From atomistics to continuum: effects of a free surface and determination of surface elasticity properties

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Abstract

We present an analysis of surface elasticity from the Born-Oppenheimer approximation for monatomic crystals. The analysis shows that the relaxations of crystal planes parallel to a free surface can be sufficiently determined by a low-rank algebraic Riccati equation instead of a full-scale molecular dynamic (MD) simulation, and gives new restrictions on physically reasonable atomistic models and simple criteria for surface reconstructions. In the case of surface relaxations, we calculate surface elasticity properties, i.e., surface tension, residual surface stress and surface elastic stiffness tensor, from atomistic models which are compared with experimental data and prior simulation results. The formulation also proves that surface relaxations always lower surface tension and surface elastic stiffness tensor. Together with the proposed algorithm, the formulation may be useful for investigating a variety of size-dependent phenomena of nano-structures.

Keywords: Surface elasticity, Atomistic-to-continuum, Size-dependent effects

1. Introduction

The surface effect of solids has been an important topic with impetus from both industries and academia. Miniaturization of electronics and nanofabrication require an in-depth understanding of surface effect on the physical properties of the bulk; some physical properties, e.g., catalysis, hydrophilicity, corrosion resistance, biocompatibility, adhesion and absorption among others, can emerge or be qualitatively improved through engineering solid surfaces which may revolutionize a number of technologies [6, 4].

In this work we focus on understanding mesoscopic effects and atomistic origin of surface elasticity [48, 49]. Surface elasticity of a liquid is conventionally modeled by postulating a surface energy that is proportional to surface area; the proportionality constant is referred to as the surface tension. The picture is, however, quite different for solids since the bulk elasticity, trivial for liquids, is intrinsically coupled with surface elasticity for solids. Moreover, it is expected that surface elasticity of solids is negligible for macroscopic bulk materials which, to some extent, explains why surface elasticity did not draw significant interest until recent years [27]. On the other hand, modern technologies allow for fabrication and

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functionalization of nanostructures with orders of magnitude larger surface to volume ratio than conventional structures where surface elasticity, presumably, plays an important role in determining overall properties of the nanostructure. This is evident from the experimental observations of size-dependent properties of nanostructures including the increase of strength [52, 53, 17, 23] and variation of the modulus of nanostructures [51, 16, 36, 20, 47, 8, 22]. Also, surfaces may induce phase transitions as shown in molecular dynamic (MD) simulations [10, 25, 50] and have been used to explain the size-dependent phase transition temperature of ferroelectric and ferromagnetic nanoparticles [21, 45, 55].

From a continuum viewpoint, the seminal works of Gurtin and Murdoch [28, 29] have laid a solid foundation for modeling surface elasticity of solids. In this theory a material surface is idealized as a two dimensional massless body adhering to the solid. Later, Steigmann and Ogden [40, 41] investigated the curvature effects of finite-thickness surfaces. By postulating a surface strain energy, we can define surface elasticity properties, i.e., surface tension, residual surface stress and surface elastic stiffness tensor. The reader is cautioned here that to be compatible with bulk elasticity and in contrast to liquid surfaces, it is more convenient to define surface elasticity properties of solids with respect to the stress-free state of the bulk. However, to our best knowledge there is not yet direct measurement of surface elasticity properties, in particular, surface elastic stiffness tensors, though acoustic measurements of surface wave dispersion relation may directly reveal surface elastic stiffness tensor [18]. Therefore, a number of authors have turned to atomistic models for assessing surface elasticity properties and their effects on the overall properties of nanostructures [46, 32, 7].

From an atomistic viewpoint, surface elasticity arises from (i) interatomic bond-breaking when new surfaces are created, (ii) surface relaxation or reconstruction [49, 30], and (iii) interatomic bond stretching and reorientation under applications of macroscopic strains. The Cauchy-Born rule [13, 31, 14] bridges the atomistic models and the Gurtin-Murdoch continuum model, which asserts that the atomic positions follow the macroscopic deformation. Upon specifying the atomistic model, one can then compute surface elasticity properties by equating the total energy of the atomistic model $E_{\text{tot}}(\mathbf{H})$ to the total strain energy of the continuum model $U_{\text{strain}}(\mathbf{H})$:

$$E_{\text{tot}}(\mathbf{H}) = U_{\text{strain}}(\mathbf{H}), \quad (1)$$

where $\mathbf{H} \in \mathbb{R}^{3 \times 3}$ is the unsymmetrized strain tensor. This strategy has been used to investigate surface/interface elasticity properties of metallic crystals [34, 46], thermoelastic properties [33], coupling of surface and bulk elasticity of nanostructures [32], noncoherent metallic interfaces [7], nanowires [8, 22], nano-multilayers/plates [43, 44] and nanocrystal superlattices [54]. Equipped with the surface elasticity properties obtained from atomistic models, the continuum theory can then be used to address many size-dependent phenomena and design new functional materials [37, 11].

