



Background and scope

Solid state materials have been a subject of intense computational studies, both using wavefunction models, discrete classical molecular dynamics (MD) and continuous finite element models, each appropriate for their own length and time scales. In my project, classical MD is utilized for studying mesoscopic phenomena in solid state structures. Two underlying phenomena in chemically homogeneous solids is the background of the calculations, fractures and friction. These are very complex processes which require accurate simulation methods on all the relevant length scales. As examples, the breaking strength of a material depends on interactions between dislocations, and the friction force depends on adhesive properties and shear strength.

I investigate the two materials Si and NaCl, materials with interatomic covalent bonds and ionic bonds, respectively. With the available computational resources, simulations with up to 20000 atoms are feasible with the potentials describing the interactions. This enables estimation of tensile and shear stress/strain, interface stress distributions, and deformation and adhesion energies. The main subject of the project is comparing trends in these quantities between the two materials.

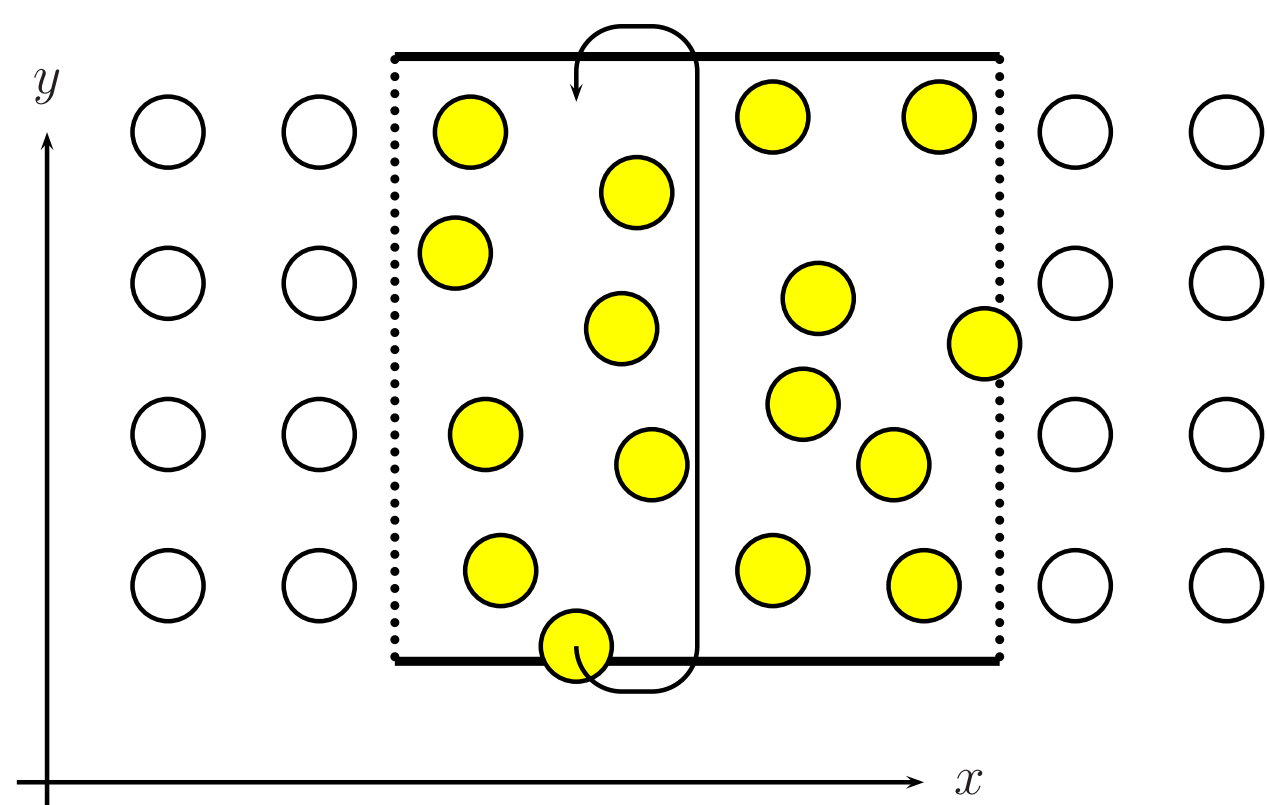
Molecular dynamics

Molecular dynamics (MD) is a theory used to simulate the motion of atoms in phase space. It has been used in materials science, biology, chemistry and astronomy to simulate both equilibrium and dynamical properties of matter. In macroscopic applications, where the discrete units are atoms, the typical scale of a simulation extends over nanometers and picoseconds.

