A tight-binding potential for the simulation of solid and liquid iodine

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Abstract
In this work, we suggest an interatomic potential for iodine applicable to the
simulation of the condensed phases of the halogen within the temperature and
density range accessible to experiments. The potential includes an attractive
term that is partitioned into directional chemical bonding with a many-particle
character and a pairwise interaction. Despite its simplicity, the potential
reproduces the crystal structure of solid iodine, the presence of atomic phases
with increasing pressure, and the metallic or insulating character of the solid
phases. Finally, we present preliminary simulation results for fluid iodine.

1. Introduction

The physics of the chemical bond in iodine poses a considerable challenge to scientists working
in the field of condensed matter theory and computer simulation. Whereas tight-binding
molecular dynamics and Monte Carlo simulations are available for VIb elements such as
Se in their liquid phases [1], we still lack a description of iodine at a comparable level. In
its condensed phases, a delicate interplay between covalent and dispersive contributions to
the chemical bond—operative on different energy and length scales—leads to the formation
of bonds distinct from ones of purely covalent or van der Waals character. At normal
conditions, iodine forms orthorhombic molecular crystals consisting of I_2 species (*Cmca* space
group [2, 3]), with nearest-neighbour distances of 2.715 Å that are elongated with respect to
those in the gas phase (2.670 Å), and next-nearest-neighbour distances of 3.496 Å that are
considerably shorter than the presumed van der Waals diameter of 4.3 Å [3]. Details of the
structure at high pressures [4] have been a matter of dispute [5, 6], but there is clear evidence
for a nonmetal-to-metal transition at a pressure of 16 GPa, as observed in the pioneering work

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of Drickamer and co-workers [7, 8]. X-ray diffraction data suggest the existence of body-centred—orthorhombic, cubic, and tetragonal—atomic phases at higher pressure values [9–13]. We note that high-quality *ab initio* studies of the solid-state phases with geometries based on the x-ray diffraction data have been performed with a special emphasis on the nature of the metal–nonmetal transition [14–17]. The formation of bands in molecular solid iodine has also been rationalized within a tight-binding scheme [18].

A crossover from nonmetallic to metallic behaviour similar to that in the solid has been observed for liquid iodine, which can be described as a molecular fluid with a local parallel alignment of I_2 molecules [19]. It is due to the work of Ricci, Buontempo, and co-workers that information on the structural properties of liquid iodine at high pressures is available [20, 21]. From these studies, the following picture emerges. For pressures of up to 6 GPa, the nearest-neighbour distance seems to exceed that of the molecular solid at comparable pressures and temperatures. At 1000 K and 4.5 GPa, indications of a dissociation of iodine molecules are found, and the conductivity rises to 10^3–10^4 S cm^{-1} at pressures of $p \simeq 3.5$ GPa and temperatures of $T \simeq 915$ K [22]. Recently, a percolation approach has been suggested to explain this crossover from nonmetallic to metallic behaviour [23].

Selenium melts exhibit a strong network character with nearest-neighbour interactions mediated by a sequence of covalent bonds of comparable strength. Consequently, a less accurate description of nonbonding interactions—or their complete absence—does not affect the global properties of a simulated system [1, 24, 25]. For iodine at normal conditions, however, only nearest-neighbour interactions within pairs of atoms are dominated by a strong covalent character, and the structure will sensitively depend on the description of the nonbonding interactions. Whereas excellent pair potentials exist for the interactions between I_2 molecules in the molecular regime [20, 26], the simulation of high-density and high-temperature phases has to take into account the possibility of breaking or forming bonds and thus requires an atomic potential that permits the unified description of intramolecular and intermolecular interactions.

In this work, we suggest a simple tight-binding potential suitable for the simulation of solid and liquid iodine. In the next section, we present details of the tight-binding model and its numerical treatment, followed by a study of the geometry, electronic structure, and thermodynamics of solid iodine. In addition, we report preliminary results on the liquid phase. In the final section, the results are discussed with reference to experimental work and theoretical concepts of the nature of the chemical bond in iodine.