In spite of recent intensive studies, MD simulations on surface elasticity, though may be a standard practice to many experts, yield few conclusive and general statements. Here we aim to systematically investigate the atomistic models themselves and consistently define surface elasticity properties as independent material properties from atomistic models and in conformity with fundamental symmetries of the system. Starting from the general Born-Oppenheimer approximation and under the assumption of small strains, we analyze the

effects of free surfaces on the crystalline structure and associated relaxations of crystal planes. It turns out that the stability of bulk crystals implies new restrictions on the atomistic models and simple criteria for surface reconstructions that appear to be unnoticed before. Also, to calculate the surface elasticity properties, it suffices to solve a low-rank algebraic Riccati equation instead of a full-scale MD simulation.

The paper is organized as follows: In Section 2 we briefly review the Gurtin-Murdoch continuum theory for surface elasticity. Based on the Born-Oppenheimer approximation, small strains and Cauchy-Born rule, we calculate the bulk and surface elasticity properties and derive the governing algebraic Riccati equation for surface relaxation in Section 3. In Section 4 we present numerical results of surface elasticity properties for FCC metallic crystals based on embedded atom potential. We conclude and summarize in Section 5.

2. Continuum surface elasticity: Gurtin-Murdoch theory

In this section we revisit the continuum theory for surface elasticity of solids that has been established by Gurtin and Murdoch [28, 29]. Let $\Omega \subset \mathbb{R}^3$ be an open bounded domain with a free surface $\Gamma = \partial\Omega$, $\mathbf{n} \in \mathbb{R}^3$ be the unit outward normal on Γ , $\mathbb{S}_{\mathbf{n}} = \{\mathbf{M} \in \mathbb{R}^{3 \times 3} : \mathbf{M}\mathbf{n} = 0 \text{ and } \mathbf{M}^T\mathbf{n} = 0\}$ be a subspace to which surface stress and strain belong, and $\mathcal{P}_{\mathbf{n}} : \mathbb{R}^{3 \times 3} \rightarrow \mathbb{S}_{\mathbf{n}}$ be the projection operator. Assume that the body undergoes a C^2 -deformation $\mathbf{y} : \Omega \rightarrow \mathbf{y}(\Omega)$. The Gurtin-Murdoch theory postulates that the surface elastic energy is given by

$$U_{\text{surf}}[\mathbf{y}] = \int_{\Gamma} W_s(\nabla \mathbf{y}, \mathbf{n}) dS, \quad (2)$$

where the derivatives in the deformation gradient $\nabla \mathbf{y}$ are defined with respect to the Lagrangian coordinates $\mathbf{x}$ of the reference configuration Ω , $W_s : \mathbb{R}^{3 \times 3} \times \mathbb{R}^3 \rightarrow \mathbb{R}$ is the surface energy density function that determines the surface stress-strain relation, and the explicit $\mathbf{n}$ -dependence of W_s reflects the fact that the surface energy density may depend on the orientation of surface. For reasonable physical behaviors, we shall assume the energy density function satisfies that for any $\mathbf{F} \in \mathbb{R}^{3 \times 3}$,

$$\begin{aligned} (i) \quad & W_s(\mathbf{F}, \mathbf{n}) = W_s(\mathcal{P}_{\mathbf{n}}\mathbf{F}, \mathbf{n}), \\ (ii) \quad & W_s(\mathbf{QF}, \mathbf{n}) = W_s(\mathbf{F}, \mathbf{n}) \quad \forall \mathbf{Q} \in SO(3), \quad \text{and} \\ (iii) \quad & W_s(\mathbf{FR}, \mathbf{n}) = W_s(\mathbf{F}, \mathbf{n}) \quad \forall \mathbf{R} \in \mathcal{G}_{\mathbf{n}}, \end{aligned} \quad (3)$$

where the first equation reflects the fact that surface energy depends only on the stretches restricted to the surface, the second follows from the principle of frame indifference with $SO(3)$ representing all rigid rotations, and the last follows from the material symmetry with $\mathcal{G}_{\mathbf{n}}$ being the local symmetry group of the surface.