With MD, atoms are described as point particles. The trajectories are approximated to solutions of Newton's second law, or equivalently, Lagrange's or Hamilton's equations. Finding the solution requires a good integrator. I use a common symplectic integrator known as the velocity Verlet algorithm. It conserves momentum and phase space volume exactly, and energy approximately.

Interactions with the surroundings of the simulated system are modelled by thermodynamical ensembles. The most common ones are the microcanonical (NVE), canonical (NVT) and pressure canonical (NPT) ensembles. In materials science the most useful is the second of these, which requires the use of methods popularly referred to as thermostats. I use a newly developed, tunable, semi-stochastic thermostat which obeys ergodicity and does not disturb dynamics [1]. Heat conduction is achieved by applying the thermostat to the atoms at the edges of the simulation box.

Periodic boundary conditions (PBC) in any number of Cartesian directions is possible. For numerical experiments with fracture or surface contact, two-dimensional PBC with fixed particles outside the non-periodic direction is desirable.



Schematic of an MD simulation with partial PBC.

Interatomic potentials

Classical molecular dynamics uses effective potentials to describe the behaviour of collections of atoms. These are mostly semi-empirical, with theoretically derived functional forms with parameters fitted to experimental data in order to reproduce cohesive energies, melting points and bulk moduli. Neighbour lists are used to reduce the computational effort of short-range potentials.

Ionic bonds

Elements close to the sides of the periodic system will engage in ionic bonds. Once atoms from these elements become ionic, they fulfill the octet rule, and their electronic densities are close to spherically symmetric. Interionic potentials can therefore be approximated as functions depending only on pairwise distances between ions. For this purpose, I utilize the popular Lennard-Jones (LJ) potential in addition to the Coulomb potential. The LJ potential was constructed with experimentally measured parameters σ_{ij} and ϵ_{ij} in the 60s and initially used to simulate liquid argon [2]. The charge distribution of an ion with a single electron deficiency or abundance is approx-

imated as a Dirac delta function with weight $\pm e$, with e being the elementary charge. The potential energy between ions i and j is (in reduced units)

$$U_{ij}^{\text{Ionic}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}. \quad (1)$$

Periodic boundary conditions complicate the matter because of the long-ranged nature of the Coulomb potential. The particle-particle Ewald method is used, in both 3D and 2D periodicity systems [3]. The reciprocal vectors \mathbf{k} are found by a spherical length cutoff, and the calculated electrostatic structure factors can exclude ions which are not periodically repeated, as those in single asperities on infinite surfaces.

Covalent bonds

Atoms have in general an angular dependence on their electronic densities, and therefore on the interatomic potentials. This fact can be taken into account by including n -body terms in the potential energy, depending on the relative positions of n atoms. By including correct n -body terms for $n \in \{2, N\}$, the exact quantum-mechanical interatomic forces are recovered. In practice, it is reasonable to stop at $n = 3$.

The Stillinger-Weber (SW) potential [4] is specially created for silicon, which I use as an example of a material with covalent bonds. Its most stable structure is the diamond lattice, where the equilibrium angle between atoms triplets, θ , satisfies $\cos \theta = -\frac{1}{3}$. The two-body part of the SW potential is

$$U_{ij}^{\text{SW2}} = A \left(\frac{B}{r_{ij}^4} - 1 \right) \exp \left(\frac{\sigma}{r_{ij} - r_c} \right) \quad \text{for } r_{ij} < r_c, \quad (2)$$