2. Model and methods

In this work, we describe the interactions between iodine atoms by a potential that incorporates both a pair contribution and the electronic energy stemming from the diagonalization of a one-electron (or tight-binding) Hamiltonian [27, 28]. Within this approach, the potential energy V of N iodine atoms is given by

$$V = \sum_{i<j} v_{ij}(r_{ij}) + 2\sum_{\alpha}^{occ} \lambda_\alpha. \tag{1}$$

The first term comprises all distinct pairs of atoms, giving rise to a potential energy contribution originating from pair potentials. The second sum runs over all occupied eigenstates with eigenvalues λ_α; the factor of two enters to account for the spin degeneracy. Whereas the pair contribution, by definition, does not depend on the mutual orientation of three or more atoms, the tight-binding energies are a function of the positions of all atoms considered within a simulation; this contribution has a genuine N-body nature. Throughout this work, we

will consider this property and do not apply any approximations—e.g. by using reduction schemes [29, 30]—to this interaction.

In the following, we specify the interactions just mentioned and present an approach for obtaining the corresponding parameters. The electronic structure of iodine is modelled by a tight-binding—or Hückel-like—Hamiltonian:

$$\hat{H} = \sum_{iajb} c_{ia}^{\dagger} c_{jb} t_{iajb} \tag{2}$$

where the $c_{ia}^{\dagger}/c_{ia}$ are creation/annihilation operators acting upon atomic orbitals i, j localized on atoms a, b. As in all simplified treatments of late-main-group elements, the atomic orbital basis is restricted to three valence p functions for each atom [1, 32, 33]. Without loss of generality, the valence orbital ionization potentials of the iodine atom can be used as the zero of energy. As a consequence, no diagonal terms appear in equation (2). All basis functions are assumed to be orthogonal. We use the potential energy curve of the di-iodide molecule, I_2, to parametrize the tight-binding interactions. It can be approximated by a potential of the form

$$V(r) = A \exp(-ar) - B \exp(-br). \tag{3}$$

In the case of $A = D_0 \exp(ar_0)$, $B = 2D_0 \exp(br_0)$, and $a = 2b$, the familiar Morse potential with a dissociation energy D_0 is recovered. We interpret the first term of equation (3) as a short-range pair repulsion induced by the core electrons and the Pauli principle. Usually, the second term is interpreted as a purely covalent contribution, which has to be recovered upon diagonalization of the Hamiltonian (2). This strategy has recently been applied by Koslowski and Vöhringer in a study of the I_3^- anion in a polarizable environment [33]. Once nonbonding interactions become important, the two-body part of the potential has to be supplemented by induced dipole interactions, with a leading term proportional to r^{-6}. As this only constitutes the leading term of a series expansion and other interactions give rise to a different scaling of $V(r)$ within a certain distance interval, we adopt the following strategy. The attractive part is subdivided into a tight-binding term weighted by $f_{TB}(r)$. In aggregates larger than the I_2 molecule, this term has a many-particle nature and depends on the position of all iodine atoms present in a system. In addition, we consider an attractive pair potential contribution with a weight $f_2(r)$, which is by definition not sensitive to orientational degrees of freedom. Summing up, we set

$$V(r) = A \exp(-ar) - B f_{TB}(r) \exp(-br) - B f_2(r) \exp(-br) \tag{4}$$

where $f_{TB}(r) + f_2(r) = 1 \; \forall r$ reproduces the I_2 potential. The function f_{TB} is equal to the bond order parameter of Sutton and co-workers [28] and Pettifor [29]. For the sake of simplicity and transparency, we set $f_{TB}(r)$ equal to a constant $c_{TB} = 1 - c_2$, although more complex forms are possible. An inverse-power-law representation of the attractive part of the long-range interaction describes the experimental potential better than the exponential used in equation (4) [34]. We arrive at