It will be useful to linearize the above general theory and obtain a linear surface stress-strain relation. The “natural” state of a free surface in general cannot coincide with the stress-free state of the bulk. Let $\mathbf{I} \in \mathbb{R}^{3 \times 3}$ be the identity tensor, $\mathbf{F}_{\mathbf{n}}^0$ be a deformation gradient that minimizes the surface energy density function:

$$W_s(\mathbf{F}_{\mathbf{n}}^0, \mathbf{n}) = \min\{W_s(\mathbf{M}, \mathbf{n}) : \mathbf{M} \in \mathbb{R}^{3 \times 3}\} =: W_s^*(\mathbf{n}),$$

and $\epsilon_{\mathbf{n}}^0 = \frac{1}{2}(\mathbf{F}_{\mathbf{n}}^{0T} + \mathbf{F}_{\mathbf{n}}^0) - \mathbf{I}$ be the linearized residual strain on the free surface. For a linearized theory, we assume that $|\epsilon_{\mathbf{n}}^0| \ll 1$ on Γ and consider only small strain in the sense that $|\nabla \mathbf{u}| = |\nabla \mathbf{y} - \mathbf{I}| \sim \delta \ll 1$ on Ω , where $\mathbf{u}(\mathbf{x}) = \mathbf{y}(\mathbf{x}) - \mathbf{x}$ is the displacement. Expanding W_s by Taylor series in a neighborhood of $\mathbf{F}_{\mathbf{n}}^0$, we rewrite the surface elastic energy (2) as a functional of displacement:

$$U_{\text{surf}}[\mathbf{u}] = \int_{\Gamma} \left[\gamma(\mathbf{n}) - \nabla \mathbf{u} \cdot \boldsymbol{\tau}_0(\mathbf{n}) + \frac{1}{2} \nabla \mathbf{u} \cdot \mathbf{C}_s(\mathbf{n}) \nabla \mathbf{u} \right], \quad (4)$$

where the terms beyond $O(\delta^2)$ are neglected, $\gamma(\mathbf{n}) := W_s^*(\mathbf{n}) + \frac{1}{2} \epsilon_{\mathbf{n}}^0 \cdot \mathbf{C}_s(\mathbf{n}) \epsilon_{\mathbf{n}}^0$ is the surface tension (of the undeformed surface), $\boldsymbol{\tau}_0(\mathbf{n}) = \mathbf{C}_s(\mathbf{n}) \epsilon_{\mathbf{n}}^0$ is the residual surface stress, and $\mathbf{C}_s(\mathbf{n})$ is the forth-order surface elasticity (or stiffness) tensor:

$$[\mathbf{C}_s(\mathbf{n})]_{piqj} = \frac{\partial^2 W_s(\mathbf{F}, \mathbf{n})}{\partial(\mathbf{F})_{pi} \partial(\mathbf{F})_{qj}} \bigg|_{\mathbf{F}=\mathbf{F}_{\mathbf{n}}^0}.$$

In addition to the major symmetry, the second of (3) implies the minor symmetry of the surface elasticity tensor:

$$[\mathbf{C}_s(\mathbf{n})]_{piqj} = [\mathbf{C}_s(\mathbf{n})]_{qjpi} = [\mathbf{C}_s(\mathbf{n})]_{pijq}.$$

Also, the first of (3) implies that $W_s(\mathbf{F}, \mathbf{n}) = W_s(\mathbf{F}_{\mathbf{n}}^0, \mathbf{n})$ if $\mathcal{P}_{\mathbf{n}}(\mathbf{F} - \mathbf{F}_{\mathbf{n}}^0) = 0$, and hence

$$\mathbf{C}_s(\mathbf{n}) = \mathcal{P}_{\mathbf{n}} \mathbf{C}_s(\mathbf{n}) \mathcal{P}_{\mathbf{n}}.$$

Further restrictions on the surface elasticity tensor $\mathbf{C}_s$ can be obtained by the last of (3) upon specifying the symmetry group $\mathcal{G}_{\mathbf{n}}$.