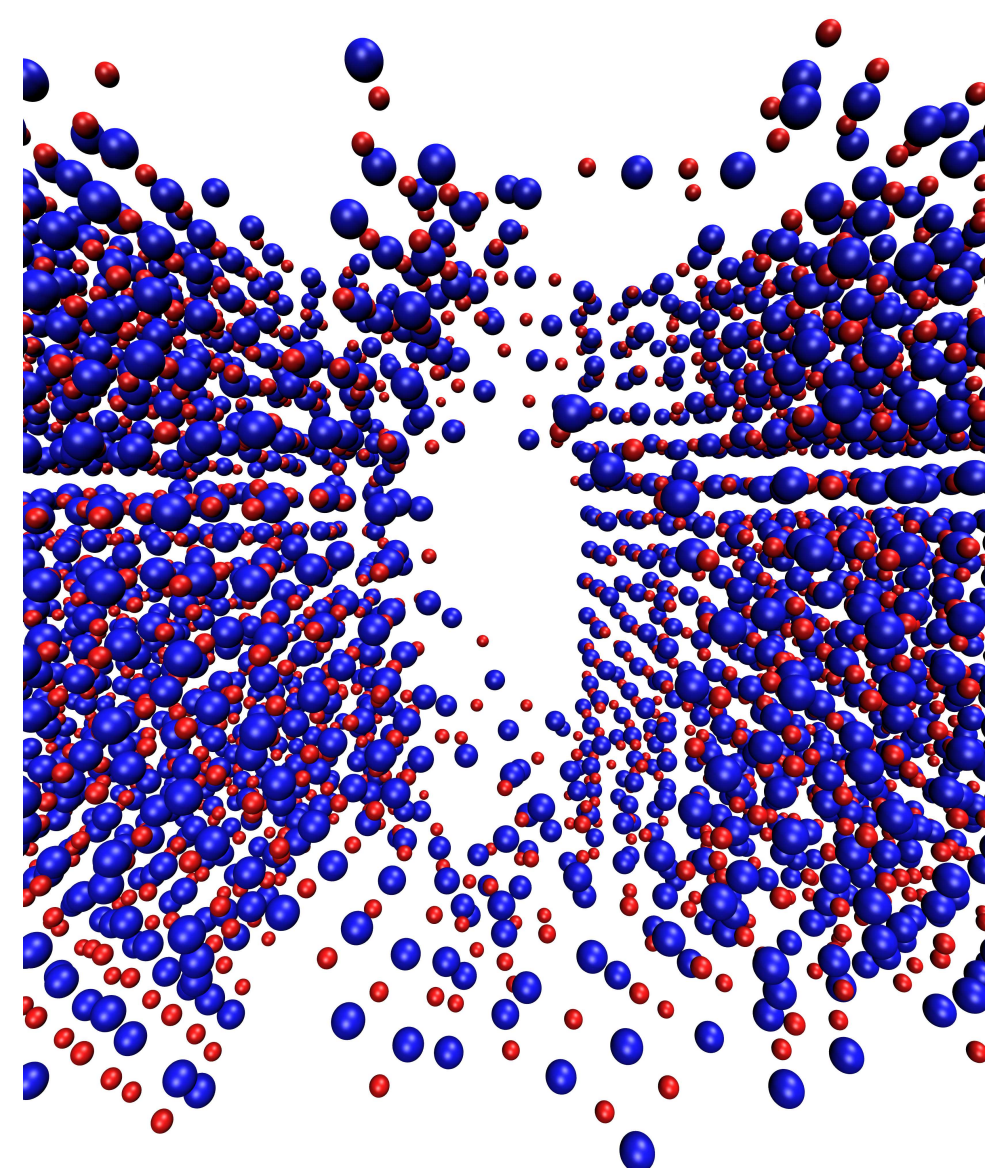
and zero otherwise. Similarly, the three-body part has the form

$$U_{ijk}^{\text{SW3}} = \lambda \exp \left(\frac{\gamma}{r_{ij} - r_c} + \frac{\gamma}{r_{ik} - r_c} \right) \left(\cos \theta_{ijk} + \frac{1}{3} \right)^2 \quad \text{for } r_{ij}, r_{ik} < r_c, \quad (3)$$

