

## MIT Open Access Articles

*Structural solution using molecular dynamics:  
Fundamentals and a case study of epoxy-silica interface*

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

**Citation:** Buyukozturk, Oral, Markus J. Buehler, Denvind Lau, and Chakrapan Tuakta. "Structural Solution Using Molecular Dynamics: Fundamentals and a Case Study of Epoxy-Silica Interface." *International Journal of Solids and Structures* 48, no. 14–15 (July 2011): 2131–2140. © 2011 Elsevier Ltd.

**As Published:** <http://dx.doi.org/10.1016/j.ijsolstr.2011.03.018>

**Publisher:** Elsevier

**Persistent URL:** <http://hdl.handle.net/1721.1/95800>

**Version:** Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

**Terms of Use:** Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.





## Structural solution using molecular dynamics: Fundamentals and a case study of epoxy-silica interface

Oral Büyüköztürk\*, Markus J. Buehler, Denvid Lau, Chakrapan Tuakta

Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

### ARTICLE INFO

#### Article history:

Received 24 November 2010

Received in revised form 14 March 2011

Available online 12 April 2011

#### Keywords:

Epoxy

Interface

Moisture

Molecular dynamics

Silica

### ABSTRACT

In this paper, the molecular dynamics (MD) simulation technique is described in the context of structural mechanics applications, providing a fundamental understanding of the atomistic approach, and demonstrating its applicability. Atomistic models provide a bottom-up description of material properties and processes, and MD simulation is capable of solving the dynamic evolution of equilibrium and non-equilibrium processes. The applicability of the technique to structural engineering problems is demonstrated through an interface debonding problem in a multi-layered material system usually encountered in composite structures. Interface debonding may lead to a possible premature failure of fiber reinforced polymer (FRP) bonded reinforced concrete (RC) structural elements subjected to moisture. Existing knowledge on meso-scale fracture mechanics may not fully explain the weakening of the interface between concrete and epoxy, when the interface is under moisture; there is a need to study the moisture affected debonding of the interface using a more fundamental approach that incorporates chemistry in the description of materials. The results of the atomistic modeling presented in this paper show that the adhesive strength (in terms of energy) between epoxy and silica is weakened in the presence of water through its interaction with epoxy. This is correlated with the existing meso-scale experimental data. This example demonstrates that MD simulation can be effectively used in studying the durability of the system through an understanding of how materials interact with the environment at the molecular level. In view of the limitation of MD simulation on both length- and time-scales, future research may focus on the development of a bridging technique between MD and finite element modeling (FEM) to be able to correlate the results from the nano- to the macro-scale.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

Some of the earliest developments of molecular dynamics (MD) simulation were reported in 1957 (Alder and Wainwright, 1957) for studies on the dynamics of a hard sphere system consisting of several hundreds of particles. Since then, advancement of MD simulation has been observed with the evolution of computational power in the last few decades. MD simulation represents a powerful tool for potential applications in various research fields including physics, chemistry, biology, bio-engineering and medicine (Allen and Tildesley, 1989; Rapaport, 1997). Recently, efforts have been made towards applying the method to structural mechanics and engineering. Traditionally, the classical continuum mechanics theories have been the basis for most computational methods used in various engineering fields including civil and mechanical engineering; examples are finite elements, finite difference, finite volume and boundary element methods. The capability of the

continuum approach is limited when structural solution at a small length scale is of concern, or if predictions about material behavior should be made from a fundamental bottom-up perspective.

MD simulation is based on modeling at atomistic level when the discrete nature of the matter at that level is explicitly considered. In an atomistic model the atomic distance provides a natural measure for the spatial discretization. The smallest unit in the atomistic model is an atom; the motion of each in the material is modeled over the course of a simulation time span. Collective behavior of the atoms allows one to understand how the material undergoes structural deformation. Atomistic models provide a fundamental chemistry-based description of material properties and processes, and MD simulation is capable of solving the dynamic evolution of equilibrium and non-equilibrium processes. Thus, a particular and detailed insight into the physics of fundamental processes can be obtained. The atomistic approach has been shown to be powerful in obtaining solutions for small scale structural mechanics problems such as, localized fracture processes in materials (see, for example (Buehler and Ackbarow, 2007) and references therein).

The objective of this paper is first to describe the MD simulation in the context of structural mechanics through a fundamental

\* Corresponding author.

E-mail address: [obuyuk@mit.edu](mailto:obuyuk@mit.edu) (O. Büyüköztürk).

understanding of the atomistic approach and, then, to apply the technique to the investigation of epoxy-silica interface under moisture as a basis for understanding of durability in multi-material structural systems. In what follows, some background on MD simulation will be provided and an organic-inorganic bi-layer system will be analyzed as an application in which structural concrete-epoxy interface under moisture can well be described. Predictions of concrete/epoxy interface behavior is an important structural mechanics problem as a basis for design and safety of structures that implement multi-material solutions such as retrofitting concrete structures using fiber-reinforced polymer materials.

## 2. Fundamentals of MD simulation

MD simulation is a numerical modeling technique for studying the molecular behavior of different substances (Allen and Tildesley, 1989; Rapaport, 1997; Fermeglia et al., 2003; Shevade et al., 2003; Fermeglia et al., 2004; Gardebien et al., 2004; Minisini and Tsobnang, 2005). The modeling process involves several key steps, namely, (1) construction of the atomistic geometry; (2) definition of atomic interaction; (3) governing equations for the system; (4) initialization and energy minimization; (5) conditions of simulation; (6) integration scheme and (7) calculation of concerned properties. These steps are included in the flowchart of the numerical approach shown in Fig. 1.

The first step in MD simulation is an accurate construction of the atomistic geometry which refers to a clear definition of the atomic location, the element type (i.e. the atomic mass and associated chemical properties), the partial charge of each atom, the bond connectivity among all atoms and the boundary conditions. This information is required for evaluating the inter-atomic interactions that describe the chemical properties. With this approach, determination of the system energy is critical throughout the simulation process, and force fields (potentials) play an important role in the accuracy of the computational modeling studies by proper description of the interaction among atoms (Lewis and Catlow, 1985). There are a number of force fields available in the literature for different types of interactions among atoms (Allen and Tildesley, 1989; Rapaport, 1997; Buehler, 2008). The choice of force field is left to the discretion of the user, based purely on the nature of forces acting between atoms for the specific material. The potential should be chosen in such a way that it mimics the nature of atomic interactions in a realistic or appropriate way, given a particular application of the model. There are different kinds of chemical bonds that exist in different substances for holding the material together; namely, ionic bonds, covalent bonds, metallic bonds, hydrogen bonds and van der Waals bonds. Each type of bond has varied strengths.

MD methods rely on Newton's second law of classical mechanics, which is given by

$$F_i = m_i a_i \quad (1)$$

where  $F_i$  is the force acting on an atom,  $m_i$  is the mass of the atom, and  $a_i$  is the acceleration of the atom. The total potential energy of the system is determined by summing up the potential energy associated with all bonded and non-bonded interactions. The total potential energy ( $U$ ) is expressed as  $U = U_{\text{bond}} + U_{\text{nonbond}}$ , where  $U_{\text{bond}}$  refers to the potential energy of the bonded atoms and  $U_{\text{nonbond}}$  refers to the potential energy of the non-bonded atoms. The force ( $F_i$ ) acting between a pair of atoms is determined by evaluating the negative gradient of the potential energy with respect to the separation distance ( $r_{ij}$ ). This is given by  $F_i = -\partial U / \partial r_{ij}$ . The net force acting on an atom 'i' is calculated by summing up the interactions between atom 'i' and the surrounding atoms 'j'. Once the net force is known, the acceleration of the individual atom can be determined using Eq. (1) as the atomic mass has been defined previously during the construction of the atomistic model. Finally, velocities and positions can be obtained by numerical integration of the equations of motion, given that their initial values are known.

