup> From reference [12].

<sup>c</sup> From references [35–37].

<sup>d</sup> From reference [34].

<sup>e</sup> From reference [40].

<sup>f</sup> From reference [32].

<sup>g</sup> From reference [52].

accuracies are about 1%–4% and 0.47%, respectively. In order to make some comparison, the structural properties of carbon in the diamond phase are listed in table 3. Despite some differences in details, the general features of the equilibrium structural results are very similar. Thus the potential parameters of *c*-BN can be derived from those conventionally accepted for carbon.

In order to test the transferability of this set of potential parameters, we study the compound BN, first under pressure, and then for varying temperature. Under pressure, BN transforms to the rock-salt structure [40]. Indeed, using the same set of parameters, we give in figure 1 the curve representing the cohesive energy versus the relative volume for BN for the high-pressure NaCl-type phase. The equilibrium lattice constant is 3.58  $\text{\AA}$  (see table 3). This result agrees well with the calculations carried out by Christensen and Gorczyca [40] and Wentzcovitch and co-workers [32] using *ab initio* methods (with an accuracy of 2%).

However, the bulk modulus of the rock-salt structure is seen to be overestimated (20% error) if we compare it to those of references [40] and [32]. This result shows that the accuracy for BN in the rock-salt phase is less than that for BN in the zinc-blende phase. This may be due to the omission of explicit ionic behaviour for the present potential.

It is also of interest to calculate the pressure of the transition between the zinc-blende and the rock-salt structure. The predicted value of the pressure of the transition obtained by using our potential corresponds to 3.94 Mbar. We point out that no experimental measurements have been made in this field. Other calculations predict that  $P_t = 8.5$  Mbar [40]. This disagreement could be due to the overestimation of the rock-salt bulk modulus that arises for the reason cited above. It has been expected that the ionic behaviour would prove rather difficult to model with this form of potential (a Tersoff potential). In particular, this potential has encountered great difficulty in describing with comparable accuracy the zinc-blende and the rock-salt structures of SiC [22]. Thus, for BN in the rock-salt phase, the

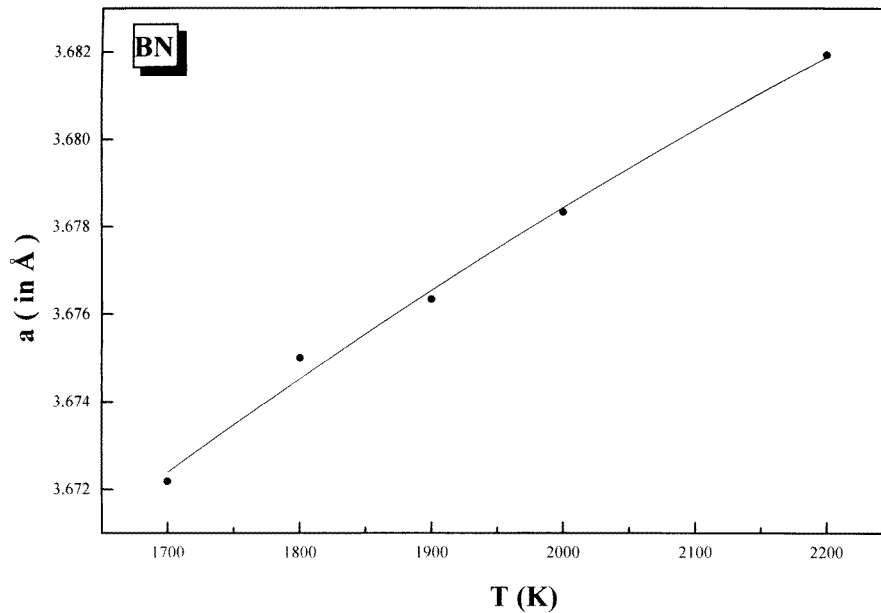
accuracy is certainly less than for the zinc-blende phase. It is not surprising that BN can be transformed under pressure to the NaCl structure with high density. Indeed, the mechanism of the structural transition from the structure with coordination number  $N_c = 4$  to that with  $N_c = 6$  is well demonstrated by the use of a computational method based on total-energy calculations [42–45]. Recent studies [46] show that the structural phase transition of the  $A^N B^{8-N}$  semiconductors is related to the bonding character.

