2.4

MODELING COVALENT BOND WITH INTERATOMIC POTENTIALS

João F. Justo
Escola Politécnica, Universidade de São Paulo, São Paulo, Brazil

Atoms, the elementary carriers of chemical identity, interact strongly with each other to form solids. It is interesting that those interactions could be directly mapped to the electronic and structural properties of the resulting materials. This connection between microscopic and macroscopic worlds is appealing, and suggests that a theoretical atomistic model could help to model and build materials with predetermined properties. Atomistic simulations represent one of the tools that can bridge those two worlds, accessing to information on the microscopic mechanisms which, in many cases, could not be sampled out by experiments.

One of the most important elements in an atomistic simulation is the model describing the interatomic interactions. In principle, such model should take into account all the particles (electrons and nuclei) of the system. Quantum mechanical (or *ab initio*) methods provide a precise description of those interactions, but they are computationally prohibitive. As a result, simulations would be restricted to systems involving only up to a thousand (or a few thousand) atoms, which is not enough to capture many important atomistic mechanisms. Some approximation, leading to less expensive models, should be implemented. A radical approach is to describe the interactions by classical potentials, in which the electronic effects are somehow integrated out, being taken into account only implicitly. The gain in computational efficiency comes with a price: a poorer description of the interactions.

Ab initio methods will become increasingly important in materials science over the next decade. Even using the fastest computers, those methods will continue being computationally expensive. Therefore, there is a demand for less expensive models to explore a number of important phenomena, to provide a qualitative view, scan for trends or insights on atomistic events, which could be later refined using *ab initio* methods. Developing an interatomic potential involves a combination of intuitive thinking, which comes out from our

S. Yip (ed.),
Handbook of Materials Modeling, 499–507.

knowledge on the nature of the interatomic bonding, and theoretical input. However, there is no theory which would directly provide the functional form for an interatomic potential. As a result, depending on the bonding type, considerably distinct approaches have been devised to describe interatomic interactions [1, 2]. In any case, the functional form should have a physical motivation and enough flexibility, in terms of fitting parameters, to capture the essential aspects underlying the interatomic interactions. The next sections discuss the specific case of modeling the covalent bonding by interatomic potentials, and the elements which should be present to properly describe such interactions.

1. Pair Potentials

The cohesive energy (E_c) is the relevant property which quantifies cohesion in a solid. It is given by $E_c(\mathbf{R}_n, \mathbf{r}_m)$, where $\mathbf{R}_n$ and $\mathbf{r}_m$ represent the degrees of freedom of the n nuclei and m electrons, respectively. While E_c could be computed by solving the quantum mechanical Schrödinger equation for the electrons of the system, one should inquire what kind of approximation could be performed to describe E_c with less expensive methods. One strategy is to average the electronic effects out, but still keeping the electronic degrees of freedom explicitly. One of these approaches, called tight-binding method, provides a realistic description of bonding in solids. However, those models are still computationally too expensive, although simulations with a few thousand atoms could be performed. An extreme approach is to remove all the electronic degrees of freedom, and E_c would be given by $E_c(\mathbf{R}_n, \mathbf{r}_m) \approx E_c(\mathbf{R}_n)$. In this last case, the electronic effects would be implicitly present in the functional form.

Several interatomic potentials for covalent bonding have been developed over the years. Only for silicon, which is considered the prototypical covalent material, there are more than thirty models which have been extensively used and tested [3]. This and the following sections discuss the relevant elements of an interatomic potential to describe a typical covalent material. The discussion focuses on the two most important models which have been developed for silicon [4, 5].

Cohesive energy could be determined by the atomic arrangement, in terms of a many-body expansion [6]

$$E_c = \sum_{i}^{n} V_1(\mathbf{R}_i) + \sum_{i,j}^{n} V_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_{i,j,k}^{n} V_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \cdots, \tag{1}$$

in which the sums are over all the n atoms of the system. In principle, E_c could be determined by an infinite many-body expansion, but the computational cost scales with n^l, where l is the order in which the expansion is truncated. The one-body terms (V_1) are generally neglected, but the two-body (V_2) and three-body (V_3) terms carry most of the relevant effects underlying bonding. While the V_2 and V_3 have a simple physical interpretation, intuition for higher order terms is not so straightforward, and most models have avoided such terms.