$$V(r) = A \exp(-ar) - c_{TB} B \exp(-br) - c_2 C/r^5. \tag{5}$$

Although this potential has been obtained from a representation of the potential energy of a pair of atoms, we reiterate that the electronic contribution in a system with more than two atoms has a many-body nature. For systems with more than two atoms, the first and the third term on the right-hand side of equation (5) give rise to the pair interactions of equation (1) via $v_{ij}(r_{ij}) = A \exp(-ar_{ij}) - c_2 C/r_{ij}^5$. The c_2-parameter can also be interpreted as a measure of dispersive interactions not incorporated in the short-ranged tight-binding term. We consider the dispersive interactions as approximately pairwise, whereas three-body and higher-order contributions such as the Axilrod–Teller interaction [31] are neglected. The singularity of the
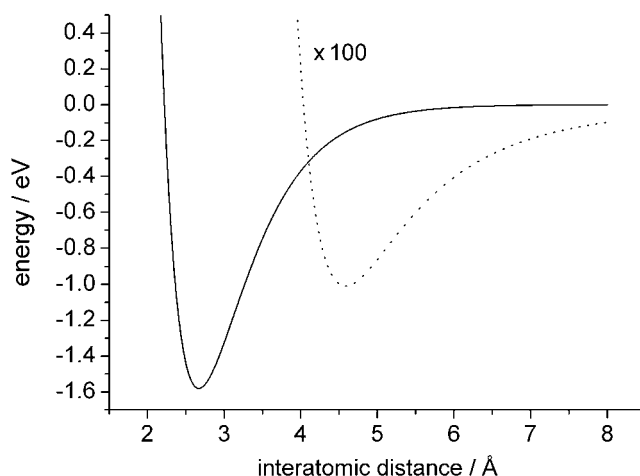
Figure 1. The potential energy of the I_2 molecule according to equation (5): total potential energy (solid curve) and classical pair contributions to the potential (dotted curve).

pair contribution to the potential at $r = 0$ can be lifted by an analytical continuation of the potential at distances small enough not to be relevant for interatomic contacts. Here, we have expanded the pair contribution around $r = 1$ Å into a Taylor series up to second order and have used this expansion to replace the original potential for $r < 1$ Å.

Details of the parametrization of a tight-binding part of a potential for iodine have been presented by Koslowski and Vöhringer [33]; we briefly summarize their approach here. Out of the six molecular orbitals of I_2 (σ, 2π, $2\pi^*$, and σ^*), five are occupied, and the σ^* MO is vacant. The resulting tight-binding energy is given by $V_{TB} = -2V_{pp\sigma}(r_0) = -B \exp(-br_0)$. For the ratio of σ and π matrix elements, we apply the Harrison parametrization leading to $V_{pp\pi}(r_0)/V_{pp\sigma}(r_0) = -0.284$ [36]. For nonlinear geometries, these matrix elements have to be weighted according to the Slater–Koster rules [37]. For the dissociation energy $D_0 = 1.58$ eV, the exponential parameters $a = 3.0$ Å^{-1} and $b = 1.6$ Å^{-1} and the equilibrium distance $r_0 = 2.670$ Å, we apply values that lie within the range given in the literature. The pre-exponential factors A, B, and C depend on these quantities via the requirements $V(r_0) = -D_0$ and $dV(r)/dr|_{r=r_0} = 0$. These requirements are fulfilled by $A = D_0 \exp(ar_0)/(a/b - 1)$, $B = D_0 \exp(br_0)/(1 - b/a)$, and $C = D_0 r_0^5/(1 - b/a)$. We arrive at $A = 4968.9$ eV, $B = 242.6$ eV, and $C = 459.4$ eV Å^5. The thus-obtained parameters do not depend on c_{TB}, and they are used for all calculations performed in this work. The c_{TB}-parameter not considered in the Koslowski and Vöhringer work is adjusted to match the crystal structure of solid iodine; details of this parametrization are provided in the next section. In the absence of chemical bonding, the expression (4) is reduced to a simple pair potential, which for the I_2 molecule exhibits an equilibrium distance of 4.1 Å and a binding energy of 10 meV for $c_{TB} = 0.93$. The interatomic distance lies close to the van der Waals diameter assumed for iodine, whereas the binding energy underestimates the depth of potentials applied to iodine's noble-gas neighbour, Xe, with 20 meV [36]. Both the total potential and its classical contributions are shown in figure 1 for a c_{TB}-parameter of 0.93. For the I_3^- anion, we obtain a $D_{\infty h}$ structure with bond lengths of 2.90 Å, which is close to the value encountered for compounds containing the ion.

Table 1. Iodine structure after the work of Bolhuis *et al* [3], Kitaigorodskii *et al* [2], and as computed in this work by MC optimizations in two and three dimensions. Unit-cell parameters a, b, c, nearest-neighbour distance r_1, next-nearest-neighbour distance within the ab-plane r_2, and $r_0 = (abc)^{1/3}$. The I_2 molecules are oriented within the ab-plane.