Before conducting the computational experiment, initialization and energy minimization should be carried out. Similar to the process of solving a partial differential equation in continuum mechanics, for example, initial conditions are necessary for a defined solution. Initial positions of all the atoms are defined by the coordinates of the corresponding atoms in the simulation cell. Here, simulation cell refers to a space in which simulation takes place. The total potential energy of the system ( $U$ ) can be calculated as a function of the current atomic positions. The entire system is then subjected to a minimization of potential energy by varying the atomic position. The new atomic positions after energy minimization will be used in the subsequent computational experiment as these positions refer to the most stable structure in the concerned domain. It should be mentioned that the energy minimization is carried out under absolute zero temperature which means the kinetic energy is zero as well.

After the stages of initialization and energy minimization, the constraints of the simulation are defined. The purpose of applying these constraints is to control the simulation process such that the computational experiment can be accurately performed; this is similar to the concept of applying boundary conditions in a finite element analysis. Here, we introduce the concept of "ensemble", which is a probability measure on the set of all possible microscopic configurations that are consistent with the macroscopic state of the system. The microscopic state of a system is defined by the atomic positions and momenta which constitute the coordinates in a multidimensional imaginary space called "phase space". For a system of  $N$  particles, this space has  $6N$  dimensions as each particle is associated with three position variables and three momentum variables. A single point in phase space represents the state of a system. A MD simulation generates a collection of points in phase space as a function of time. An ensemble can be defined as a collection of points in phase space satisfying the conditions of a particular thermodynamic state. In advance of the computation we need to fix the type of ensemble that the system is desired to perform during the computation experiment, just like when finite element analysis is being performed, the boundary conditions need to be defined at the beginning of the analysis. There are three commonly used ensembles in MD: (1) micro-canonical ( $NVE$ ), where the number of atoms ( $N$ ), the volume ( $V$ ) and the energy ( $E$ ) of the system are kept constant; (2) canonical ( $NVT$ ) where, the number of atoms ( $N$ ), the volume ( $V$ ) and the temperature ( $T$ ) of the system are constant; (3) Gibb's ensemble ( $NPT$ ), where, the number of atoms ( $N$ ), the pressure ( $P$ ) and the temperature ( $T$ ) of the system are maintained constant. Depending on the type of ensemble used, a thermostat or barostat need to be chosen for the MD simulations. Generally, thermostats are intended to

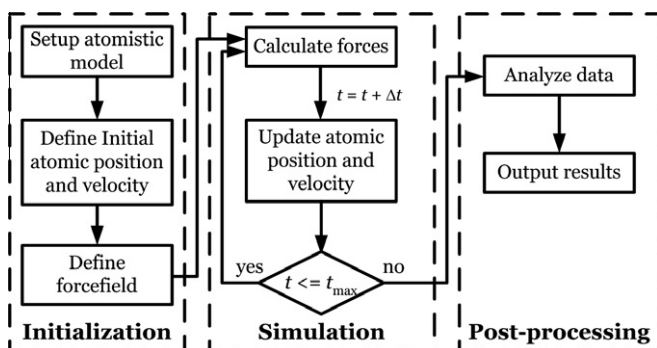


Fig. 1. Numerical approach of MD simulation.

control the temperature of the system. Some of the popular barostats used to control the pressure of the system (*NPT*) are Berendsen and Nose–Hoover barostat (Allen and Tildesley, 1989; Rapaport, 1997). It should be mentioned that macroscopic quantities are always related to their associated microscopic quantities. For instance, temperature (*T*) is a macroscopic quantity and its associated microscopic quantity is the atomic velocity (*v*). Their relationship can be established by considering the kinetic energy stored in the system macroscopically and microscopically, and given by the following equation:

$$\frac{3}{2}k_B T = \frac{1}{N} \sum_i \frac{1}{2} m_i v_i^2 \quad (2)$$

where  $k_B$  is the Boltzmann constant and  $m_i$  is the mass of the *i*th atom. The left hand side of Eq. (2) describes the kinetic energy of the system from a macroscopic point of view using the quantity *T*, while the right hand side of Eq. (2) describes the kinetic energy of the system from a microscopic point of view using the quantity *v*.

As mentioned earlier, the fundamental equation governing the molecular motion is the Newton's second law. In the simulation process, integration of this governing equation must be carried out. There are several numerical algorithms for integrating Eq. (1) using finite difference methods. A relatively simple algorithm called Verlet algorithm is discussed in this paper. Besides Verlet algorithm, the velocity-Verlet algorithm and the leapfrog-Verlet or the r-RESPA integration schemes are also widely used for implementation. The Verlet algorithm is one of the commonly used methods in MD simulation and is described as,

$$r_i(t_0 + \Delta t) = 2r_i(t_0) - r_i(t_0 - \Delta t) + a_i(t_0)\Delta t^2 \quad (3)$$

where  $r_i(t_0)$  is the position vector at time  $t_0$ ,  $r_i(t_0 - \Delta t)$  is the position vector at time  $t_0 - \Delta t$ , and  $a_i(t_0)$  is the acceleration vector at time  $t_0$ . This representation assumes that the atomic positions, velocities and accelerations can be approximated by a Taylor series expansion and uses the positions and accelerations at time  $t_0$ , and the positions from previous time step at time  $t_0 - \Delta t$  to calculate the new positions at the next time step at time  $t_0 + \Delta t$ . Hence, once we have the initial conditions in terms of atomic position in the system, as well as a well defined force field which is used for evaluating the acceleration vector, the subsequent motion can be calculated by this algorithm.

In order to reduce the computation time, a cut off radius ( $r_{cut}$ ) is usually specified in the simulation to limit the number of interactions associated with individual atoms. A list of neighboring atoms is generated for each atom in the system so that only the interactions with those listed in the neighbor list are accounted for the force calculation. This avoids the time-consuming step of calculating all possible interactions between an atom and the rest in the system for each time step.

Based on Eq. (3), the atomic displacements for all atoms can be calculated from a pre-set time step which is usually 1 fs ( $1 \times 10^{-15}$  s), and the atomic velocities can be calculated accordingly. After computing the atomic displacements, velocities and accelerations for all atoms under a desirable ensemble, the material properties can be determined and interpreted through post-processing of the calculated quantities. Usually an existing post-processing program, such as the visualization tool in Visual Molecular Dynamics (VMD) (Humphrey et al., 1996), is used. Interpreting the MD results usually means performing time averages of physical properties. Post-processing using appropriate theoretical models is required in order to evaluate some of the material properties from the MD simulation result, such as the adhesive energy of a bonded system.

### 3. Application of MD to layered composites in structures

Study of organic–inorganic interfaces for various applications has been of interest to numerous researchers. Development of molecular dynamics simulation based on the atomic and molecular motions has offered opportunities for the application of the method to interface problems. The study of organic–inorganic interfaces using MD was mainly carried out in the fields of biological and chemical engineering since the early 1990's (Galema et al., 1994; Sprous et al., 1999) but typically the focus was not on mechanical properties. With the expansion of the computational methods and capabilities, application can now be extended to structural mechanics and engineering problems. An example of organic–inorganic interface in structural engineering is the layered bonded material systems. Deterioration and debonding of interfaces in a multi-layer material system is of concern since such failures at local regions might lead to a system or structural failure. One example is the possible premature failure of reinforced concrete (RC) structural elements strengthened by fiber reinforced polymer (FRP) composite after prolonged exposure to moisture affecting the FRP/concrete interface. In practice, FRP-strengthened system for a RC beam is typically designed such that failure occurs in the form of either steel reinforcement yielding followed by concrete crushing, or FRP rupture, providing early warning when the load capacity is exceeded (ACI440.2R-08, 2008). However, when the interface becomes weak, failure can occur in the form of delamination in a tri-layer material system formed by the FRP, epoxy adhesive (organic), and the concrete material (inorganic) at various critical locations along the beam soffit, leading to a significantly lower load capacity of the FRP-retrofitted system. Fig. 2 shows possible debonding configurations in a FRP-retrofitted reinforced concrete beam.

When a strengthened RC beam is loaded to failure, cracks can initiate and propagate in different interfaces and material locations depending on loading configuration, and mechanical properties of the constituent materials and the interfaces. In general, crack can either propagate in bulk materials (material decohesion) or along the interfaces (interface separation). Reported empirical and analytical formulae available to predict interfacial fracture behavior include crack kinking by energy release rate (Hutchinson and Suo, 1992; Nishioka et al., 2003), crack kinking by maximum hoop stress (Yuuki and Xu, 1992), and crack kinking by zero complex stress intensity factor,  $K_{II}$  (Akisanya and Fleck, 1992).