Could the expansion (1) be truncated in a two-body expansion and still capture the essential properties of covalent bonding? For a long period, pair potentials were used to investigate materials properties, and revealed a number of fundamental atomistic processes. Models including higher order expansions, later developed, provided results which were qualitatively consistent with those early investigations. This sets light on the discussion of pair potentials. Although they provide an unrealistic description of covalent bonding, they still capture some of the essential aspects of cohesion.

A typical V_2 function has a strong repulsive interaction at short interatomic separations, changing to an attractive interaction at intermediate separations which goes smoothly to zero at longer distances. The V_2 interaction, between atoms i and j, can be written as combination of a repulsive (V_R) plus an attractive (V_A) interaction in terms of the interatomic distance, $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$.

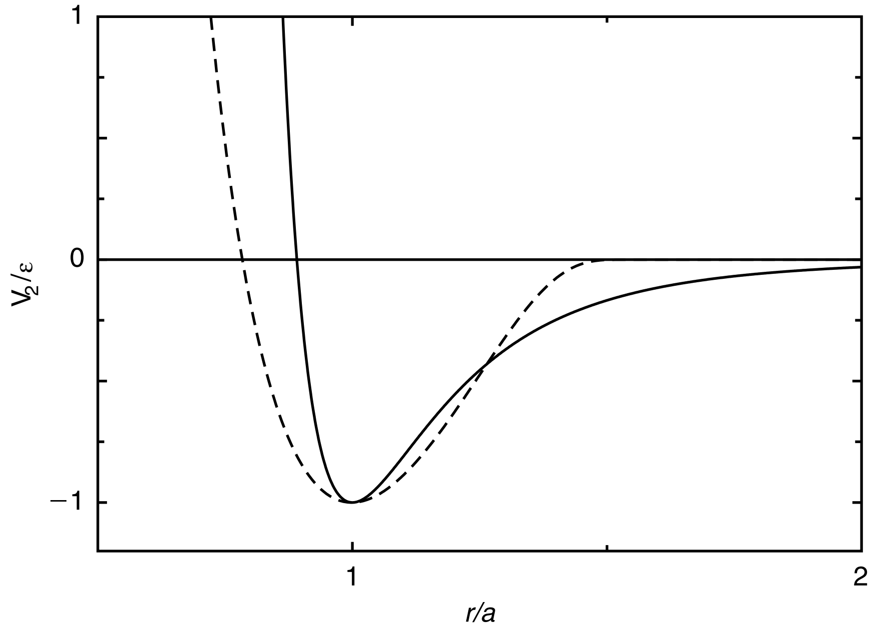

Figure 1. The two-body interatomic potential. The figure presents V_2 for two models: the Lennard–Jones (full line) and the Stillinger–Weber (dashed line) potentials. The functions are plotted normalized in terms of the minimum in energy and equilibrium separation (a).

The Lennard–Jones potential, shown in Fig. 1, is an example of a pair potential used to model cohesion in a solid

$$V_2(r) = V_R(r) + V_A(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{2}$$

where ε and σ are free parameters which can be fitted to properties of the material. The equilibrium interatomic distance (a) is related to the crystalline lattice parameter, while the curvature of the potential near a is directly correlated to the macroscopic bulk modulus.

The functional form in Eq. (2) is long ranged, and the computational cost scales with n^2. On the other hand, this cost could scale linearly with n if a cut-off function $f_c(r)$ were used. This $f_c(r)$ function should not change substantially the interaction for the relevant region of bonding, near the minimum of $V_2(r)$, and should vanish at a certain interatomic distance R_c, defined as the cut-off of the interaction. Therefore, the two-body interaction is described by an effective potential $V_2^{\text{eff}}(r) = V_2(r) f_c(r)$.

The functional form of the Lennard–Jones potential can provide a realistic description of noble gases in condensed phases. Although pair potentials capture some essential aspects of bonding, there are still some important elements missing in order to properly describe covalent bonding. If interatomic interactions were described only by pair potentials, there would be a gain in cohesive energy if an atom increased its coordination (number of nearest neighbors). Since there is no energy penalty for increasing coordination, pair potentials will always lead to closed packed crystalline structures. However, atoms in covalent materials sit in much more open crystalline structures, such as hexagonal or the diamond cubic. Pair potentials alone cannot describe the covalent bonding, and many-body effects must be introduced in the description of cohesion.