We remark that the linearized Gurtin-Murdoch theory has recently attracted quite some interest and been used to explain size-dependent properties of nanostructures and nanocomposites [38, 12, 11, 19].

3. Determination of surface elastic properties from atomistic models

Though the continuum theory of surface elasticity has been well established, the surface elasticity properties, i.e., $\gamma(\mathbf{n})$, $\boldsymbol{\tau}_0(\mathbf{n})$ and $\mathbf{C}_s(\mathbf{n})$ defined in (4), appear to be elusive to experimental investigations. Microscopically speaking, surface energy and surface elasticity arise from bond breaking and stretching between two half-space bodies. Besides possible surface reconstruction, planes of atoms relax in the out-of-surface direction so as to significantly change electrical, optical and thermal properties of the materials. Therefore, it is of great importance to understand the origin of surface energy, surface elasticity and surface relaxation from the atomistic point of view. Below we describe a general atomistic model that will be used for our subsequent calculations of surface elasticity properties.

3.1. An atomistic model of a finite crystal

We begin with an infinite body that, in the equilibrium state, would have its atomic positions at lattice points $\mathcal{L} \subset \mathbb{R}^3$. Let a be the atomic lengthscale and consider a macroscopic

thin slab $\Omega = [0, L] \times [0, L] \times [0, h]$ with $L \gg h \gg a$. Upon removing all atoms that are not in the domain Ω , we are left with a finite crystal with reference atomic positions at $\Omega \cap \mathcal{L}$. Due to the bond-breaking at the boundary $\partial\Omega$, the atoms will deviate from the reference positions so as to reach a new equilibrium state. Denoted by $\mathbf{x}_\nu$ the new positions of the atom with a reference position $\mathbf{x}_\nu^0 \in \Omega \cap \mathcal{L}$, where $\nu \in \{1, \dots, M\}$ labels the atom and M is the total number of atoms in the finite crystal. We assume the displacement of all atoms $\mathbf{u}_\nu$ are small, i.e, $\mathbf{u}_\nu = \mathbf{x}_\nu - \mathbf{x}_\nu^0 \sim \delta \ll a$.

By the general Born-Oppenheimer approximation, we write the total internal energy of this finite body as a function of the positions of all atoms:

$$E_{\text{tot}} = E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M), \quad (5)$$

where $E_{\text{tot}} : \mathbb{R}^{3M} \rightarrow \mathbb{R}$ is assumed to be a smooth function. It is clear that the total energy function shall be invariant with respect to the Galilean transformations:

$$E_{\text{tot}}(\mathbf{Q}\mathbf{x}_1 + \mathbf{c}, \dots, \mathbf{Q}\mathbf{x}_M + \mathbf{c}) = E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M) \quad \forall \mathbf{c} \in \mathbb{R}^3, \mathbf{Q} \in SO(3). \quad (6)$$

For small displacements, we approximate the total internal energy by a quadratic function of atomic displacements:

$$E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M) = E_{\text{tot}}(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0) + \sum_{\nu=1}^M \mathbf{f}_\nu \cdot \mathbf{u}_\nu + \frac{1}{2} \sum_{\nu, \mu=1}^M \mathbf{u}_\nu \cdot \mathbf{K}_{\nu\mu} \mathbf{u}_\mu + o(\delta^2), \quad (7)$$

where $\mathbf{f}_\nu \in \mathbb{R}^3$ and $\mathbf{K}_{\nu\mu} \in \mathbb{R}^{3 \times 3}$ are given by

$$\mathbf{f}_\nu = \left. \frac{\partial E_{\text{tot}}}{\partial \mathbf{x}_\nu} \right|_{(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0)}, \quad \mathbf{K}_{\nu\mu} = \left. \frac{\partial^2 E_{\text{tot}}}{\partial \mathbf{x}_\nu \partial \mathbf{x}_\mu} \right|_{(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0)}. \quad (8)$$