However, these criteria may not fully explain the interface fracture behavior involving complex material interaction when the interface is under moisture attack. Knowledge on the debonding behavior of FRP-concrete bonded systems under the effect of moisture is crucial in predicting the service-life and improving the safety of civil structures strengthened using this technique. Inter-

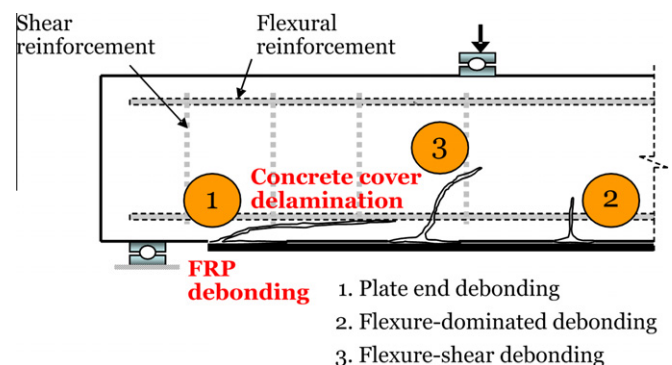


Fig. 2. Typical failure modes of FRP-retrofitted reinforced concrete beam (Buyukozturk et al., 2004).

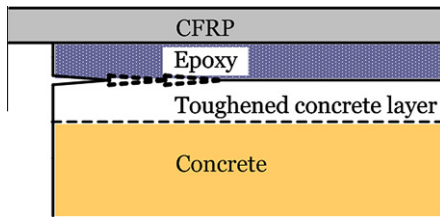


Fig. 3a. Plasticization of epoxy-penetrated concrete layer.

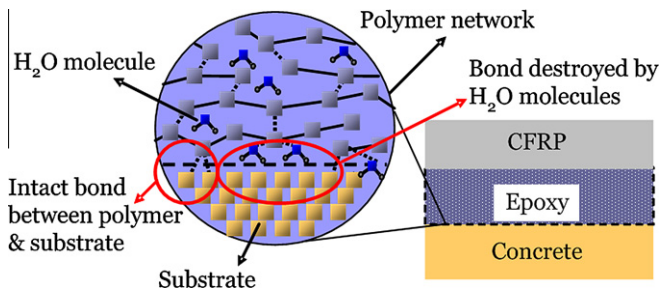


Fig. 3b. Weakening of bond between epoxy and concrete.

face fracture tests were conducted on tri-layer specimens consisting of carbon FRP, epoxy adhesive, and concrete (Au and Büyüköztürk, 2006a; Au and Büyüköztürk, 2006b; Lau and Büyüköztürk, 2010). The specimens were loaded under displacement control in peel and shear loading configurations separately. Effect of moisture on bond strength was studied by conditioning specimens in various moisture levels at room and elevated temperatures. It was found that the presence of moisture may significantly decrease fracture toughness of the tri-layer material system. Furthermore, for both peel and shear loadings, while the dry specimens failed by concrete delamination, in all cases the wet specimens failed by concrete-epoxy interface separation. Using material properties (Young's modulus and Poisson's ratio) from material characterization test program, the crack kinking criterion could well predict crack propagation observed in the dry specimens. However, these criteria failed to explain the decrease in strength and shift in failure mode observed in wet specimens, in which interaction at the material level between water, epoxy, and concrete may have occurred in the bulk material and at the interface. The two possible explanations may be that, first, there may be a toughened epoxy-penetrated concrete layer in the vicinity of the interface under moist environment (Fig. 3a). As a result, the initial crack at the interface between concrete and epoxy may not propagate into concrete due to this toughened top concrete layer staying at the interface instead. Second, the adhesive force at the interface may be weakened due to interaction between

epoxy and water (Fig. 3b). The initial crack, therefore, may stay at the interface which requires less energy for crack propagation. There is a need to study the debonding mechanism of the interface under the presence of water molecules using a more fundamental approach. Atomistic modeling approach employing molecular dynamics (MD) simulation may be used as a basis for a fundamental study.

#### 4. MD simulation of epoxy-silica interface

One of the challenges in MD simulation is to construct an atomistic model which can accurately describe the system. A known chemical formula for the concerned material is necessary in order to create a realistic atomistic model. Concrete is a heterogeneous material which is primarily composed of hydrated cement and aggregate. However, among all the constituent materials in concrete, silica, which has a well defined chemical formula, constitutes a large proportion as aggregate, usually more than 40 percent by weight of the solid ingredients. By investigating the epoxy-silica interface in an atomistic scale, it is expected that the structural behavior of concrete-epoxy interface can also be interpreted. Note that the chemical formula for hydrated cement has also been provided in a recent study on cement chemistry (Pellenq et al., 2009).

In our study, the atomistic model consists of crystalline silica ( $\text{SiO}_2$ ) and a single chain of epoxy. Figs. 4a and 4b show the atomistic model of the crystalline silica used in MD simulation. A silica block is constructed from a unit cell of crystalline silica shown in Fig. 4. By repeating the unit cell in  $x$ -,  $y$ -, and  $z$ -directions, a bulk silica crystal can be obtained as shown in Fig. 4b. The bulk silica crystal is then cleaved in such a way that the normal vector of the cleaved surface (to be in contact with epoxy) is at  $[001]$  direction. All the atoms in the crystalline silica are covalently bonded by a harmonic bond potential. Non-periodic boundary conditions are applied on the  $\text{SiO}_2$  substrate which means that hydrogen atoms are used for bond termination at the free surface of the  $\text{SiO}_2$  substrate as shown in Fig. 4b. The entire  $\text{SiO}_2$  substrate has dimensions  $a = 9.421 \text{ \AA}$ ,  $b = 36.84 \text{ \AA}$ ,  $c = 3.881 \text{ \AA}$ , with  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$  and consists of 2540 atoms. The epoxy employed in this paper is diglycidyl ether of bisphenol A (DGEBA) and its molecular structure is shown in Fig. 5. For simplification, there is no hardener included in the atomistic model. Only one chain of DGEBA, with five repeating units ( $n = 5$  as shown in Fig. 5), is used in this model. In the case describing a wet environment, a water box is created which embraced the DGEBA- $\text{SiO}_2$  system entirely. Fig. 6 shows the models for both dry (a) and wet (b) cases. Partial charges of all atoms in the simulation cell are calculated by the charge equilibrium (QEq) method (Rappe and Goddard, 1991).

Interaction between dissimilar molecular entities such as polymer and silica is formulated through the definition of force field.

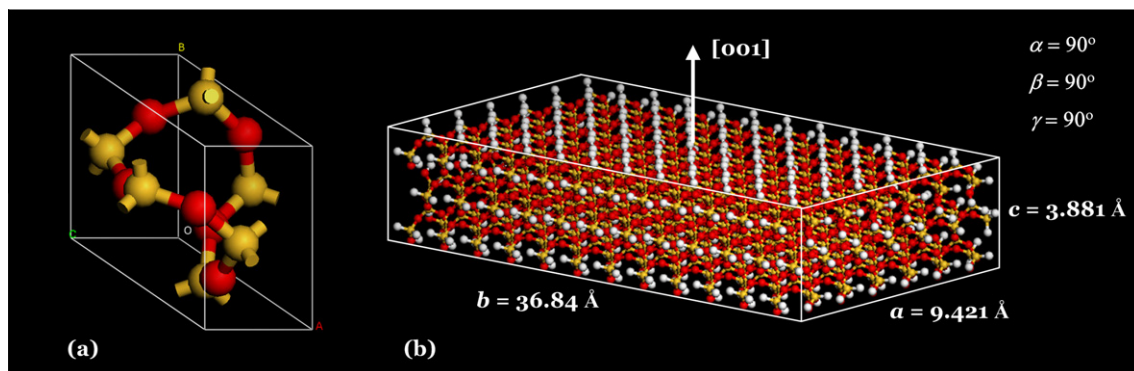


Fig. 4. (a) Unit cell of  $\text{SiO}_2$  and (b) Atomistic model of  $\text{SiO}_2$  substrate.