Parameters (Å)	Reference [3]	Reference [2]	2D	3D
a	4.686	4.79	4.856	4.763
b	9.784	9.78	9.713	9.432
c	7.136	7.26	—	7.341
r_1	2.715	2.68	2.721	2.721
r_2	3.496	3.56	3.492	3.478
r_0	6.891	6.98	—	6.909

3. The solid state

For the molecular crystal, the coupling between layers of iodine molecules is considered to be small, and basically involves nonbonding interactions. In order to study large systems, we have thus first focused on the geometry of a plane of iodine molecules representing the molecular phase of the halogen, and then extended these calculations to three dimensions. Structures were relaxed applying a zero-temperature Monte Carlo procedure until an energy convergence of 10^{-6} eV/atom was achieved. For the two-dimensional computations, we have used an extended unit cell containing 64 atoms with cyclic boundary conditions. Starting from a quadratic arrangement of iodine molecules, the following degrees of freedom have been the subject of the MC optimization: intramolecular distances, molecular orientation with reference to the underlying lattice, and the dimensions of the unit cell with the constraint of a constant area.

The structure of the global minimum depends sensitively on the partitioning of the attractive part of the total energy into contributions corresponding to covalent bonding and van der Waals-like interactions, as expressed by the c_{TB}- or c_2-parameter, respectively. With increasing c_{TB}, we observe the following structural and energetic trends: the atomic volume at the minimum increases, and this is accompanied by a decrease in the cohesive energy. The intramolecular distances decrease, and their intermolecular counterparts increase. This implies that a strong tight-binding contribution to the attractive part of the potential induces a stronger molecular character in terms of the chemical bond; the intramolecular distances approach the gas phase value, the cohesive energy vanishes, and the structure expands. This behaviour can be rationalized by the closed-shell nature of the iodine molecule; these entities do not interact by the formation of chemical bonds any more. We note that for c_{TB}-values larger than or equal to 0.97, we do not observe a minimum in the cohesive energy at all. For $c_{TB} = 0.93$, we find the closest agreement of the computed geometry with the experimental structure data; the results for this minimum are presented in table 1. To achieve a qualitative comparison of energy as a function of the system volume between the computed geometry and structures of higher symmetry, the area of the unit cell for planar arrangements has been multiplied by the experimental interlayer distance, $c = 3.568$ Å.

To extend these computations to more realistic three-dimensional structures, we have studied the energetics of models with four coupled layers as a function of the interlayer distance, where the geometry of each layer was taken from the calculations for two dimensions with a unit cell shifted by $a/2$ for every other layer. Compared to the 2D calculations, the minimum is shifted as regards both the atomic volume and the energy parameters (cf table 1). It is located at an atomic volume of 41.67 Å and an energy of -1.875 eV. With ~0.3 eV, the cohesive energy with reference to isolated I_2 molecules is only a small multiple of $k_B T$ at room temperature.
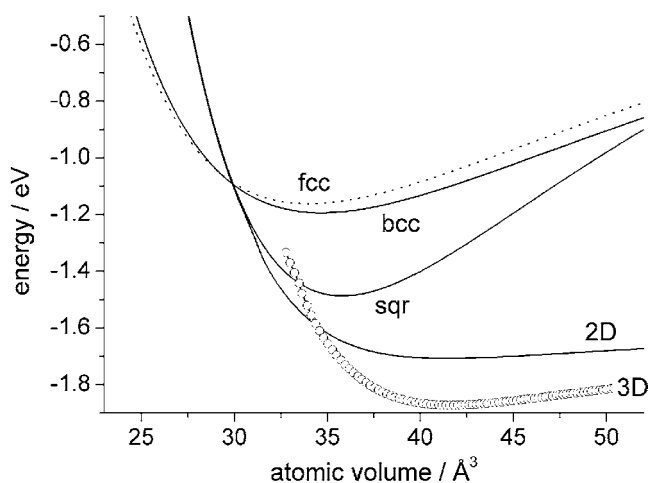
Figure 2. Internal energy per pair of iodine atoms in electronvolts as a function of the atomic volume in Å^3: the system relaxed by Monte Carlo simulations in two (2D) and three (3D, open circles) dimensions, the square lattice (sqr), and the bcc (solid curve) and the fcc (dashed curve) arrangements of iodine atoms.

This is in qualitative accord with the experimentally observed high vapour pressure of solid iodine.