### 3.2. Thermodynamic properties

In this paper, we will concentrate on the results for the thermal expansion and specific heat of BN in the zinc-blende phase. Since the molecular-dynamics method treats the motion of the atoms classically, it will correctly determine the thermal expansion coefficient ( $\alpha$ ) and the specific heat ( $C_v$ ) above the Debye temperature, where quantum effects can be neglected. The quantum mechanics corrections will be important for thermodynamic quantities like the specific heat and thermal expansion below the Debye temperature. Therefore, in the present paper, we will display results for temperatures above 1700 K (the Debye temperature for BN being 1700 K) [47]. In MD simulation, the linear thermal expansion coefficient  $\alpha_l$  can be computed directly from the definition

$$\alpha_l = \frac{1}{a} \left. \frac{\partial a}{\partial T} \right|_P \quad (4)$$

where  $a$  is the lattice parameter. Therefore, we consider the temperature variation of the lattice constant of cubic BN above 1700 K at zero pressure. A molecular-dynamics simulation is performed on an  $NVT$ -ensemble at each temperature to equilibrate the system and then to determine the corresponding zero-pressure lattice constant. In figure 2, we display the variation of the lattice parameter versus temperature, which is a polynomial



**Figure 2.** The lattice parameter as a function of temperature for BN in the zinc-blende structure.

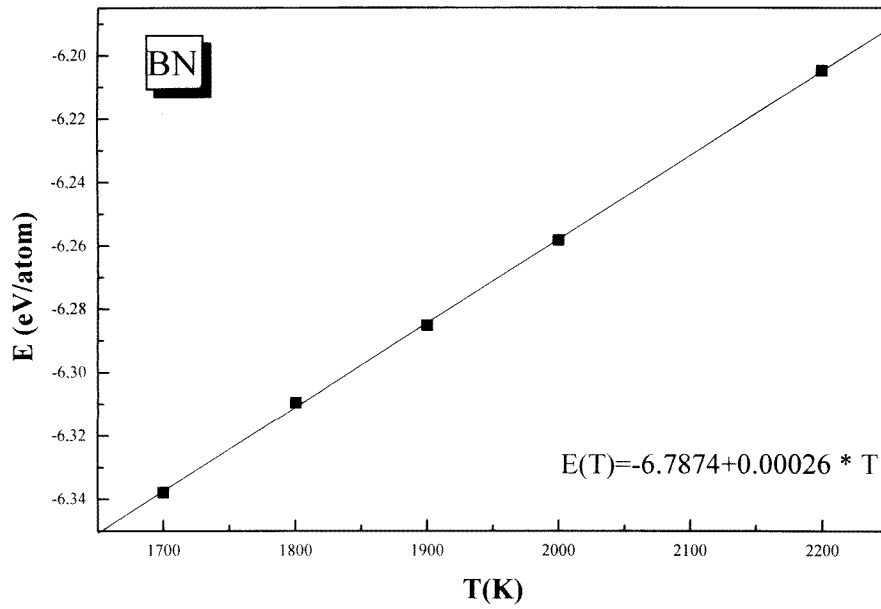


Figure 3. The total energy (per atom) of the system as a function of temperature.

