Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Acta Materialia 59 (2011) 4437–4447

Acta MATERIALIA

www.elsevier.com/locate/actamat

Surface eigen-displacement and surface Poisson's ratios of solids

Tong-Yi Zhang *, Hang Ren, Zhi-Jia Wang, Sheng Sun

Department of Mechanical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Received 21 February 2011; received in revised form 21 March 2011; accepted 27 March 2011

Abstract

Theoretical analysis and molecular dynamics simulations were conducted to study systematically surface eigen-displacement and surface Poisson's ratios of solids, which play essential roles in surface energy, surface strain and surface stress. Face-centered cubic (0 0 1) Au thin films were taken as typical examples to illustrate the physical picture. The surface eigen-displacement is a critical surface strain at the equilibrium state after normal relaxation and thus an intrinsic surface property. Surface Poisson's ratios are also intrinsic surface properties. Combining surface eigen-displacement and surface Poisson's ratios with surface eigen-stress and surface tangential elastic constants lays foundations of surface elasticity of solids.

Keywords: Surface energy; Surface elasticity; Surface eigen-displacement; Relaxation; Solids

---

1. Introduction

Surface stress and surface energy of solids play a central role in the thermodynamics of solid surfaces, which offer descriptions of macroscopic phenomena without the detailed knowledge about underlying atomistic processes. The role becomes even more significant in nanomaterials, where the surface-to-bulk ratio is much larger than that in bulk materials. Surface stress of solids has been studied by many researchers over a half century [1–9].

An interface is a boundary between two phases, say between phase α and phase β. If one of the two phases is vacuum or air, the interface is called surface. The interfacial boundary is physically a transition zone with a thickness, in which the thermodynamic property density changes from that of phase α to that of phase β. In thermodynamic study, surfaces and interfaces are treated in the same way [10]. There are three common approaches to study the properties of interface and thus the interface is called the diffusive interface, the interphase and the sharp or two-dimensional (2-D) interface. Theoretically, diffusive interface is described by a gradient term, e.g., the concentration gradient [11] or the polarization gradient [12]. The interphase approach treats an interface as a thermodynamic phase. However, the boundaries of the interphase are somewhat arbitrary and are usually chosen to be at locations at which the properties are no longer varying significantly with position. The interphase then has a finite volume and may be assigned thermodynamic properties in the normal way. Zhang and Hack [13] used the interphase approach to study the effect of grain boundaries on the elastic properties of nano-grained materials. Both diffusive interface and interphase approaches treat interfaces to be three-dimensional (3-D), while in the sharp interface approach where a single dividing interface (of zero thickness) is used to separate the two homogeneous phases, the interface contribution to the thermodynamic properties is defined as the excess over the values that would obtain if the bulk phases retained their properties constant up to the dividing surface. The sharp interface approach and the concept of a dividing surface were first introduced by Gibbs [10]. In this paper, we adopt the sharp interface approach.

---

* Corresponding author. Tel.: +852 2358 7192; fax: +852 2358 1543.
E-mail address: mezhangt@ust.hk (T.-Y. Zhang).

1359-6454/$36.00 © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2011.03.067

Following Gibbs' approach to interfacial excess quantities [10], Müller and Saúl analyzed the excess of elastic energy at an interface by decomposing stress and strain tensors into perpendicular and parallel contributions [14], i.e.,

$$\omega = \omega^{//} + \omega^{\perp} = \begin{pmatrix} \omega_{11}^{//} & \omega_{12}^{//} & 0 \\ \omega_{21}^{//} & \omega_{22}^{//} & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & \omega_{13}^{\perp} \\ 0 & 0 & \omega_{23}^{\perp} \\ \omega_{31}^{\perp} & \omega_{32}^{\perp} & \omega_{33}^{\perp} \end{pmatrix} \tag{1}$$

where ω is either stress tensor or strain tensor. Based on traction continuity and non-gliding at the interface, they defined interfacial stress tensor, σ_{ij}^{s}, and interfacial strain tensor, ε_{ij}^{s}, as

$$\sigma_{ij}^{s} = \frac{1}{A}\left[\int_{z_\alpha}^{z_\beta} \sigma_{ij}^{//} dV - \sigma_{ij}^{//\alpha} V^{\alpha} - \sigma_{ij}^{//\beta} V^{\beta}\right] \tag{2a}$$

$$\varepsilon_{ij}^{s} = \frac{1}{A}\left[\int_{z_\alpha}^{z_\beta} \varepsilon_{ij}^{\perp} dV - \varepsilon_{ij}^{\perp\alpha} V^{\alpha} - \varepsilon_{ij}^{\perp\beta} V^{\beta}\right] \tag{2b}$$

where A is the interfacial area, V^{α} and V^{β} are the volumes of bulk phases α and β extrapolated to the dividing surface, and the integration limits, z_α and z_β, include the entire interfacial transition zone. Then, the change in interface energy due to mechanical loading is given by

$$dW^{s} = A\sum_{i,j}\left[\sigma_{ij}^{s}\delta\varepsilon_{ij}^{//} + \varepsilon_{ij}^{s}\delta\sigma_{ij}^{\perp}\right] \tag{2c}$$