The results of the simulations are presented in figure 2, supplemented by the data for body-centred cubic, face-centred cubic, and square arrangements of iodine atoms. The latter has been computed as that two-dimensional representative of the body-centred orthorhombic lattice with the strongest interiodine interactions. The simulation curves exhibit minima that are well separated in terms of both the potential energy and the atomic volume. The total minimum has an orthorhombic character; the corresponding structure is displayed in figure 3. We observe a nearest-neighbour distance of $r_1 = 2.721$ Å that lies close to the experimental value of Bolhuis *et al* [3], 2.715 Å. The simulation value of the next-nearest-neighbour distance, $r_2 = 3.478$ Å, lies again close to the experimental one, 3.496 Å. We note that the electron densities stemming from x-ray diffraction data obtained by Kitaigorodskii *et al* [2] have been described as rather diffuse and of a cylindrical shape, making a precise assignment of interiodine distances difficult. For completeness, we provide the corresponding values of $r_1 = 2.68$ Å and $r_2 = 3.56$ Å. For the size of the unit cell, we obtain $a = 4.763$ Å and $b = 9.432$ Å, in an arrangement close to that with the experimental values. In terms of the cubic root of the volume of the unit cell, we arrive at $r_0 = (abc)^{1/3} = 6.909$ Å, which lies closer to the value of Bolhuis *et al* of 6.891 Å than to that of Kitaigorodskii *et al* (6.98 Å). We note a small deviation from a perpendicular arrangement of iodine molecules in both the simulation results and the experimental crystal structures. A characterization of the geometries is also presented in table 1.

With increasing atomic volume, the potential energy of the simulated two-dimensional system approaches the gas phase value of 1.58 eV/molecule. With decreasing atomic volume (or increasing pressure), the simulation results finally merge into that obtained for a quadratic arrangement of atoms, representing a plane of a body-centred orthorhombic phase. With further decreasing volume, we arrive at the face- and body-centred cubic phases, which lie too close to be distinguished in terms of thermodynamic stability by a semiempirical calculation like that performed here.
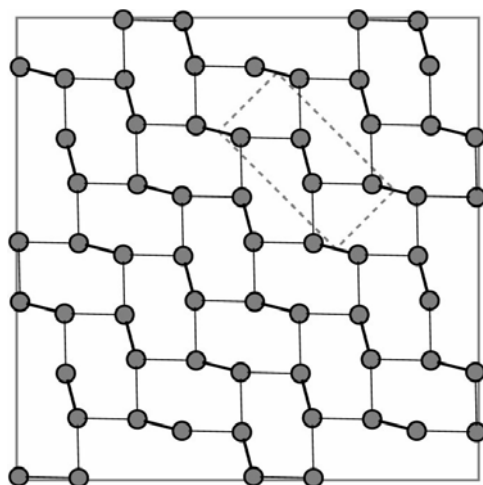
Figure 3. A representation of the optimized geometry in two dimensions. The spheres represent iodine atoms, the strong lines indicate intramolecular distances, the weak lines the smallest intermolecular distances. In the top right corner, the unit cell is displayed in dashed light grey.

Although we do think that the potentials are hardly accurate enough to permit thermodynamic calculations, we cannot refrain from performing a Maxwell construction at zero temperature to estimate an order of magnitude for the pressure of phase coexistence between the Monte Carlo curve (3D orthorhombic phase) and bcc phase; we arrive at $p \simeq 7.5$ GPa. Experimental values for phase transitions in solid iodine lie in the range of small multiples of 10 GPa [4].

We have computed the densities of states for systems based on the geometries described above with at least 64 atoms using the Hamiltonian that enters the tight-binding potential, equation (5). At the corresponding minima of the potential energy curves, the Monte Carlo simulation results indicate an insulating behaviour, whereas the quadratic, bcc, and fcc phases are metallic, again in accord with both experiments and *ab initio* calculations based upon crystalline geometries. For the gaps at the minimum of the potential energy, we obtain 1.38 eV both for the 2D and for the 3D simulation. The gaps for the fcc, bcc, and square arrangements vanish at the minima and at the points relevant to the aforementioned Maxwell construction.

4. Liquid iodine

Using the tight-binding potential derived above, we have studied a model of liquid iodine at elevated temperatures applying a Monte Carlo scheme. The following moves have been the subject of importance sampling: atomic translation, and the translation and rotation of an iodine atom and its nearest neighbour. The latter two steps speed up the calculations considerably for conditions under which I_2 molecules form the dominant species. The simulation has been performed for a system of 64 atoms, 5000 Monte Carlo steps have been used to equilibrate the system, and the subsequent 10 000 were used for the analysis via the radial distribution function. A Monte Carlo step is defined as an attempt to move each atom once on average. The standard Metropolis Monte Carlo method was applied to an NVT ensemble.