This is similar to the concept of constitutive model used in FEM to formulate the material behavior. For different atoms, the corresponding parameters adopted in the chosen force field are obtained either by experimental methods such as nuclear magnetic resonance (NMR) spectroscopy or from rigorous *ab initio* quantum mechanics calculations. Some of the commonly used force fields are Amber (Weiner et al., 1984, 1986), DREIDING (Mayo et al., 1990), CHARMM (Brooks et al., 1983; Momany and Rone, 1992), consistent force field (CFF91) (Hagler and Ewig, 1994; Hwang et al., 1994; Maple et al., 1994) and consistent valence force field (CVFF) (Dauber-Osguthorpe et al., 1988; Maple et al., 1988). These force fields were optimized and well tested for simulating different proteins and polymers. Epoxy is a typical polymer in which the above mentioned force fields are applicable. Meanwhile, efforts have been made to parameterize the CVFF for inorganic materials including silica as well as the interface between epoxy and silica. Therefore, in this paper, CVFF is adopted for studying the interaction between epoxy and silica under both dry and wet condition.

The total potential function in CVFF is represented by the superposition of valence and non-bonded interactions. The valence terms are the bonded interactions consisting of bond stretch, bond angle bending, dihedral angle torsion terms, while non-bonded interactions consist of Van der Waals and electrostatic terms. Fig. 7 shows the potential terms adopted in the CVFF. In this sim-

ulation, we use the CVFF potential energy function given by Maple et al. (1988). This is a reduced form of CVFF potential function using harmonic form for bond stretching term, which is useful for simulating structures consisting of organic and inorganic phases (Ritschla et al., 2002). In this reduced form, the CVFF potential function is described as,

$$E = \sum_b K_b (b - b_o)^2 + \sum_\theta K_\theta (\theta - \theta_o)^2 + \sum_\phi K_\phi (1 + s \cos n\phi) + \sum_{ij} \varepsilon_{ij} \left[ \left( \frac{r_{ij}^*}{r_{ij}} \right)^{12} - \left( \frac{r_{ij}^*}{r_{ij}} \right)^6 \right] + \sum_{ij} \frac{q_i q_j}{\varepsilon r_{ij}} \quad (4)$$

where  $K_b$ ,  $K_\theta$ ,  $K_\phi$  are force constants,  $b_o$ ,  $\theta_o$  and  $\phi$  are equilibrium bond length, equilibrium bond angle and dihedral angle, respectively;  $b$  and  $\theta$  are bond length and bond angle,  $r_{ij}$  is the distance between the  $i$ th and  $j$ th particles with charges  $q_i$  and  $q_j$ , respectively. The terms  $\varepsilon_{ij}$  and  $r_{ij}^*$  determine the minimum and zero values of the van der Waals terms, respectively. The CVFF has been parameterized against a wide range of experimental observables for amino acids, water, and a variety of other functional groups, as well as some inorganic materials including silica (details and parameters described in Maple et al. (1988)). The parameters of the force field used in this paper are included in the appendix. In this paper, we use the CVFF water potential, a three-site model with internal geometry corresponding to the gas-phase experimental structure (Lau et al., 1994). Flexibility of water molecules is modeled through the use of harmonic bond stretching and angle bending potentials. With the exception of the hydrogen atom size, the non-bonded parameters are comparable to those of simple point charge (SPC) model. An important aspect of choosing an interaction function for the epoxy-silica system including explicit water molecules is the consistency between different parts of the interatomic function, for example the epoxy-silica, epoxy-solvent, silica-solvent and solvent-solvent terms. When combining a water model with a force field used in the epoxy-silica system, the definition of the solvent-related interaction requires special attention. In most cases, this interaction is defined using the so-called combination rules (Gunsteren et al., 1994). If epoxy-silica system and solvent force fields are of different types, the application of combination rules may lead to an imbalance between epoxy-silica, epoxy-solvent, silica-solvent, and solvent-solvent interactions.

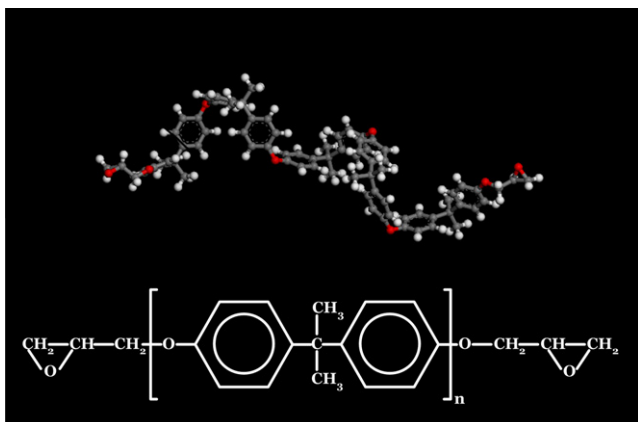


Fig. 5. Molecular structure and chemical formula of DGEBA with  $n = 5$ .

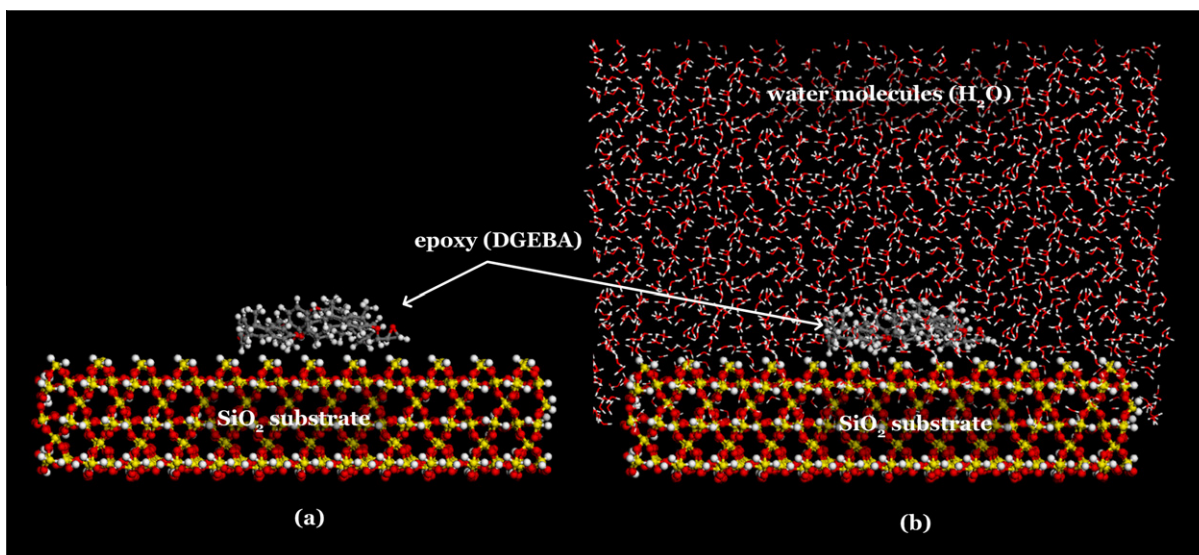


Fig. 6. Simulation model for (a) dry case and (b) wet case.

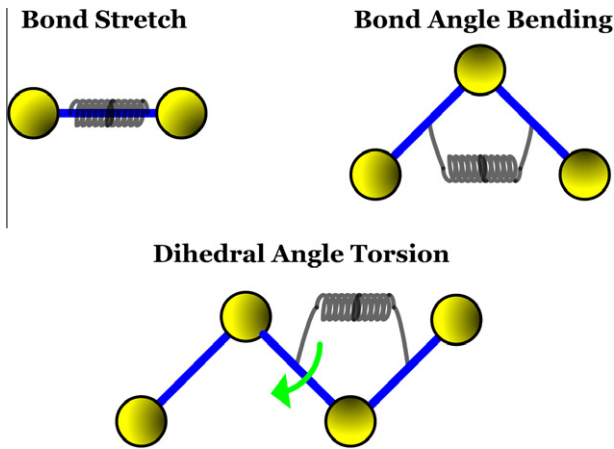


Fig. 7. Major potential terms in the CVFF used here (Ritschla, et al., 2002), applied to describe the silica substrate, epoxy chain and water.