Physically, the vectors $\mathbf{f}_\nu$ can be interpreted as the force acting on the atom at $\mathbf{x}_\nu^0$ and $\mathbf{K}_{\nu\mu} \in \mathbb{R}_{\text{sym}}^{3 \times 3}$ can be interpreted as the ‘spring constants’ between atoms at $\mathbf{x}_\nu^0$ and $\mathbf{x}_\mu^0$ in the reference configuration $\Omega \cap \mathcal{L}$. We note that the general form of energy (7) can account for the angular and nonlocal dependence of atoms’ energy. From (6) we infer that for any skew-symmetric tensor $\mathbf{W} = -\mathbf{W}^T \in \mathbb{R}^{3 \times 3}$ and $\mathbf{c} \in \mathbb{R}^3$,

$$\sum_{\nu=1}^M \mathbf{f}_\nu \cdot (\mathbf{W}\mathbf{x}_\nu^0 + \mathbf{c}) + \frac{1}{2} \sum_{\nu, \mu=1}^M (\mathbf{u}_\nu + \mathbf{W}\mathbf{x}_\nu^0 + \mathbf{c}) \cdot \mathbf{K}_{\nu\mu} (\mathbf{u}_\mu + \mathbf{W}\mathbf{x}_\mu^0 + \mathbf{c}) - \frac{1}{2} \sum_{\nu, \mu=1}^M \mathbf{u}_\nu \cdot \mathbf{K}_{\nu\mu} \mathbf{u}_\mu = 0.$$

Therefore,

$$\begin{aligned} \sum_{\nu=1}^M \mathbf{f}_\nu &= 0, & \sum_{\nu=1}^M \mathbf{K}_{\nu\mu} &= \sum_{\mu=1}^M \mathbf{K}_{\nu\mu} = 0, \\ \sum_{\nu=1}^M \mathbf{f}_\nu \cdot \mathbf{W}\mathbf{x}_\nu^0 &= 0, & \sum_{\mu=1}^M \mathbf{K}_{\nu\mu} \mathbf{W}\mathbf{x}_\mu^0 &= 0. \end{aligned} \quad (9)$$

Figure 1: *Surface atoms and bulk atoms*

Moreover, we anticipate that two atoms cannot directly interact if the distance between them exceeds, say, R . To be precise, we introduce the concept of *cut-off radius*. As shown in Fig. 1, for the ν th atom in the reference state its “*neighboring atoms*” are defined as $\mathcal{N}_\nu = \{\mathbf{x}_\mu^0 \in \Omega : |\mathbf{x}_\nu^0 - \mathbf{x}_\mu^0| \leq R\}$. By the distance to the surface $\partial\Omega$, we refer to $\mathcal{B} = \{\mathbf{x}_\nu^0 \in \Omega : \text{dist}(\partial\Omega, \mathbf{x}_\nu^0) > R\}$ as the *bulk atoms* and $\mathcal{S} = \{\mathbf{x}_\nu^0 \in \Omega : \text{dist}(\partial\Omega, \mathbf{x}_\nu^0) \leq R\}$ as the *surface atoms*. The *cut-off radius* R is such that

$$\begin{cases} \mathbf{K}_{\nu\mu} = 0 & \text{if } |\mathbf{x}_\nu^0 - \mathbf{x}_\mu^0| > R, \\ \mathbf{f}_\nu = 0 & \forall \mathbf{x}_\nu^0 \in \mathcal{B}, \end{cases} \quad (10)$$

where the first reflects the physical intuition that two-atoms do not interact if they are far apart, and the second follows from the assumption that the reference state would be the equilibrium state for a perfect infinite crystal.

We remark that besides the reference lattice structure $\mathcal{L}$, the coefficients $\mathbf{K}_{\nu\mu}$ and $\mathbf{f}_\nu$ defined by (8) are the only atomistic parameters needed for our subsequent calculations of bulk and surface elasticity properties for small strains. Also, equations (9) impose fundamental restrictions on an atomistic model that may be relevant to some fundamental conceptual problems [1]. If the cut-off radius R is small enough such that only the nearest neighbors interact, the total energy (7) can be identified as the strain energy in a discretized finite element model for the classic linearized elasticity; for larger cut-off radius that takes into account interactions beyond nearest neighbors, the energy (7) can be regarded as the total energy in a discretized model for the linearized peridynamics with R being the *peridynamic*

horizon [39]. Also, the energy (7) can be a reasonable starting point for studying a variety of properties of harmonic crystals including bulk linear elasticity, phononic dispersion relations, surface elasticity, thermal fluctuations among others [2, 14]. For example, we can find the bulk elasticity tensor by equating the continuum strain energy per unit volume to the change of total energy per unit volume in the atomistic model for a large crystal:

$$\frac{1}{2}\mathbf{H} \cdot \mathbf{C}\mathbf{H} = \frac{1}{V}[E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M) - E_{\text{tot}}(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0)],$$

where V ($V \gg 1$) is the volume of the finite crystal, $\mathbf{C} : \mathbb{R}^{3 \times 3} \rightarrow \mathbb{R}^{3 \times 3}$ is the forth-order bulk elasticity tensor, $\mathbf{H} \in \mathbb{R}^{3 \times 3}$ is the unsymmetrized strain, and

$$\mathbf{x}_\nu = \mathbf{x}_\nu^0 + \mathbf{H}\mathbf{x}_\nu^0 \quad (\nu = 1, \dots, M)$$

are the new positions of the atoms that follow from the Cauchy-Born rule. Assuming $\mathbf{H}\mathbf{x}_\nu^0 \sim \delta \ll a$ ($\nu = 1, \dots, M$), by (7) we have

$$\frac{1}{2}\mathbf{H} \cdot \mathbf{C}\mathbf{H} = \frac{1}{V} \left[\sum_{\mathbf{x}_\nu^0 \in \mathcal{S}} \mathbf{f}_\nu \cdot \mathbf{H}\mathbf{x}_\nu^0 + \frac{1}{2} \sum_{\mu, \nu=1}^M (\mathbf{H}\mathbf{x}_\nu^0) \cdot \mathbf{K}_{\nu\mu}(\mathbf{H}\mathbf{x}_\mu^0) \right]. \quad (11)$$

To proceed, we now assume that the crystal is monatomic and the reference lattice $\mathcal{L}$ is a simple Bravais lattice $\mathcal{L} = \{i_1\mathbf{a}_1 + i_2\mathbf{a}_2 + i_3\mathbf{a}_3 : i_1, i_2, i_3 \in \mathbb{Z}\}$, where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \in \mathbb{R}^3$ are the lattice vectors. By periodicity we can verify the following properties for *bulk atoms*:

$$\mathbf{K}_{\nu_1\mu_1} = \mathbf{K}_{\nu_2\mu_2} \quad \text{if } \mathbf{x}_{\nu_1}^0 - \mathbf{x}_{\mu_1}^0 = \mathbf{x}_{\nu_2}^0 - \mathbf{x}_{\mu_2}^0, \mathbf{x}_{\nu_1}^0, \mathbf{x}_{\nu_2}^0, \mathbf{x}_{\mu_1}^0, \mathbf{x}_{\mu_2}^0 \in \mathcal{B}. \quad (12)$$

By (10) and (11), we find that

$$\begin{aligned} \frac{1}{2}\mathbf{H} \cdot \mathbf{C}\mathbf{H} &= \frac{1}{V} \sum_{\mathbf{x}_\nu^0 \in \mathcal{S}} \mathbf{f}_\nu \cdot \mathbf{H}\mathbf{x}_\nu^0 + \frac{1}{2V} \sum_{\mu, \nu=1}^M (\mathbf{H}\mathbf{x}_\nu^0) \cdot \mathbf{K}_{\nu\mu}(\mathbf{H}\mathbf{x}_\mu^0) \\ &\rightarrow \frac{M}{2V} \sum_{\mathbf{x}_\mu^0 \in \mathcal{N}_\nu} (\mathbf{H}\mathbf{x}_\nu^0) \cdot \mathbf{K}_{\nu\mu}(\mathbf{H}\mathbf{x}_\mu^0) \quad \text{as } V \rightarrow +\infty. \end{aligned} \quad (13)$$

Therefore, the bulk elasticity tensor of the crystal is given by

$$[\mathbf{C}]_{piqj} = n_0 \sum_{\mathbf{x}_\mu^0 \in \mathcal{N}_\nu} (\mathbf{x}_\nu^0)_i [\mathbf{K}_{\nu\mu}]_{pq} (\mathbf{x}_\mu^0)_j \quad \forall \nu \in \mathcal{B}, \quad (14)$$

where the crystal constant $n_0 = M/V$ is the number of atoms per unit volume, and by (12) the value $[\mathbf{C}]_{piqj}$ is independent of the index ν . Also, we notice that the properties in (9) guarantee that the bulk elasticity tensor satisfies the usual symmetries: $[\mathbf{C}]_{piqj} = [\mathbf{C}]_{qjpi} = [\mathbf{C}]_{pijq}$.