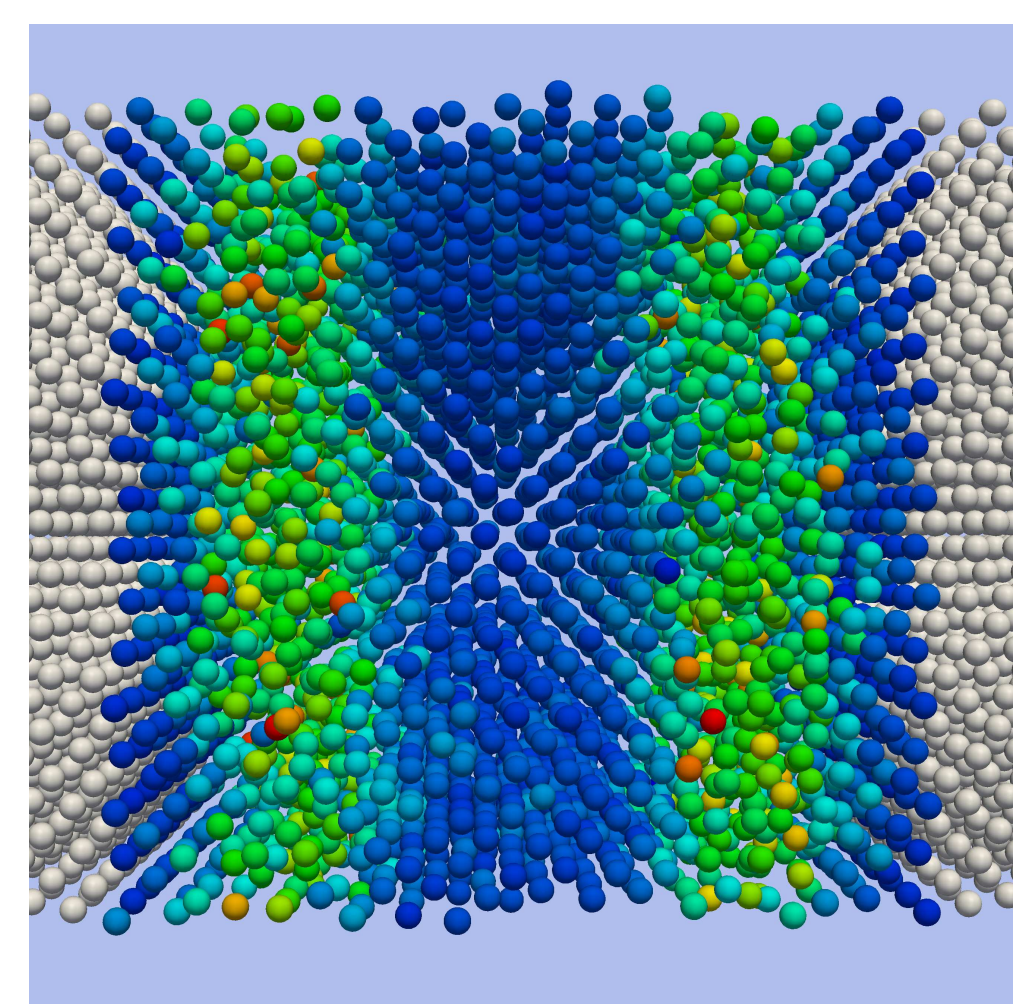
where θ_{ijk} is the angle between the three interacting atoms.

Fracture mechanics

Simulating fracture processes can give great insight in how the lattices of different atoms behave on a nanoscale. I have simulated both mode I (tensile) and mode II (shear) fractures. Visualizations are presented below.



Fracture of bulk NaCl.