Initiation and energy minimization of the simulation cell containing epoxy and silica (and water in the wet condition) are then performed. After constructing the atomistic models for both dry and wet cases with the clear definition of the model geometry and the interaction among atoms, the following computation experiments are carried out under *NVT* ensemble at 300 K in an existing MD code called LAMMPS (Plimpton, 1995).

Computational peel and shear tests on the silica-epoxy system are performed through steered molecular dynamics (SMD) by systematically varying the pulling velocity over four orders of magnitude, ranging from 2 to 1000 m/s. The basic idea of SMD is to apply an external force to one or a group of atoms, while keeping another group of atoms fixed and study the behavior of the molecule. Essentially, the SMD approach applies a moving spring force under constant velocity (i.e. the force is not constant). The SMD approach mimics an atomic force microscope (AFM) experiment. In our simulation, only the silica substrate is fixed. All atoms in water and epoxy are allowed to move freely. The end carbon atom in the epoxy is connected to a virtual spring in the entire process of SMD. The pulling direction to this carbon atom is normal away from the epoxy-silica interface under peeling condition and parallel with the interface under shear loading. Fig. 8 describes the peel and shear computational experiments schematically.

As discussed previously, a suitable model is required in quantifying certain mechanical property. Here, we extend the applicability of the model as done previously for investigating the adhesion between protein structures (Ackbarow et al., 2007). It is based on the conventional Bell's model (Bell, 1978) which was developed and applied to the study on cell adhesion at larger scales. Similar to earlier work (Ackbarow et al., 2007) here we apply Bell's approach so that simulation at various pulling speeds can be used to gain information on the free energy landscape of the bi-material system, postulating a phenomenological theory in explaining the competing process due to the mechanical induced stabilities. Through the Bell analysis, we can find the energy barrier  $E_b$  and the distance between the equilibrated state and the transition state  $x_b$  (see Fig. 9). In the modified Bell model (Ackbarow et al., 2007), we have a relationship between the pulling speed and the bond associated properties:

$$v = v_0 \exp\left(\frac{f \cdot x_b}{k_B T}\right) \quad (5)$$

where  $f$  is the external applied force,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, with  $v_0$  as the natural bond breaking speed, which is defined as

$$v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_B T}\right) \quad (6)$$

Substituting Eq. (6) into Eq. (5) and rearranging the equation with  $f$  as the subject, we have:

$$f = \left(\frac{k_B T}{x_b}\right) \ln v - \frac{k_B T \ln v_0}{x_b} = A \cdot \ln v + B \quad (7)$$

where  $A = k_B T/x_b$  and  $B = k_B T \cdot \ln v_0/x_b$ . Eq. (7) predicts that the applied force depends logarithmically on the pulling speed in a non-equilibrated system. It should be mentioned that the maximum force recorded during the whole simulation process under the constant velocity is taken as the value of  $f$  for the Bell analysis. By plotting  $f$  against  $\ln(v)$ , we can quantify the  $E_b$  and  $x_b$  for this system through the slope and the y-intercept of the curve. The resulting value of  $E_b$  represents the adhesive energy between silica and epoxy in an atomistic scale.

The maximum force  $f$  is plotted as a function of the pulling speed in Figs. 10a and 10b for the peel case under dry and wet conditions, respectively. Figs. 10c and 10d show the maximum force  $f$  for the shear case as a function of the pulling speed under dry and wet conditions, respectively. It should be mentioned that  $v^*$  is for the normalization purpose which equals 1 m/s. By fitting the extended Bell theory to the MD results of the peel case, we obtain  $E_b = 9.10$  kcal/mol and  $x_b = 0.69$  Å for the dry condition. In the wet case,  $E_b = 7.74$  kcal/mol and  $x_b = 0.16$  Å. Similar values are found for the shear case. For the dry case, the obtained values are  $E_b = 7.06$  kcal/mol and  $x_b = 0.48$  Å. In the wet case,  $E_b = 5.99$  kcal/mol and  $x_b = 0.11$  Å. These results are summarized in Fig. 11. The decrease in the adhesive energy  $E_b$  from 9.10 to 7.74 kcal/mol in the peel case and from 7.06 to 5.99 kcal/mol in the shear case, indicates that the adhesive strength between epoxy and silica is weakened in the presence of water with 14.9% reduction in the peel case and 15.2% reduction in the shear case. A close examination of the MD simulation process under wet condition shows that some water molecules can seep into the gap between epoxy and silica as shown in Fig. 12. Hence, the interaction between epoxy and silica is interfered by the presence of these water molecules, causing a change in the epoxy-silica interface from a bonded stage to a detached stage, which results in a reduction of energy barrier. The trend of deterioration is consistent with the results from meso-scale fracture based studies of the concrete-epoxy specimens (Lau and Büyüköztürk, 2010) and FRP-bonded concrete specimens (Au and Büyüköztürk, 2006b). In these papers, it is reported that there is a substantial decrease in the interfacial fracture toughness of concrete-epoxy system under prolonged moisture, which is accompanied with a shift of failure mode from material decohesion to interface separation. Both the experimental and simulation works show the reduction in the energy required for debonding in the presence of water. The MD result validates our hypothesis that the adhesive strength of the interface is weakened due to

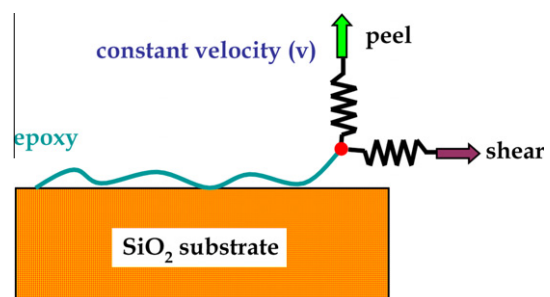


Fig. 8. Schematic diagram of the computational experiments for both peel and shear loading.

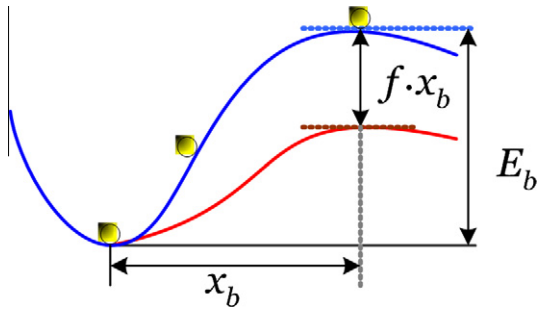


Fig. 9. Schematic diagram of the energy profile.

interaction between epoxy and water and provides a detailed chemistry-based view on the mechanical properties of the interface.

In practice, the length scale of structural models is much larger than that of the atomistic models. In order to implement the fundamental knowledge of local interface behavior in the entire model of the structural system, MD modeling should be coupled with the conventional finite element modeling (FEM). Due to the limitation of MD modeling on both length and time scales, bridging between MD and FEM needs to be established. In a multi-scale simulation framework, this would allow the exchange of information between atomistic and continuum regions. This process, in most cases, takes place in a region called hand-shaking region, which interconnects the two descriptions of materials. The location of atoms in this specialized region usually coincides with the nodes of finite elements adjacent to the atomistic region. The size of the interface region must ensure that information can be transferred seamlessly between the two regions. A conceptual description of various length scales and relationship of atomistic to continuum approaches is given in Fig. 13.

The research on bridging MD and FEM began in mid 1990s and the quasicontinuum model is one of the earliest methods to deal with this problem, initially applied to crystalline materials such as metals (Tadmor et al., 1996; Shenoy et al., 1998; Shenoy et al., 1999; Knap and Ortiz, 2001; Miller and Tadmor, 2002; Curtin and Miller, 2003; Shimokawa et al., 2004; Miller and Tadmor, 2007). This model is based on the observation that in many large-scale atomistic simulations a large section of atomic degrees of freedom can be described by effective continuum models and only a small subset of atomic degrees behave differently. Recently, several techniques have become available to bridge MD and FEM (Nakano et al., 2001; Fish, 2006; Liu et al., 2006). The main objective of these techniques is to avoid wave reflection at MD and FE interface. A concurrent coupling technique based on the idea of

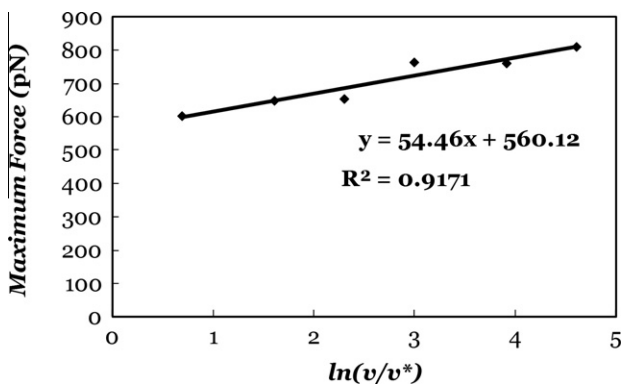


Fig. 10a. Maximum force as a function of varying pulling speed under peel and dry conditions.