2. Beyond Pair Potentials

The many-body effects [6] could be introduced in E_c by several procedures: inside the two-body expansion (pair functionals), by an explicit many-body expansion (cluster potentials), or a combination of both (cluster functionals). Models which have been successfully developed to describe covalent systems fit into one of these categories. The Stillinger–Weber [4] and the Tersoff [5] models can be classified as a cluster potential and as a cluster functional, respectively.

In a description using only pair potentials, as given by Eq. (2), the cohesive energy of an individual bond inside a crystal is constant for any atomic coordination. However, this departs from a realistic description. Figure 2(a) shows the cohesive energy per bond as a function of atomic coordination for several crystalline structures of silicon. There is a weakening of the bond strength

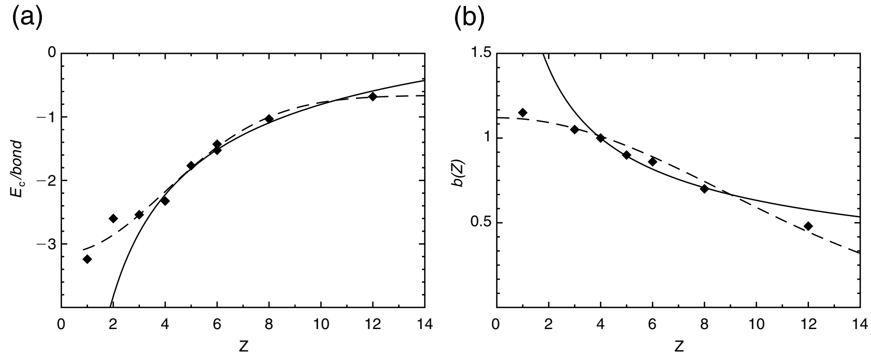

Figure 2. (a) Cohesive energy per bond ($E_c/bond$) as a function of atomic coordination (Z). Cohesive energies are taken from *ab initio* calculations (diamond), and the full and dashed lines represent fitting with a $Z^{-1/2}$ and $\exp(-\beta Z^2)$, respectively. (b) Bond order term $b(Z)$ as a function atomic coordination taken from *ab initio* calculations (diamond), and fitted to $Z^{-1/2}$ (full line) and $\exp(-\beta Z^2)$ (dashed line).

with increasing coordination, a behavior that is observed in any material. However, bond strength weakens very fast with coordination in molecular crystals and very slow in most metals. That is why molecular solids favor very low coordinations and metals favor high coordinations. Covalent solids fall between those two extremes.

Cohesive energy can be written as a sum over all the individual bonds V_{ij}

$$E_c = \frac{1}{2}\sum_{i,j} V_{ij} = \frac{1}{2}\sum_{i,j} \left[V_R(r_{ij}) + b_{ij} V_A(r_{ij})\right], \tag{3}$$

where the parameter b_{ij} controls the strength of the attractive interaction in V_{ij}. The attractive interaction between two atoms, i.e., the interaction controlling cohesion, is a function of the local environment. This dependence could be translated into a physical quantity called local coordination (Z). As the coordination increases, valence electrons should be shared with more neighbors, so the individual bond between an atom and its neighbors weakens. Using chemistry arguments, it can be shown that the bond order term (b_{ij}), can be given as a function of the local coordination (Z_i) in atom i by

$$b_{ij}(Z_i) = \eta\, Z_i^{-1/2}, \tag{4}$$

where η is a fitting parameter. Figure 2(b) shows the bond order term as a function of coordination for several crystalline structures. The $Z^{-1/2}$ function is a good approximation for high coordinations, but fails for low coordinations. It has been recently shown [7] that an exponential behavior for b_{ij} would be more adequate. The introduction of the bond order term in V_2 considerably improves the description of cohesion in a covalent material. With this new term, the equilibrium distance and strength of a bond is also determined by the local coordination at each atomic center.

Even using a bond order term, covalent bonding still requires a functional form with some angular dependence to stabilize the open crystalline structures. Angular functions could be introduced inside the bond order term $b(Z)$, as developed by Tersoff [5], which becomes $b(Z, \theta)$, where θ represents the angles between adjacent bonds around each atom of the system. Another procedure is to use an explicit three-body expansion [4]. In terms of energetics, there is a parallel between two-body and three-body potentials. In the former case, there is an energy penalty for interatomic distances differing from a certain equilibrium value. In the later case, there is a penalty for angles differing from a certain equilibrium value θ_0.

