

Activation volumes of mechanochemical reactions in amorphous materials

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Ab initio simulations of mechanochemical reactions in amorphous materials under stress are used to investigate activation volumes, an empirical quantity whose physical meaning is not well-understood at an atomic scale. Constant (stress-independent) activation volume are observed and quantified on the scale of a single chemical reactions for compression and shearing processes in amorphous carbon-hydrogen (a-C:H) and amorphous silicon dioxide, respectively. The conditions that lead to a constant activation volume and their geometric meaning are discussed.

Keywords (from 3 to 5 max): activation volume, mechano chemistry, ab initio simulations

1. Introduction

Experimental findings over the past few decades have supported the view of wear as the removal of individual atoms from a surface via the formation and breakage of bonds across an interface. A transition state theory treatment of this atomic loss leads to an Arrhenius model to describe the rate Γ of mechanically induced reactions [1]:

$$\Gamma = \nu \exp\left(\frac{\Delta G_{\text{act}}(\sigma)}{k_B T}\right).$$

Here, ν is the so-called attempt frequency, $\Delta G_{\text{act}}(\sigma)$ is the generally stress-dependent Gibbs free energy of activation, k_B is the Boltzmann constant and T is the temperature. Experimentally it is often observed that $\Delta G_{\text{act}}(\sigma)$ depends linearly on the applied mechanical stress σ :

$$\Delta G_{\text{act}}(\sigma) = \Delta G_{\text{act}}(0) - \sigma V_{\text{act}}. \quad (1)$$

The constant of proportionality V_{act} has the units of a volume. However, it is mostly an empirical parameter and its meaning is not well-understood.

In this study, we use ab initio simulations to test whether the linear relation (1) also holds on the scale of single bond breaking and forming events in amorphous materials and to quantify V_{act} for elementary processes. Moreover, we derive a condition under which (1) holds which also allows a geometrical interpretation of the activation volume.

2. Methods

We used density functional theory (DFT) to simulate the mechanical load dependence of the energetics of single plastic events. For this purpose, we conducted quasistatic simulations where we successively deformed the simulation box and relaxed the atomic positions at each step. Both compressive and shear deformations were investigated to evaluate the effects of normal load and shear stress, respectively. Then we extracted the thermodynamic enthalpies of the reactant, product and transition states of the plastic event of interest from the energy-deformation curves.

3. Discussion

A pronounced effect by the external deformation on the

energetics of mechanically-induced plastic events along the reaction path is found. In Fig. 1 the energy profiles along the reaction path of a C-C bond formation in a-C:H under compression are shown. The reaction changes from endothermic to exothermic and the activation energy decreases drastically. We will demonstrate that the reaction and activation enthalpies indeed scale linearly with the applied mechanical load over a wide range, as well as discuss the origin and the limits of the linear scaling behavior of equation (1) and give typical quantities for the activation volumes.

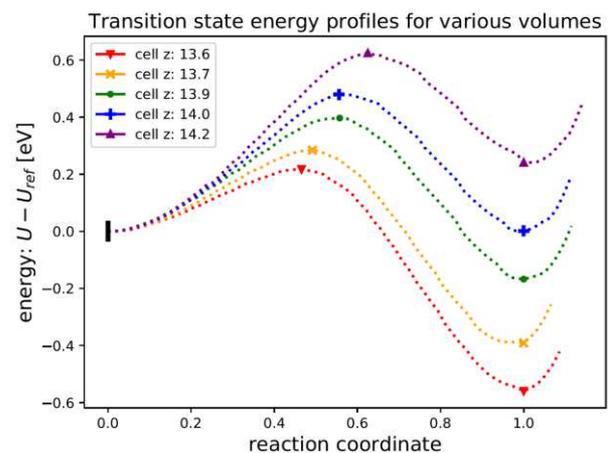
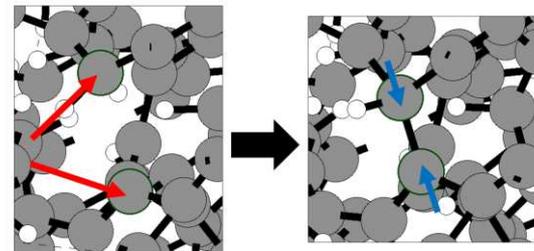


Figure 1: a) C-C bond formation in a-C:H under pressure. Large (small) spheres represent C (H) atoms. b) Change of reaction energy profiles of the process shown in a) under compressive deformation of the simulation box.

4. References

- [1] Jacobs, T.D.B. *et al.*, "On the Application of Transition State Theory to Atomic-Scale Wear," *Tribol. Lett.* 39, 2010, 257–271.