Effects of surfaces on the mechanical properties of nanoscale materials. A simulation study.

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Introduction

The emergence of refined fabrication techniques has given rise to structures on the tiniest length scales. Understanding the mechanical properties of such nanosized materials (where at least one dimension is comparable to the size of atoms) is key for various applications ranging from nanocomposites to microelectronic or microoptic devices. At the same time, there is also an increasing interest in understanding the mechanics of materials containing voids of nanoscopic size i.e. nanoporous structures. Such materials have been gaining importance in applications as high surface area activated adsorbents or in the production of fossil fuel from unconventional source rocks.

The usual equations within the realm of classical continuum theories fall short to explain the mechanical properties of such materials. For example, the 60-fold drop of the bulk modulus of some activated carbons containing 50% nanoporosity (i.e. pores in the order of less than or equal to 2 nm) with respect to the modulus of the solid carbonaceous matrix cannot be captured by classical poromechanics. The shortcomings of the classical theories at this scale are related to the fact that nano-sized structures can be characterized by a very large surface-to-volume ratio. Indeed, atoms at surfaces experience a lack of interaction and hence an increased energy environment. Atoms tend to minimize this increased energy state by rearranging themselves, which can lead to drastic adjustments of the structure at the surface as well as high equilibrium strains and stresses. For the correct description it is thus necessary to consider surface atoms a separate 'phase' with distinct mechanical behavior and elastic constants.

Methods and results

Atomistic simulations provide a unique tool to directly observe the mechanical behavior and rearrangements of atoms or any subgroups of atoms under arbitrary loading conditions. Indeed, molecular simulation studies of atomic plates and rods showed that the size dependence of elastic moduli can be very different depending on the material or the studied crystallographic surfaces.[1] These findings have later been confirmed by experimental investigations.

In this contribution we present an atomistic simulation study conducted on nanoscopic objects of varying characteristic size. Our main goal is to understand the role of large free surfaces in determining the overall mechanical properties of nanoscopic systems of different size and shape. We consider a model crystalline (fcc) system with different crystallographic surfaces. The observed behavior is decomposed into effective contributions of the 'core' and the 'surface' (as a region displaying different behavior from the 'core') which allows us to characterize the 'surface' in terms of its thickness and effective mechanical properties.

The studied crystalline structures lend themselves to defining reasonable quasi-homogeneous atomic layers and evaluating spatially resolved stress fields and mechanical properties. However, attributing stress locally in the system is a non-trivial task especially if the system is inhomogeneous. There exist two kinds of techniques to compute the stress field in atomistic simulations: one kind is based on volume averaging techniques and the other one makes use of a force-area concept. [2] We compare and discuss the physicality of the observed stress profiles calculated with different methods. As an example, Figure 1 compares the distribution of the normal stress in an infinite sheet of crystalline structure. The stress is evaluated in a

direction normal to the sheet based on atomic stress tensors as well as the so called 'method of planes'.[2] While with the former method we observe non-physical stress oscillations near the surface, the latter method gives vanishing stress throughout the system in the direction of the orthotropy. Most of our results are obtained at 0 K in a crystalline system, but we present results at finite temperatures as well as those obtained in disordered systems. In the last part of this contribution, based on the 'thin layer analogy', [3] we discuss the implications and the lower bounds on the macroscopic constants that are introduced by considering the interface as a 3D solid phase (i.e. and 'interfacial transition zone') instead of a 2D surface. [4]
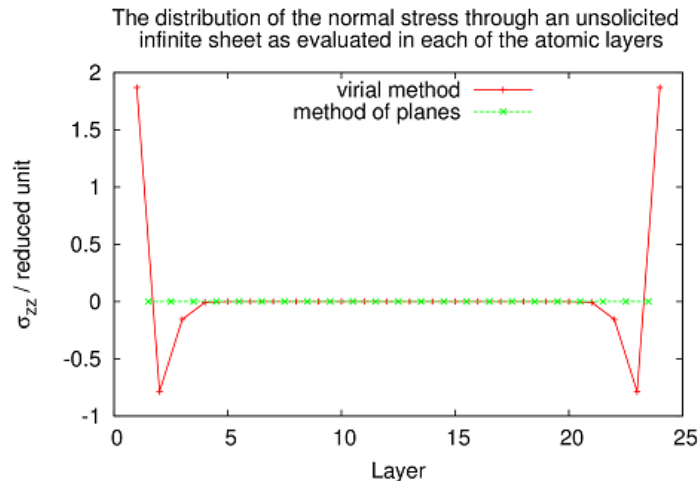

Figure 1. The stress computed in an infinite sheet of 24 atomic layers perpendicular to the direction of orthotropy. While the usual method based on atomic virials display unphysical oscillations at the surface, the method of planes, as expected, gives vanishing stress in all layers.

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