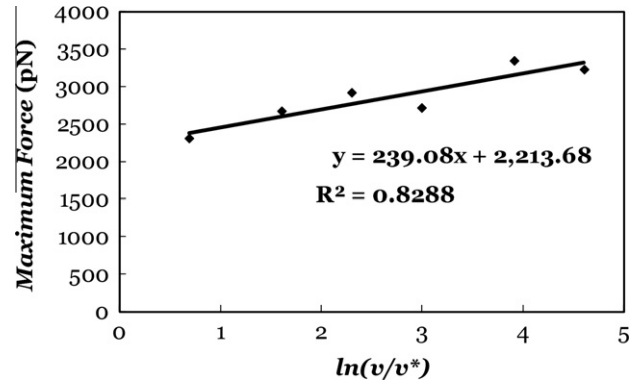


Fig. 10b. Maximum force as a function of varying pulling speed under peel and wet conditions.

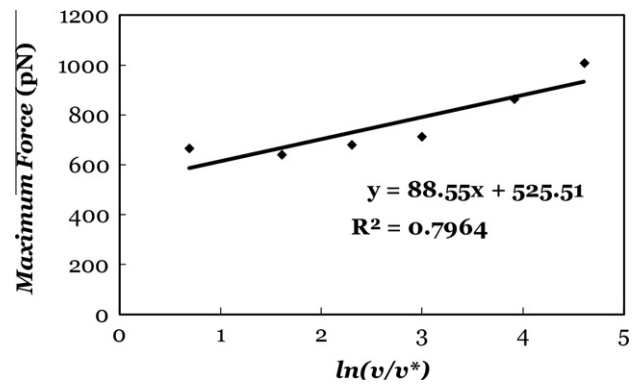


Fig. 10c. Maximum force as a function of varying pulling speed under shear and dry conditions.

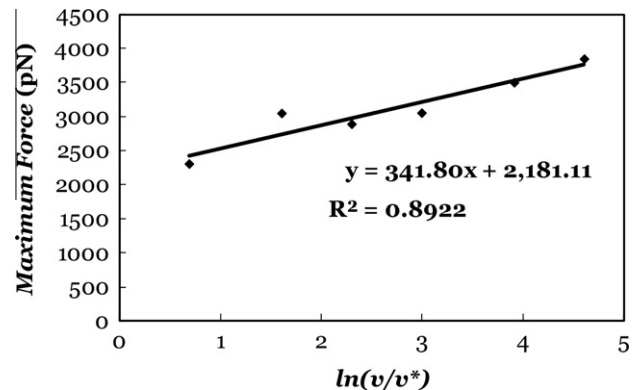


Fig. 10d. Maximum force as a function of varying pulling speed under shear and wet conditions.

quasicontinuum method is found to be suitable in bridging the atomistic and continuum paradigms. This technique reduces the degrees of freedom in the atomistic region by employing the Cauchy–Born (CB) rule, which postulates that a uniform deformation gradient at the macro-scale can be mapped to the same uniform deformation at atomistic scale (Klein and Gao, 1998; Miller and Tadmor, 2002). Given that Eq. (1) is quite similar in form to the semi-discrete FEM momentum equation with a lumped mass matrix, the time step stability when linking up MD and FEM can be interpreted based on the work developed in FEM because of the fact that the same time integrators can be used in integrating both MD and FEM equations of motion in time. It is noted that the FEM



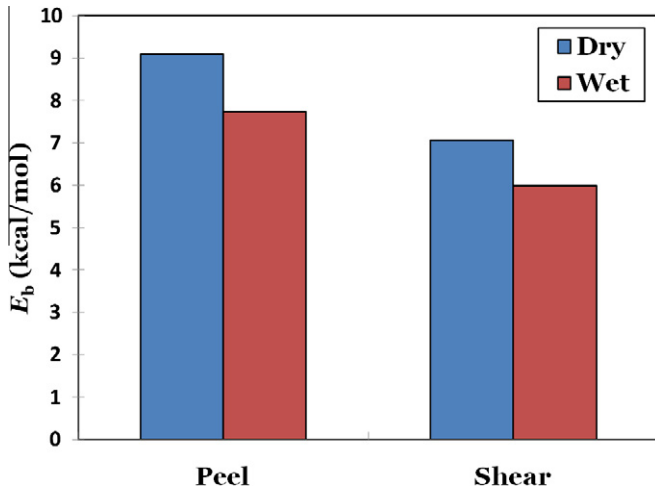


Fig. 11. Summary of the difference between peel and shear loading cases under both dry and wet conditions. This result implies that adhesion between silica and epoxy is weakened by about 15% in the presence of water.

internal force can be obtained using the CB hypothesis in conjunction with the atomistic forces utilizing the same interatomic potential. The connection between the FEM equations of motion could be achieved if a CB continuum model is used and the FEM mesh is meshed down to the atomic spacing. A correction can be made to the CB rule to account for non-uniform deformation in some materials (Tadmor et al., 1999; Zhang et al., 2002) and free surfaces when extracting information at continuum scale (i.e. force and energy) from representative atoms in the atomistic region and subsequently performing energy minimization (Park et al., 2006; Park and Klein, 2008). This will allow seamless information transfer between MD and FEM regions because, unlike other techniques, no boundary will be present between them.

In the multiscale modeling of non-crystalline structure such as the epoxy-silica system, a development of a coarse-grain model (Bertaud et al., 2009, 2010) which is constructed based on the information from a full atomistic simulation is important as it can utilize the information from the full atomistic simulation in a larger length and time scale. Besides improving the computational time, a larger model can be constructed and combined with the FEM region at a larger length scale. The main challenge of building

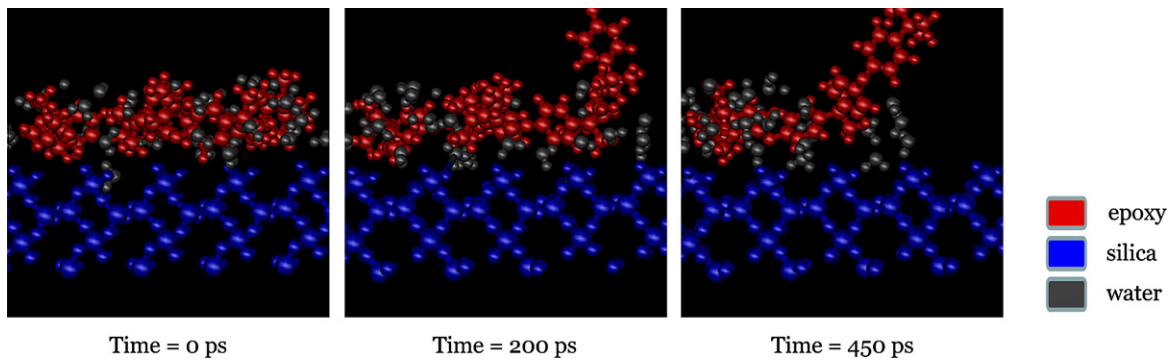


Fig. 12. Snapshots of the MD simulation in wet condition.