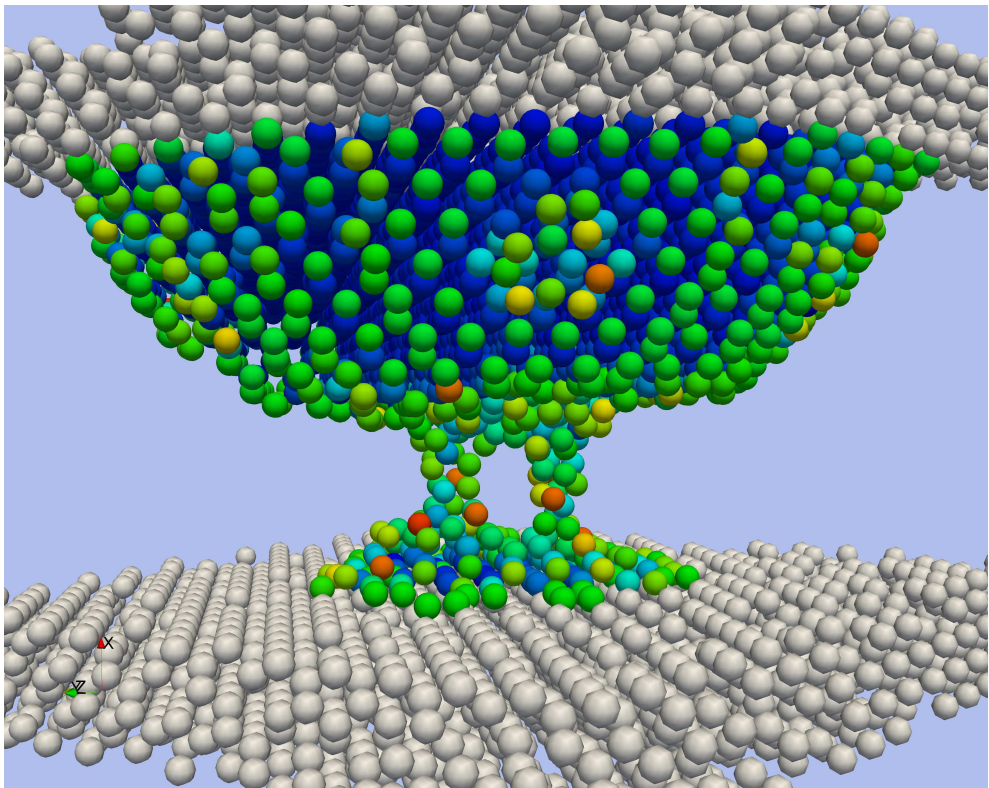


Shear fracture of bulk Si. Atoms are coloured by potential energy.

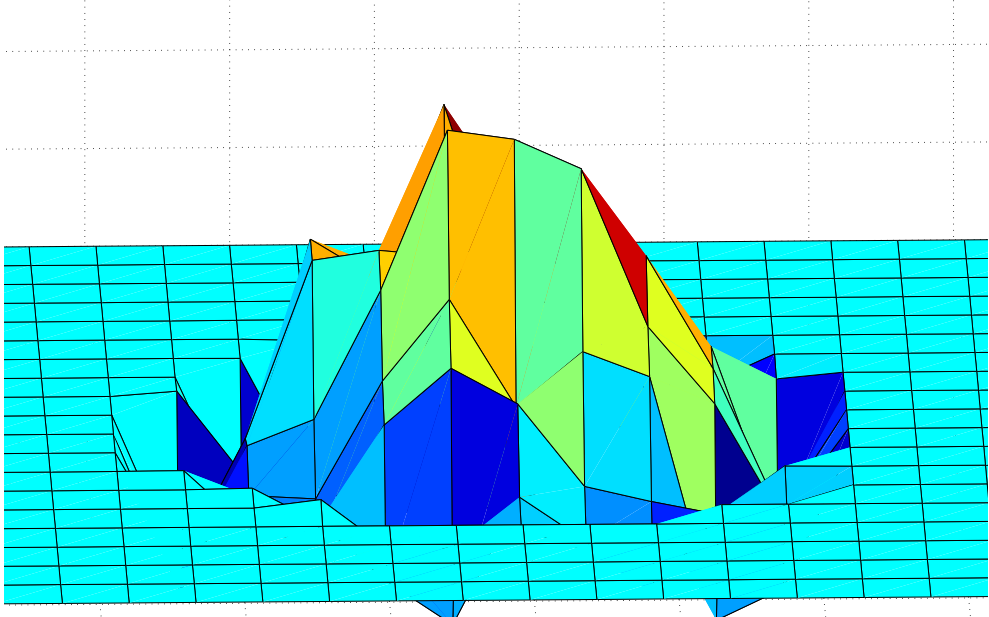
The most prominent difference in the behaviour of the two materials is the organization of atoms in the fracture areas. NaCl tends to keep its crystal structure, and keep fracture surfaces plain when possible. Shear deformations induce periodic slip motions. Silicon is a brittle material and stores great amounts of potential energy before fracturing in a more violent fashion. When shear stress is applied, channels of liquid Si will eventually form through the bulk and act as a lubricant between the two oppositely moving surfaces.

Tribology

The cause of friction is roughness of surfaces. The real area of contact between two surfaces is the sum of interfaces between asperities at the nanoscale. Thus studies of forces between asperities (e.g. sphere segments) and plane surfaces are important. Again, silicon atoms arrange randomly upon inflicted stress, while sodium chloride preserves its crystal structure. The stress distributions are similar to those obtained with harmonic spring and pure LJ potentials for similar atom organization [5]. On a side note, the force varies drastically when the NaCl surfaces are relatively rotated.