The three-body potentials are generally positive, being null at an equilibrium angle. The interaction for the (i, j, k) set of atoms is described by

$$V_3(r_{ij}, r_{ik}, r_{jk}) = h(r_{ij})h(r_{ik})g(\theta_{ijk}), \tag{5}$$

where the radial functions $h(r)$ goes monotonically to zero with increasing the interatomic distance. Figure 3 shows the behavior of typical angular functions $g(\theta)$. The Stillinger–Weber model used a three-body expansion, and the V_3 potential was developed as a penalty function with a minimum

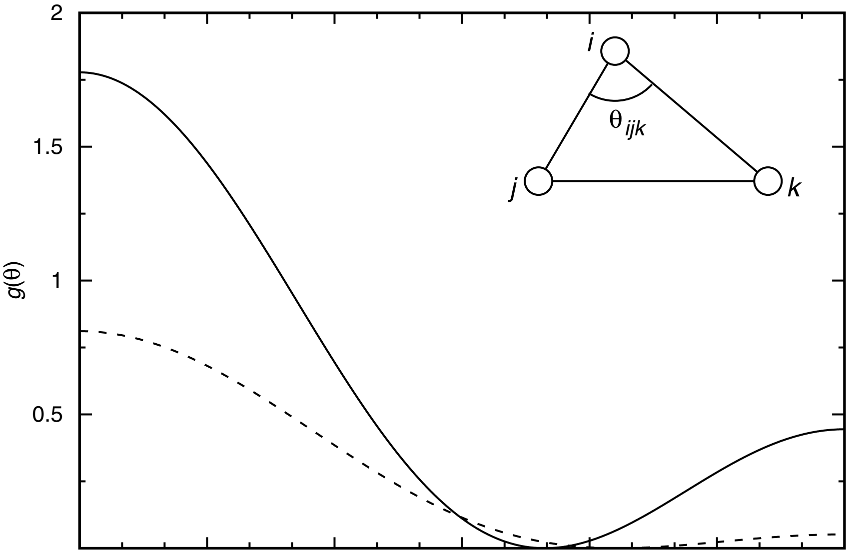

Figure 3. Angular function $g(\theta)$ from the Stillinger–Weber (full line) and Tersoff (dashed line) models.

at the tetrahedral angle (109.47°). On the other hand, the Tersoff potential introduced an angular function inside the bond order term, and the minimum of the angular term was a fitting parameter.

3. Models

Developing an interatomic potential involves several elements. The first one is the functional form, which should capture all the properties of covalent bonding. The functions should have enough flexibility, in terms of number of free parameters, to allow a description of a wide set of the materials properties. The second element is the fitting procedure used to find the set of free parameters that better describes a predetermined database. The database comprises a set of crystalline properties (such as cohesive energy, lattice parameter, elastic constants) and other specific properties (such as the formation energy of point defects) obtained from experiments or *ab initio* calculations. Additionally, the interatomic potential should be transferable, i.e., it should provide a realistic description of relevant configurations away from the database.

Two interatomic potentials [4, 5] have prevailed over the others in studies of covalent materials. The Tersoff model is described by a two-body expansion, including a bond order term

$$E_c = \frac{1}{2}\sum_{i\neq j} V_{ij}, \tag{6}$$

$$V_{ij} = f_c(r_{ij})\left[f_R(r_{ij}) + b_{ij} f_A(r_{ij})\right], \tag{7}$$

where $f_R(r_{ij})$ and $f_A(r_{ij})$ are respectively, the repulsive and attractive terms given by

$$f_R(r) = A\exp(-\lambda_1 r) \quad \text{and} \quad f_A(r) = -B\exp(-\lambda_2 r). \tag{8}$$

The $f_c(r)$ is a cut-off function which is one for the relevant region of bonding $r < S$, going smoothly to zero in the range $S < r < R$. The R and S, which control the range of interactions, are fitting parameters.

The b_{ij} is the bond order term which is given by

$$b_i j = \left(1 + \beta^n \zeta_{ij}^n\right)^{1/2n}, \tag{9}$$

$$\zeta_{ij} = \sum_{k\neq i,j} g(\theta_{ijk}) \exp\left[\alpha^3 (r_{ij} - r_{ik})^3\right], \tag{10}$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}, \tag{11}$$

where θ_{ijk} is the angle between ij and ik bonds.