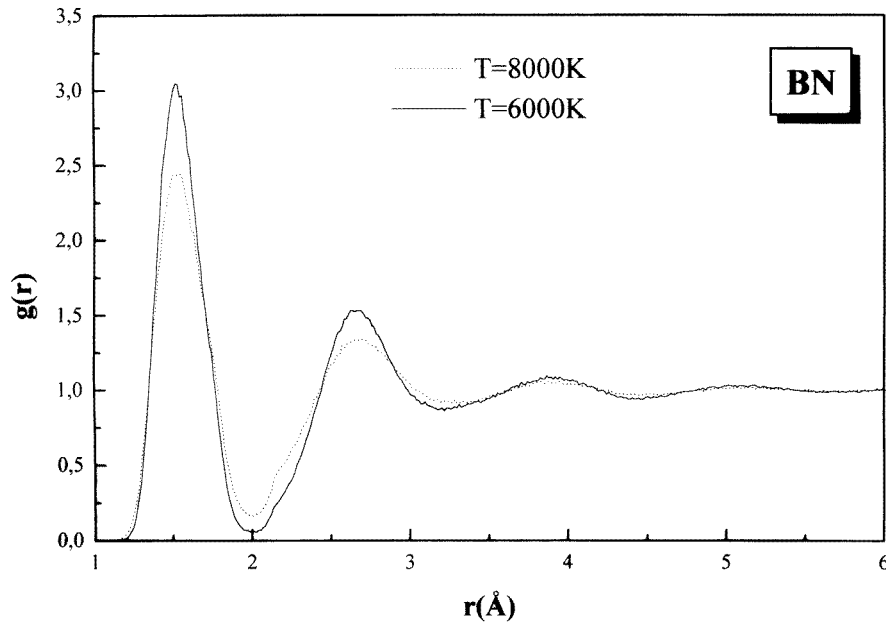


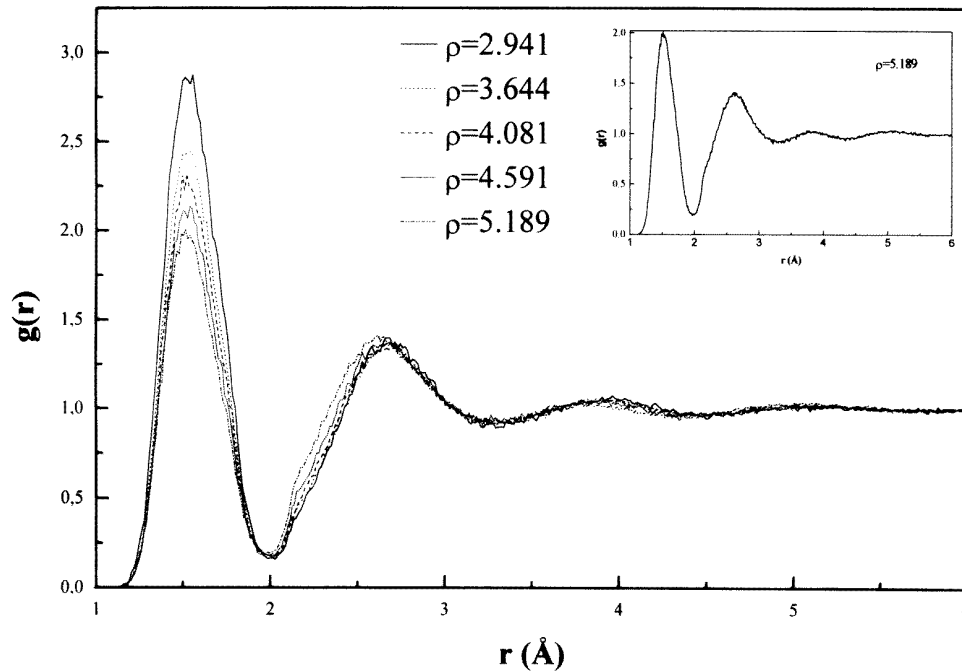
Figure 4. Calculated pair correlation functions for liquid c-BN at 6000 K (solid line) and 8000 K (dotted line).

function given by the following equation:

$$a(T) (\text{Å}) = 3.6180 + 4.1972 \times 10^{-5} T - 5.8971 \times 10^{-9} T^2. \quad (5)$$



