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Molecular simulation of the effects of humidity and of interfacial Si- and B-hydroxyls on the adhesion energy between glass plates

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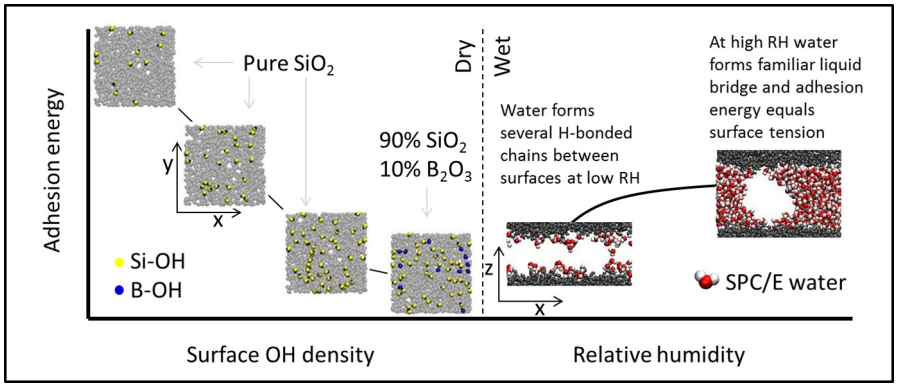
GRAPHICAL ABSTRACT



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ABSTRACT

Adhesion energies for sub-micron particles cannot be accurately calculated with macro-scale theories, in part because heterogeneities in surface morphology and chemistry play a significant role. Atomistic models have been used previously to quantify adhesion energies in wet environments for pure silica surfaces. To extend such modeling to more complex glass materials, we adopt a more comprehensive amorphous glass potential, and use a simplified approach to define the interaction between the hydroxylated surface and SPC/E water. We compute adhesion energies for pure SiO_2, and 90 mol% SiO_2 + 10 mol% B_2O_3, in dry and humid conditions. We find that the addition of B_2O_3 reduces adhesion, due to multiple effects which result in reduced hydrogen bonding. At high RH, the water between the plates forms a clear liquid bridge, whereas at the lowest RH, the water connects in chains of hydrogen bonded molecules that form and break during the adhesion process, so that capillary forces do not come into play. We also find that for under-hydroxylated pure SiO_2 surfaces, a transitional state which may be found after heating or during glass formation, adhesion energies are the highest.

1. Introduction

The use of silicate glass materials is ubiquitous in many industries including laboratory and consumer products, pharmaceuticals, and environmental applications. Understanding and controlling adhesion between glass surfaces is important, for example,

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in the manufacture of some labware (like multi-well plates), glass panels for automotive or architectural applications, and glass screens for consumer products like computers, tablets, and TVs. The relevant length scales which determine performance are becoming ever smaller as fabrication of micro and nanoscale devices is achievable. For many applications, understanding the interfacial behavior is key to improving quality and performance. At such small length scales, capillary forces can have significant impact on how surfaces interact. The existence of numerous interaction potentials devoted specifically to describing the interaction of silica and water underscores this fact [1–9].

Adhesive energy is a characteristic interfacial property which can be approximated using theories based on the Young–Laplace and Kelvin equations and assuming the particle has some ideal shape, such as a sphere, cylinder or cone [10], and that the surface is either another particle or a flat surface, either smooth or with some specific roughness [11]. The computed adhesion values depend heavily on these factors as well as empirical quantities such as a Hamaker coefficient which can be off by several orders of magnitude due to assumptions about particle–surface geometry [12], and do not capture local variations on the surface. While these approximations are generally considered reasonable at length scales of tens of microns and above [13], we are interested in how local variations in composition and the presence of water will affect adhesive behavior.

Adhesion can be measured experimentally by atomic force microscopy (AFM) where, for example, a pyramid-shaped glass tip at the end of a cantilever arm is brought into contact with a surface and the force to remove the tip is computed based on a spring constant [14]. In some cases a glass shard is attached to the end of the tip [15]. Adhesion values measured this way vary by a factor of 2 to 10 [16] and depend heavily on assumptions about the tip size and the radius of curvature, which will change the contact surface area, and which can change sometimes dramatically over a series of measurements as the tip is worn down.

Published experimental and simulation results show varying dependence of adhesion on relative humidity, including monotonically increasing [15], increasing to a plateau [17,18], and running through a maximum at intermediate RH values [16,13]. In some simulation studies the adhesive force vanishes with dry surfaces [1,19].