The Tersoff potential was fitted to several silicon polytypes, being extended to other covalent systems, including multi-component materials. The Brenner potential [8], a model which resembles the Tersoff potential, is widely used to study hydrocarbon systems.

The Stillinger–Weber potential is the most used model for covalent materials. It was developed as a three-body expansion

$$E = \sum_{i,j} V_2(r_{ij}) + \sum_{i,j,k} V_3(r_{ij}, r_{ik}, r_{jk}). \tag{12}$$

The two-body term $V_2(r)$ is given by

$$V_2(r) = A\left[\frac{B}{r^{\rho}} - 1\right] f_c(r), \tag{13}$$

where the cut-off function $f_c(r)$ is given by

$$f_c(r) = \exp\left[\mu/(r - R)\right], \tag{14}$$

if $r < R$ and null otherwise.

The three-body potential V_3 is given by:

$$V_3(r_{ij}, r_{ik}) = h(r_{ij})h(r_{ik})g(\theta_{ijk}), \tag{15}$$

$$h(r) = \exp\left[\gamma/(r - R)\right], \tag{16}$$

$$g(\theta) = (\cos\theta + 1/3)^2. \tag{17}$$

This model was fitted to properties of the diamond cubic structure and local order of liquid silicon.

Other models have been developed to describe covalent materials. Those models have used different approaches, such as functional forms with up to 50 parameters and extensive database. Some of those models have been compared with each other, specially in the case of silicon [3]. Such comparisons revealed that no interatomic potential is suitable for all situations, such that there is still space for further developments. Recently, a new model for covalent materials was developed [7] and included the features of both the Tersoff and the Stillinger–Weber models. That model included explicitly bond order terms in the two-body and three-body interactions, which allowed a better description of covalent bonding as compared to previous models.

4. Perspectives

Interatomic potentials will continue playing an important role in atomistic simulations. Although potentials have been successfully applied to investigate covalent materials, they still face several challenges. As new models are developed, theoretical input will increasingly prevail over empirical input. So far, the physical properties of bonding have been introduced by trial and error. Attempts to improve models have been in the direction of trying new functional forms, going to higher order expansions or increasing the number of fitting parameters. This will give place to more sophisticated approaches, in which the functional forms could be directly extracted from theory.

Interatomic potentials also face the challenge to describe materials with mixed bonding character (metallic, covalent, and ionic altogether). The Tersoff potential, for example, has been extended to systems with some ionic character, but still with prevailing covalent character. That model would not work for materials with stronger ionic character, requiring at least the introduction of a long-ranged Coulomb interaction term. Finally, even if sophisticated interatomic potentials are developed, one should keep in mind that every model has its limited applicability and should always be used with caution.

References

[1] A.F. Voter, "Interatomic potentials for atomistic simulations," *MRS Bulletin*, 21(2), 17–19, (and additional references in the same issue, 1996).

[2] R. Phillips, *Crystals, Defects and Microstructures: Modeling Across Scales*, Cambridge University Press, Cambridge, UK, 2001.

[3] H. Balamane, T. Halicioglu, and W.A. Tiller, "Comparative study of silicon empirical interatomic potentials," *Phys. Rev. B*, 46, 2250–2279, 1992.

[4] F.H. Stillinger and T.A. Weber, "Computer simulation of local order in condensed phases of silicon," *Phys. Rev. B*, 31, 5262–5271, 1985.

[5] J. Tersoff, "New empirical-approach for the structure and energy of covalent systems," *Phys. Rev. B*, 37, 6991–7000, 1988.

[6] A.E. Carlsson, "Beyond pair potentials in elemental transition metals and semiconductors," In: H. Ehrenreich and D. Turnbull (eds.), *Solid State Physics*, vol. 43, Academic Press, San Diego, pp. 1–91, 1990.

[7] J.F. Justo, M.Z. Bazant, E. Kaxiras, V.V. Bulatov, and S. Yip, "Interatomic potential for silicon defects and disordered phases," *Phys. Rev. B*, 58, 2539–2550, 1998.

[8] D.W. Brenner, "Empirical potential for hydrocarbons for use in simulating the chemical vapor-deposition of diamond films," *Phys. Rev. B*, 42, 9458–9471, 1990.