The linear ( $\alpha_l$ ) and bulk ( $\alpha_v$ ) thermal coefficients determined from equation (5) are  $5.96 \times 10^{-6} \text{ K}^{-1}$  and  $1.79 \times 10^{-5} \text{ K}^{-1}$ , respectively. Recently, Solozhenko [48] has determined the volume coefficient of thermal expansion ( $\alpha_v = 3\alpha_l$ ) and found that, above 1300 K,  $\alpha_v$  becomes temperature independent, and is equal to  $1.76 \times 10^{-5} \text{ K}^{-1}$ . This last result agrees well with our calculation. We point out that the thermal expansion coefficient of cubic BN is smaller than those of many semiconductors such as AlN, BP, GaP, Si, and Ge; only diamond has a slightly smaller value [49]. The total energy of the system as a function of temperature is plotted in figure 3. From the slope of the energy–temperature curve, we estimate the specific heat of the system to be  $C_v = 3.02k_B$  at high temperatures. This constant value corresponds to the classical Dulong–Petit result ( $3k_B$ ), which is obtained at high temperatures for all solids.



**Figure 5.** A comparison of the pair correlation functions of liquid boron nitride obtained by using different densities.

In order to test the behaviour of the zinc-blende structure of BN at high temperature within the Tersoff potential model, we have run the molecular-dynamics simulation at a number of temperatures ranging from 6000 K to 8000 K. The heating is performed for 121 picoseconds for each temperature using Andersen's method [50] for temperature control. The pair correlation functions  $g(r)$  at  $T = 6000 \text{ K}$  and  $T = 8000 \text{ K}$ , plotted in figure 4, exhibit sharp nearest-neighbour peaks and have an oscillatory tail around the value of 1. The corresponding densities are found to be  $4.59 \text{ g cm}^{-3}$  for  $T = 6000 \text{ K}$  and  $4.08 \text{ g cm}^{-3}$  for  $T = 8000 \text{ K}$ . The pair correlation functions obtained from our simulation are in general similar to those of liquid carbon [21]. It appears that this potential model also gives a qualitatively correct description for liquid BN between 6000 K and 8000 K.

We have also performed further simulations to study the structure of the liquid BN for  $T = 8000 \text{ K}$  but using different densities. The resulting of pair correlation functions

**Table 4.** The variation of the coordination number of liquid BN as a function of density.

Density $\rho$ (g cm <sup>-3</sup> )	Coordination number
2.941	2.47
3.644	2.58
4.081	2.75
4.591	2.87
5.189	3.07

are compared in figure 5. Table 4 lists the average coordination numbers for liquid BN. It is interesting to note that the coordination number obtained for liquid BN decreases significantly with decreasing density. We found that as the density becomes lower, the percentage of twofold atoms increases. This tendency is clearly seen from table 4. Similar trends were found for liquid carbon [51].

We found that the structure of liquid boron nitride for high density (5.189 g cm<sup>-3</sup>) is qualitatively different to that for low density (2.941 g cm<sup>-3</sup>). Indeed, we notice that, on going from low to high density, the first peak mainly decreases when a slight increase in the second peak occurs. It is important to notice that the first and second peaks tend to have the same magnitude at high density (see figure 5). This feature is also similar to the tight-binding molecular-dynamics result obtained for liquid carbon [51].

#### 4. Conclusion

In conclusion, we have presented a simulation method for the calculation of the structural and thermodynamic properties of BN. The results confirm the validity of the model used ( Tersoff potentials) for the BN compound. This empirical approach also gives a good description of liquid BN. We have shown that our potential has sufficient accuracy and efficiency for a realistic simulation study of the structural and thermodynamic properties of BN. Now, it will be interesting to use the molecular-dynamics method with the Tersoff potential to simulate the growth of BN for application in device fabrication. Finally, we hope that this simple model can be used to simulate new phase transformations of the group III nitride family.

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