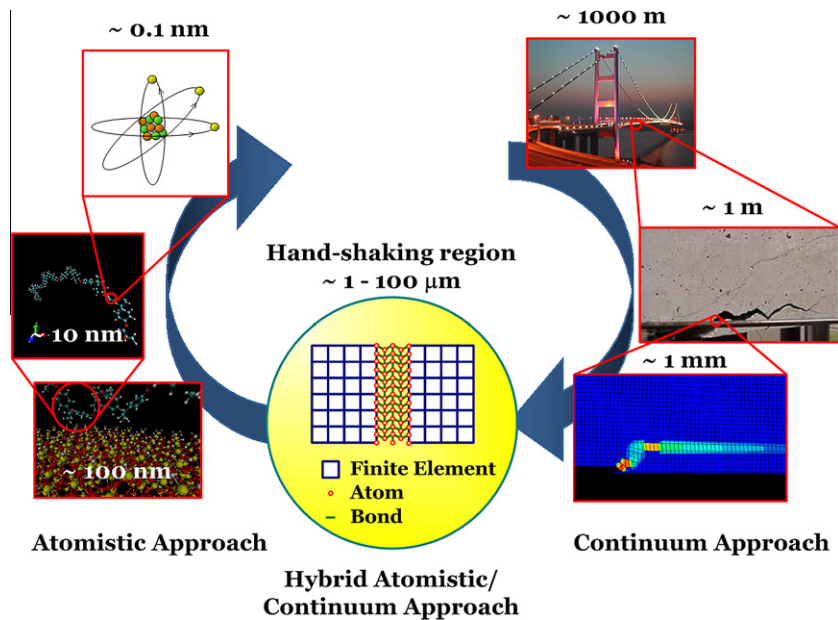


Fig. 13. Atomistic and continuum approaches connected in the hand-shaking region.

up a coarse grain model is to correctly describe the spring connecting various coarse-grain particles (so-called beads) in the model.

## 5. Conclusion

Research on MD simulation contributes to our understanding of the interaction between structural materials and environment at an atomistic scale providing a bottom-up “first principles” approach to structural engineering. Especially, MD is useful for studying the fracture related problems which can be intrinsically described in this length scale. The work reported in this paper has demonstrated that solution from MD simulation can give us an insight into the failure mechanism of layered material system under moisture effect. In this work, the bonded structural system consisting of epoxy and silica has been investigated and it is found that the weakening of the adhesive strength between epoxy and silica can be quantified by the decrease of the energy barrier  $E_b$ . However, the results from standard MD simulation only describe the considered system correctly on limited length and time scales (albeit methods such as Replica Exchange, Metadynamics, Hyperdynamics etc. (Voter, 1997; Sugita and Okamoto, 1999; Laio and Parrinello, 2002) can be used to bridge to large time-scales). In order to correlate the result from nano- to macro-scale, a bridging technique between MD and FEM is required. Research in this area is still in an infant stage, and particularly in applying the method to important problems in the field that often span many structural scales. MD may also enable synthesis of novel complex structural materials, designed from the nano- to the macro-scale upwards. It is anticipated that the long term impact of our work will be in extending our ability to perform structural engineering at the macro-scale, as related to the local phenomena that is modeled at the nano-scale.

## Acknowledgments

This research was supported by the National Science Foundation (NSF) through the CMS Grant #0856325 to Massachusetts Institute of Technology. The authors are grateful to Dr. Lawrence C. Bank, the cognizant NSF official, for his interest and support of this work. We acknowledge help from Dr. Zhiping Xu in setting up the simulation model.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijsostr.2011.03.018.

## References

- ACI440.2R-08, 2008. Guide for the design and construction of externally bonded FRP systems for strengthening concrete structures. Michigan (USA), American Concrete Institute (ACI), Committee 440.
- Ackbarow, T., Chen, X., Keten, S., Buehler, M.J., 2007. Hierarchies, multiple energy barriers, and robustness govern the fracture mechanics of  $\alpha$ -helical and  $\beta$ -sheet protein domains. *Progress of National Academy of Sciences of the United States of America* 104, 16410–16415.
- Akisanya, A.R., Fleck, N.A., 1992. Brittle fracture of adhesive joints. *International Journal of Fracture* 58, 93–114.
- Alder, B.J., Wainwright, T.E., 1957. Phase transition for a hard sphere system. *Journal of Chemical Physics* 27, 1208–1209.
- Allen, M.P., Tildesley, D.J., 1989. *Computer Simulation of Liquids*. Oxford University Press.
- Au, C., Büyüköztürk, O., 2006a. Debonding of FRP plated concrete: a tri-layer fracture treatment. *Engineering Fracture Mechanics* 73, 348–365.
- Au, C., Büyüköztürk, O., 2006b. Peel and shear fracture characterization of debonding in FRP plated concrete affected by moisture. *Journal of Composites for Construction, ASCE* 10, 35–47.
- Bell, G.I., 1978. Models for the specific adhesion of cells to cells. *Science* 200, 618–627.
- Bertaud, J., Qin, Z., Buehler, M.J., 2009. Atomistically informed mesoscale model of alpha-helical protein domains. *Journal for Multiscale Computational Engineering* 7, 237–250.
- Bertaud, J., Hester, J., Jimenez, D.D., Buehler, M.J., 2010. Energy landscape, structure and rate effects on strength properties of alpha-helical proteins. *Journal Physics: Condensed Matter* 22, 035102.
- Brooks, B.R., Brucoleri, R.E., Olafson, B.D., States, D.J., Swaminathan, S., Karplus, M., 1983. CHARMM: a program for macromolecular energy, minimization, and dynamics calculations. *Journal of Computational Chemistry* 4, 187–217.
- Buehler, M.J., 2008. *Atomistic Modeling of Materials Failure*. Springer, New York.
- Buehler, M.J., Ackbarow, T., 2007. Fracture mechanics of protein materials. *Materials Today* 10, 46–58.
- Buyukozturk, O., Gunes, O., Karaca, E., 2004. Progress on understanding debonding problems in reinforced concrete and steel members strengthened using FRP composites. *Construction and Building Materials* 18, 9–19.
- Curtin, W.A., Miller, R.E., 2003. Atomistic/continuum coupling in computational material science. *Modelling and Simulation in Materials Science and Engineering* 11, 33–68.
- Dauber-Osguthorpe, P., Roberts, V.A., Osguthorpe, D.J., Wolff, J., Genest, M., Hagler, A.T., 1988. Structure and energetics of ligand binding to proteins: E. coli dihydrofolate reductase-trimethoprim, a drug-receptor system. *Proteins: Structure, Function and Genetics* 4, 31–47.
- Fermeglia, M., Ferrone, M., Pricl, S., 2003. Computer simulation of nylon-6/organoclay nanocomposites: prediction of the binding energy. *Fluid Phase Equilibria* 212, 315–329.
- Fermeglia, M., Ferrone, M., Pricl, S., 2004. Estimation of the binding energy in random poly(butylene terephthalate-co-thiodiethylene terephthalate) copolyesters/clay nanocomposites via molecular simulation. *Molecular Simulation* 30, 289–300.
- Fish, J.J., 2006. Bridging the scales in nano engineering and science. *Journal of Nanoparticle Research* 8, 577–584.
- Galema, S.A., Howarth, E., Engberts, J.B.F.N., Grigera, J.R., 1994. The effect of stereochemistry upon carbohydrate hydration. A molecular dynamics next term simulation of  $\beta$ -D-galactopyranose and ( $\alpha,\beta$ )-D-talopyranose. *Carbohydrate Research* 265, 215–225.
- Gardebien, F., Gaudel-Siri, A., Brédas, Jean-Luc, Lazzaroni, R., 2004. Molecular dynamics simulations of intercalated poly( $\epsilon$ -caprolactone)-montmorillonite clay nanocomposites. *Journal of Physical Chemistry B* 108, 10678–10686.
- Gunsteren, W.F.V., Luque, F.J., Timms, D., Torda, A.E., 1994. *Molecular Mechanics in Biology: From Structure to Function, Taking Account of Solvation*. Annual Review of Biophysics and Biomolecular Structure 23, 847–863.
- Hagler, A.T., Ewig, C.S., 1994. On the use of quantum energy surfaces in the derivation of molecular force fields. *Computer Physics Communication* 84, 131–155.
- Humphrey, W., Dalke, A., Schulten, K., 1996. VMD – Visual Molecular Dynamics. *Journal of Molecular Graphics* 14, 33–38.
- Hutchinson, J.W., Suo, Z., 1992. Mixed mode cracking in layered materials. *Advances in Applied Mechanics* 29, 63–191.
- Hwang, M., Stockfisch, T.P., Hagler, A.T., 1994. Derivation of class II force fields. 2. Derivation and characterization of a class II force field, CFF93, for the alkyl functional group and alkane molecules. *Journal of the American Chemical Society* 116, 2515–2525.
- Klein, P., Gao, H., 1998. Crack nucleation and growth as strain localization in a virtual-bond continuum. *Engineering Fracture Mechanics* 61, 21–48.
- Knap, J., Ortiz, M.J., 2001. An analysis of the quasicontinuum method. *Journal of the Mechanics and Physics of Solids* 49, 1899–1923.
- Laio, A., Parrinello, M., 2002. Escaping free-energy minima. *Progress of National Academy of Sciences of the United States of America* 99, 12562–12566.
- Lau, D., Büyüköztürk, O., 2010. Fracture characterization of concrete/epoxy interface affected by moisture. *Mechanics of Materials* 42, 1031–1042.
- Lau, K.F., Alper, H.E., Thacher, T.S., Stouch, T.R., 1994. Effects of switching functions on the behavior of liquid water in molecular dynamics simulations. *Journal of Physical Chemistry* 98, 8785.
- Lewis, G.V., Catlow, C.R.A., 1985. Potential models for ionic oxides. *Journal of Physics C: Solid State Physics* 18, 1149–1161.
- Liu, W.K., Park, H.S., Qian, D., Karpov, E.G., Kadowaki, H., Wagner, G.J., 2006. Bridging scale methods for nanomechanics and materials. *Computer Methods in Applied Mechanics and Engineering* 195, 1407–1421.
- Maple, J.R., Dinur, U., Hagler, A.T., 1988. Derivation of force fields for molecular mechanics and dynamics from ab initio energy surfaces. *Progress of National Academy of Sciences of the United States of America* 85, 5350–5354.
- Maple, J.R., Hwang, M.J., Stockfisch, T.P., Dinur, U., Waldman, M., Ewig, C.S., Hagler, A., 1994. Derivation of class II force fields. 1. Methodology and quantum force field for the alkyl functional group and alkane molecules. *Journal of Computational Chemistry* 15, 162–182.
- Mayo, S.L., Olafson, B.D., Goddard, W.A., 1990. DREIDING: a generic force field for molecular simulations. *Journal of Physical Chemistry* 94, 8897–8909.
- Miller, R.E., Tadmor, E.B., 2002. The quasicontinuum method: overview, application, and concurrent directions. *Journal of Computer-Aided Materials Design* 9, 203–239.
- Miller, R.E., Tadmor, E.B., 2007. Hybrid continuum mechanics and atomistic methods for simulating materials deformation and failure. *Material Research Society Bulletin* 32, 920–926.
- Minisini, B., Tsohnang, F., 2005. Molecular mechanics studies of specific interactions in organomodified clay nanocomposite. *Composite Part A* 36, 531–537.