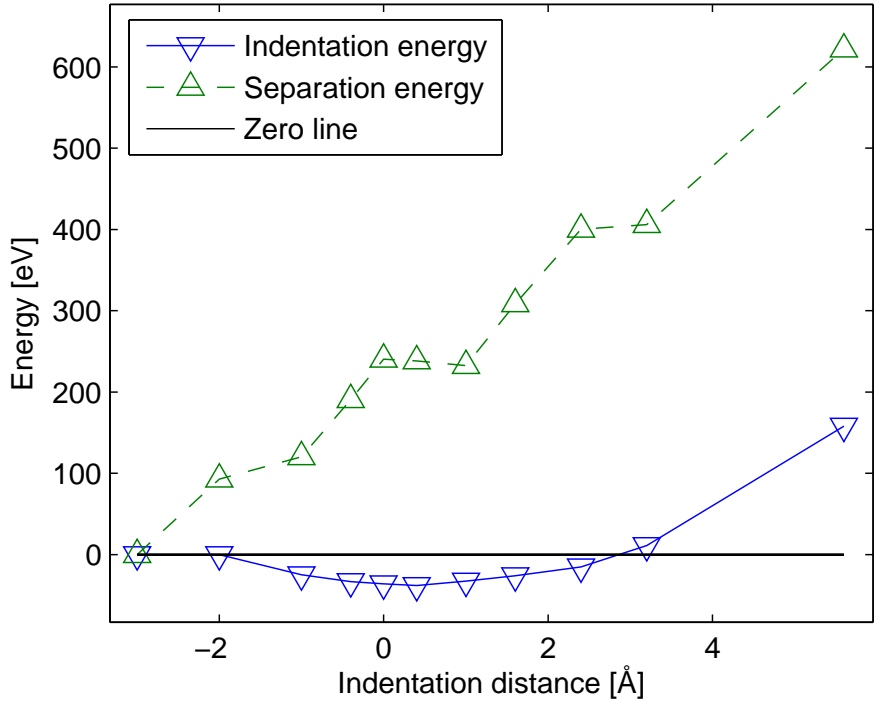


Adhesion between an Si asperity and surface.

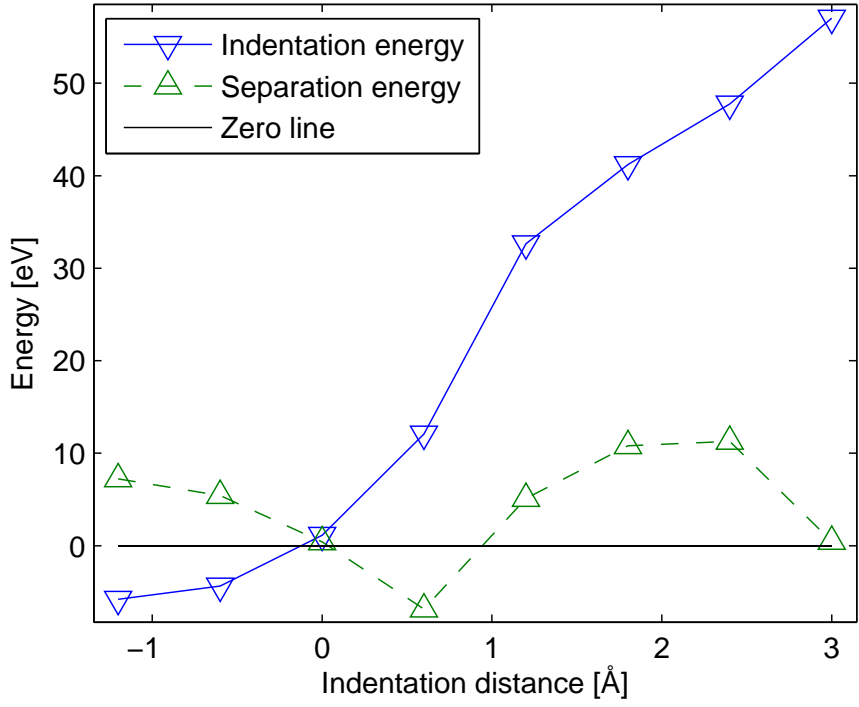


Asperity-surface interface stress for Si.

Differences between the two materials is more visible when a plastic deformation occurs. The figures below show the results from many simulations where an asperity is brought in contact with a plane surface and separated again. The energy required to deform the Si structure is very low, but great amounts of energy is needed to pull the surfaces apart again. NaCl stores energy from elastic stress, but once a (slip) deformation occurs, the potential energy lowers a lot because the contact area is increased. In big systems with several deformation stages, the bow pattern of separation energy is expected to repeat itself.



Silicon indentation



Sodium chloride indentation

References

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- [4] F. H. Stillinger and T. A. Weber, "Computer simulation of local order in condensed phases of silicon," *Phys. Rev. B*, vol. 31, pp. 5262–5271, Apr 1985.
- [5] B. Luan and M. O. Robbins, "The breakdown of continuum models for mechanical contacts," *Nature*, vol. 435, 2005.