The radial distribution function $g(r)$ for a model liquid at $T = 409$ K and $\rho = 0.0186$ atoms Å^{-3} is displayed in figure 4. For these conditions, the experimental atom–
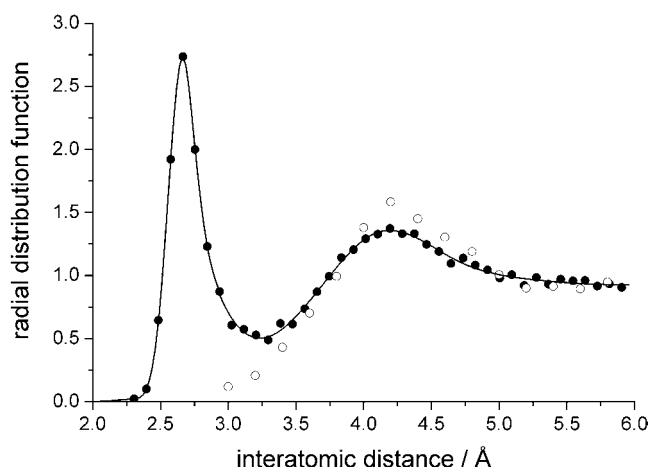
Figure 4. The iodine–iodine radial distribution function for $\rho = 0.0185$ atoms Å^{-3} and $T = 409$ K. Experimental data (open circles) from [35] are compared to computer simulation results as obtained in this work (full symbols). The line is a guide to the eye.

atom pair correlation function $g(r)$ obtained by neutron diffraction experiments is available in tabulated form [35] with the omission of the intramolecular contribution. At small interatomic distances, two peaks can be identified, which can be attributed to a distribution of intramolecular distances around the gas phase value and an intermolecular counterpart with a maximum at 4.3 Å, which lies close to the expected van der Waals diameter and is identical to the experimentally observed value of 4.3 Å. This reproduces the main structural features of liquid iodine, although further oscillations of the radial distribution functions beyond the experimental maximum of 4.3 Å ($g(r) \simeq 1.5$) could not be resolved due to the small system sizes studied here.

As we apply a full Monte Carlo simulation with a complete diagonalization of the Hamiltonian matrix for each attempt to move an atom or a molecule, the number of arithmetic operations required for an N-particle system scales like N^4 (N^3 for the diagonalization times N for attempted moves within a Monte Carlo step). We are thus limited to small system sizes and sample calculations. Future work will address the issue of the structure and the metallic or nonmetallic nature of liquid iodine as a function of temperature and density using more efficient methods.

5. Conclusions

In this work, we have suggested an empirical tight-binding potential suitable for the computer simulation of the molecular, solid, and liquid phases of iodine in the temperature and density regime accessible to experiments. As expected for a late VIIb member of the periodic table of elements, both covalent and van der Waals interactions play an important role and become operative on different length and energy scales. Starting from the I_2 molecule, we have partitioned the potential energy represented by a modified Morse potential into a pairwise repulsive, a pairwise attractive, and a many-body tight-binding part. By definition, the I_2 potential energy is not sensitive to this partitioning, but the geometry of the solid state crucially depends on the relative strength of the attractive pair interaction—representing the attractive part of a van der Waals interaction—and the tight-binding part, which reflects the chemical

bond. Consequently, numerical values that can be assigned to the strengths of these two interactions can replace vague chemical concepts and their application to the nature of the chemical bond in solid iodine.

We have performed a Monte Carlo relaxation procedure to obtain the geometry of planar and three-dimensional arrangements of iodine atoms as a function of the atomic volume without any bias towards a specific crystal structure. The resulting arrangement of I_2 molecules within the orthorhombic structure is not only in qualitative, but—considering the simplicity of the model—remarkable quantitative agreement with the experimental crystal structure. With increasing pressure, we obtain a crossover to the fcc or bcc structure. This trend is in qualitative agreement with x-ray diffraction experiments at high pressure, as are the predicted insulating or metallic natures of these phases. Preliminary tight-binding Monte Carlo results have been reported for the liquid, giving rise to both an intra-atomic and an interatomic peak in the radial distribution function.

Whereas we consider the application of density functional methods to the high-density phases of iodine as an important contribution to the understanding and prediction of the electronic structure and the equation of state, the sensitivity of the structure to the presence and the strength of nonbonding interactions as encountered here for a tight-binding computation suggests that the introduction of appropriate correction terms into simple *ab initio* schemes— e.g. those based on the local density approximation—is necessary before thermodynamical accuracy can be achieved there.

Acknowledgments

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