- Momany, F.A., Rone, R., 1992. Validation of the general purpose QUANTA<sup>®</sup>32/CHARMm<sup>®</sup> force field. *Journal of Computational Chemistry* 13, 888–900.
- Nakano, A., Bachlechner, M.E., Kalia, R.K., Lidorikis, E., Vashishta, P., Voyiadjis, G.Z., Campbell, T.J., Ogata, S., Shimojo, F., 2001. Multiscale simulation of nanosystems. *Computing in Science & Engineering* 3, 56–66.
- Nishioka, T., Syano, S., Fujimoto, T., 2003. Concepts of separated J-integrals, separated energy release rates, and the component separation method of the J-integral for interfacial fracture mechanics. *Journal of Applied Mechanics-Transactions of the ASME* 70, 505–516.
- Park, H.S., Klein, P.A., 2008. Surface stress effects on the resonant properties of metal nanowires: the importance of finite deformation kinematics and the impact of the residual surface stress. *Journal of the Mechanics and Physics of Solids* 56, 3144–3166.
- Park, H.S., Klein, P.A., Wagner, G.J., 2006. A surface Cauchy–Born model for nanoscale materials. *International Journal for Numerical Methods in Engineering* 68, 1072–1095.
- Pellenq, R.J.-M., Kushima, A., Shahsavari, R., Van Vliet, K.J., Buehler, M.J., Yip, S., Ulm, F.-J., 2009. A realistic molecular model of cement hydrates. *Progress of National Academy of Sciences of the United States of America* 106, 16102–16107.
- Plimpton, S., 1995. Fast parallel algorithms for short-range molecular dynamics. *Journal of Computational Physics* 117, 1–19.
- Rapaport, D.C., 1997. *The Art of Molecular Dynamics Simulation*. Cambridge University Press, Cambridge.
- Rappe, A.K., Goddard, W.A.I., 1991. Charge equilibration for molecular dynamics simulations. *Journal Physical Chemistry* 95, 3358–3363.
- Ritschla, F., Fäitb, M., Fiedler, K., Jkohlere, J.E.H., Kubiasb, B., Meisela, M., 2002. An extension of the consistent valence force field (CVFF) with the aim to simulate the structures of vanadium phosphorus oxides and the adsorption of n-Butane and of 1-Butene on their crystal planes. *ZAAC Zeitschrift für Anorganische und Allgemeine Chemie* 628, 1385–1396.
- Shenoy, V., Miller, R., Tadmor, E.B., Phillips, R., Ortiz, M., 1998. Quasicontinuum methods of interfacial structure and deformation. *Physical Review Letter* 80, 742.
- Shenoy, V., Miller, R., Tadmor, E.B., Rodney, D., Phillips, R., Ortiz, M., 1999. An adaptive methodology for atomic scale mechanics – the quasicontinuum method. *Journal of the Mechanics and Physics of Solids* 73, 611–642.
- Shevade, A.V., Ryan, M.A., Homer, M.L., Manfreda, A.M., Zhou, H., Manatt, K.S., 2003. Molecular modeling of polymer composite – analyte interactions in electronic nose sensor. *Sensor and Actuators B* 93, 84–91.
- Shimokawa, T., Mortensen, J.J., Schiotz, J., Jacobsen, K.W., 2004. Matching conditions in the quasicontinuum method: removal of the error introduced at the interface between the coarse-grained and fully atomistic region. *Physical Review B* 69, 214104.
- Sprou, D., Young, M.A., Beveridge, D.L., 1999. Molecular dynamics studies of axis bending in d(G5-(GA4T4C)2-C5) and d(G5-(GT4A4C)2-C5): effects of sequence polarity on DNA curvature. *Journal of Molecular Biology* 285, 1623–1632.
- Sugita, Y., Okamoto, Y., 1999. Replica-exchange molecular dynamics method for protein folding. *Chemical Physics Letters* 314, 141–151.
- Tadmor, E.B., Ortiz, M., Phillips, R., 1996. Quasicontinuum analysis of defects in solids. *Philosophical Magazine A* 73, 1529.
- Tadmor, E.B., Smith, G.S., Bernstein, N., Kaxiras, E., 1999. Mixed finite element and atomistic formulation for complex crystals. *Physical Review B* 59, 235–245.
- Voter, A.F., 1997. Hyperdynamics: accelerated molecular dynamics of infrequent events. *Physical Review Letters* 78, 3908.
- Weiner, S.J., Kollman, P.A., Case, D.A., Singh, U.C., Ghio, C., Alagona, G., Profeta, S., Weiner, P., 1984. A new force field for molecular mechanical simulation of nucleic acids and proteins. *Journal of the American Chemical Society* 106, 765–784.
- Weiner, S.J., Kollman, P.A., Nguyen, D.T., Case, D.A., 1986. An all atom force field for simulations of proteins and nucleic acids. *Journal of Computational Chemistry* 7, 230–252.
- Yuuki, R., Xu, J.Q., 1992. Stress based criterion for an interface crack kinking out of the interface in dissimilar materials. *Engineering Fracture Mechanics* 41, 635–644.
- Zhang, P., Huang, Y., Geubelle, P.H., Klein, P.A., Hwang, K.C., 2002. The elastic modulus of single-wall carbon nanotubes: a continuum analysis incorporating interatomic potentials. *International Journal of Solids and Structures* 39, 3893–3906.