Molecular dynamics simulations have been used previously to compute the adhesion energy between silica surfaces and particles in the presence of varying amounts of water corresponding to a range of relative humidities [1,20,13]. These works give a baseline of comparison for our study, where we compare the behavior for our fully hydroxylated pure silica system and then extend to a composition containing B_2O_3, as well as pure silica with reduced amount of surface hydroxylation, a transitional state which may be found after heating or during glass formation. In this way, we hope to gain insight about how the isolated effects of composition and surface energy influence adhesion. We use the Pedone force field [21] to describe our bulk material because it is a fairly simple, non-bonded potential which accurately predicts many bulk structural properties of amorphous glass materials and includes parameters for many typical glass components. Using methods similar to those used by Hassanali et al. to extend the BKS potential [3], and by Cole and Payne for a Stillinger–Weber based potential [1], we use density functional theory (DFT) energies to estimate Lennard-Jones parameters between each hydroxyl type and SPC/E water [22]. Using these parameters we study the wetting and adhesion behavior of surfaces of both compositions under several levels of relative humidity ranging from dry to fully saturated.

There are numerous models to describe the water–silica interaction [1–7], many of which use complicated three-body terms, correction terms, chemical bonding, polarization, or other effects that make them not transferable to systems other than silica and water. We selected the Pedone potential and a compatible, simplified interaction potential for the hydroxylated surface with water in hopes that the comprehensive set of Pedone potential parameters can be leveraged to make this approach extensible to adhesion studies of more complex bulk compositions.

The remainder of this article is organized as follows: In Section 2 we describe the computational details of the simulated systems, hydroxylation of surfaces, development of the potential between the hydroxylated glass surface and water, and how we compute the adhesion energies. In Section 3 we analyze the wetting and adhesion behavior we computed for each condition and compare to available published results, and discuss the effect of hydrogen bonding and affinity for water. In Section 4 we present our concluding remarks.

2. Methods

2.1. Creating the systems

We consider two compositions of amorphous material: one pure SiO_2 and one with 10 mol% B_2O_3. The surface hydroxylation was selected to represent a nearly fully hydroxylated surface (3.0 OH/nm^2) as well as two lower density (0.7 and 1.5 OH/nm^2), more energetic and transitional surfaces. Each system is created by first simulating a bulk mixture of the relevant oxides, then making two surfaces by cleaving the bulk and equilibrating, hydroxylating the surfaces, and finally adding water between the surfaces. Each of these steps is described in more detail below.

The bulk glass structure is created through a series of molecular dynamics (MD) and Metropolis Monte Carlo (MC) steps, as the glass is annealed from 4273 K down to 673 K in steps of 200 K, with a final step of 100 K. This combination of MD and MC runs while quenching has been shown to be an efficient and accurate process for creating atomistic glass structures [23]. At each temperature step the system is run for 4×10^5 MD steps of 0.001 ps at constant temperature, followed by 2×10^7 trial moves with an acceptance ratio of 0.35 in constant pressure MC. The starting locations of O, Si and B atoms are random within a cubic periodic simulation box, with the number of each type of atom defined by the desired molar concentrations, and the simulation box size defined by the estimated final density (2.4 g/cc, based on SiO_2). The MD runs of the anneal cycle are performed using the NVT ensemble in GROMACS [24], and an in-house program is used for the MC portion. A final NPT step is used to relax the structure. In the final structure, bond lengths and coordination numbers are compared to known values. This process is described in more detail elsewhere [23].

The pure silica system has 5001 atoms (1667 Si and 3334 O) and the equilibrated cubic system is 41.3 Å per side. The borosilicate system has 5440 atoms (1688 Si, 376 B and 3376 O), and measures 42.95 Å per side. These sizes are for the final equilibrated bulk systems (before cleaving, hydroxylating and duplicating).

The remainder of the MD simulations are performed using LAMMPS [25], in the NVT ensemble at 300 K using a Nose–Hoover thermostat with a damping parameter of 0.018 timesteps, unless otherwise noted. For each system, two surfaces are created by opening the periodic boundary conditions in the z-dimension, and exposing the glass at those boundaries to a vacuum. The x and y dimensions do not change. In the z dimension the length is fixed at 140 Å and the slab option is used to properly handle calculations of the long-range interactions, which are solved using PPPM [26] with accuracy of 10^{-7} and order 7. The system is allowed to equilibrate until the energy stops changing. Surfaces created in this way have only molecular scale roughness, and high energy due to