The same definition of interfacial stress tensor as Eq. (2a) was given by Kollár et al. and Ibach [15,16]. The interfacial stress tensor is an in-plane tensor, while the interfacial strain tensor is an out-plane tensor. In terms of strains, Weissmüller and Kramer separated surface deformation into surface-parallel deformation (the tangential strain) and surface-normal deformation (the normal strain) [17]. Surface-parallel deformation is related to the interfacial stress tensor with the surface stress–strain relationship, while surface-normal deformation can be gauged by the interfacial strain tensor of Eq. (2b). Weissmüller and Kramer proved that surface-parallel deformation and surface-normal deformation are both state variables in the surface free energy [17]. By atomistic simulations, Diao et al. found that surface relaxation induced the change in the wire length of gold nanowires [18]. Kwon et al. investigated the normal relaxation-induced changes in surface energy and surface stress by using ab initio total-energy methods [19]. The ab initio calculations indicate that relaxation of the outmost surface layer is significantly larger than the relaxations of the subsurface layers. Normal relaxation reduces not only surface energy, but also surface stress. Gupta studied normal relaxation of metal surfaces with Morse and LJ potentials and Friedel's tight-binding model [20]. Dingreville and Qu re-analyzed the problem of interfacial excess energy, excess stress and excess strain of planar interfaces and obtained the same results as those of Eq. (2) [21]. Their analysis indicates that surface stress and surface strain are not intrinsic properties of materials; rather, the in-plane interfacial stiffness tensor, the out-plane interfacial compliance tensor, and the coupling tensor, which accounts for the Poisson's effect of interface, describe fully the elastic behavior of a coherent interface upon deformation.

Huang et al. conducted coherent diffraction experiments to measure the movements of surface atoms of Au nanocrystals of 3–5 nm in diameter in comparison with the lattice constant of stress-free bulk counterpart. Clearly, such movements of surface atoms are caused by relaxations [22]. By examining diffraction intensity oscillations around the Bragg peaks and molecular dynamics simulations, they suggested that the relaxations were inhomogeneous, which involved large out-plane bond length contractions for the edge atoms (0.02 nm); a significant contraction (0.013 nm) for {1 0 0} surface atoms; and a much smaller contraction (0.005 nm) for atoms in the middle of the {1 1 1} facets.

Zhang et al. re-analyzed surface energy, surface stress, and surface elastic constants of a nanowire by treating a nanowire as a composite of a 3-D hypothetical nanowire, namely the core, 2-D geometric surfaces, and one-dimensional (1-D) geometric edges [23]. Note that here 3-D is used on the core to indicate that the core is geometrically 3-D and has a finite volume, in spite of whether theoretical analysis of the properties of the 3-D core is 2-D or 1-D. When a free-standing nanowire subjected to no external loads is at equilibrium after relaxation, the core usually presents an initial deformation along the nanowire length direction with respect to the stress-free bulk counterpart. When the initial stress field in the core is known, surface stress is determined from the force balance [23]. Following the same approach, Chan et al. investigated the bending behaviors of nanowires [24,25]. Taking solid films as a typical example, Zhang et al. studied surface stress of solids. If the bulk counterpart of a nanomaterial is taken as reference, a newly created nanomaterial relaxes inevitably because new surfaces are created [26]. Zhang et al. separated the relaxation process into normal relaxation and parallel relaxation and proposed a surface eigen-stress model to calculate the energy change during parallel relaxation [26]. Parallel relaxation induces in-plane deformation, called initial deformation, which could be large and nonlinear. After parallel relaxation, a tensile (or compressive) surface eigen-stress causes a compressive (or tensile) initial strain in the thin film with respect to its bulk lattice. Due to initial deformation, surface energy density and surface stress are both dependent on the film thickness, whereas surface elastic constants are independent of the film thickness. Furthermore, a general scaling law about the nominal Young's modulus is derived naturally and directly from the eigen-stress model, indicating that the nominal modulus of a thin film is determined generally by nonlinear elastic properties of its core and surfaces with initial strain. If initial deformation is linear, the general scaling law will be reduced to the linear scaling law. A tensile (or compressive) surface eigen-stress makes the nominal modulus of a thin film lager (or smaller), resulting in