Figure 2: Layer number $l \in \{1, 2, \dots, \Theta\}$ labels crystal planes parallel to the free surfaces.

3.2. Surface elasticity properties

We now calculate the surface elasticity properties in terms of atomistic parameters for the bulk stiffness tensor. In addition to the assumption that the reference crystal $\mathcal{L}$ is monatomic and a simple Bravais lattice, we assume that (i) the top surface $\{z = h\}$ and the bottom surface $\{z = 0\}$ are rational crystal planes, and (ii) upon creation of the top and bottom free surfaces, there occurs only surface relaxation instead of surface reconstruction; all crystal planes that are perpendicular to $\mathbf{b}_3 := \mathbf{a}_1 \times \mathbf{a}_2$ move as a whole. Without loss of generality, assume the our Cartesian coordinate basis vector $\mathbf{e}_3 = \mathbf{b}_3/|\mathbf{b}_3|$. The assumption (i) enables us to label crystal planes perpendicular to $\mathbf{e}_3$ sequentially from bottom to top by $1, 2, \dots, \Theta$, see Fig. 2. Let $d_0 = |\mathbf{a}_3 \cdot \mathbf{e}_3|$ be the distance between two neighboring crystal planes. For ease of notation, we introduce a mapping between the atomic label and the layer number:

$$\begin{cases} \theta : \{1, 2, \dots, M\} \rightarrow \{1, 2, \dots, \Theta\}, \\ \nu \mapsto \theta(\nu) = 1 + |\mathbf{x}_\nu^0 \cdot \mathbf{e}_3|/d_0, \end{cases}$$

and denote the set of atoms on the l th crystal plane by

$$\theta^{-1}(l) := \{\nu \in \{1, \dots, M\} : \theta(\nu) = l\}.$$

By the assumption (ii) we infer that upon applying an average unsymmetrized strain $\mathbf{H} \in \mathbb{R}^{3 \times 3}$, the new positions of atoms can be written as

$$\mathbf{x}_\nu = \mathbf{x}_\nu^0 + \mathbf{H}\mathbf{x}_\nu^0 + w_{\theta(\nu)}\mathbf{e}_3, \quad (15)$$

where the first two terms follow from the Cauchy-Born rule, and $w : \{1, \dots, \Theta\} \rightarrow \mathbb{R}$ characterizes the out-of-surface relaxations of crystal planes upon the creation of free surfaces.

We are interested in the elastic energy associated with *traction-free* surfaces and how it depends on surface strain. From the viewpoint of bulk elasticity, the traction on an interface with unit normal $\mathbf{n} = \mathbf{e}_3$ is given by

$$\mathbf{t} = (\mathbf{CH})\mathbf{n}, \quad (16)$$

which, in general, would not vanish for planar strain $\mathbf{H} \in \mathbb{S}_{\mathbf{n}}$ because of the Poisson's effect. Therefore, we shall restrict ourselves to applied deformations such that (16) vanishes, i.e.,

$$\mathbf{H} \in \mathbb{H}_0 = \{\mathbf{H} \in \mathbb{R}^{3 \times 3} : (\mathbf{CH})\mathbf{n} = 0\}.$$

Then the surface energy density in the atomistic model as a function of the strain tensor $\mathbf{H}$ and relaxations $(w_1, \dots, w_\Theta)$ can be identified as (c.f., (18) and (14))

$$E_{\text{surf}}(\mathbf{H}, w_1, \dots, w_\Theta) = \frac{1}{2L^2} \left[E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M) - \frac{1}{2} V \mathbf{H} \cdot \mathbf{CH} - V \varphi_0 \right], \quad (17)$$

where $\frac{1}{2} V \mathbf{H} \cdot \mathbf{CH}$ represents bulk strain energy, and φ_0 is the ground state energy per unit volume of the perfect crystal and given by

$$\frac{1}{V} E_{\text{tot}}(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0) \rightarrow \varphi_0 \quad \text{as } V \rightarrow +\infty. \quad (18)$$

Let

$$\gamma^0 = \frac{1}{2L^2} [E_{\text{tot}}(\mathbf{x}_1^0, \dots, \mathbf{x}_M^0) - V \varphi_0]. \quad (19)$$

By (7), (15) and neglecting higher order terms, we rewrite the surface energy density (17) as

$$\begin{aligned} E_{\text{surf}}(\mathbf{H}, w_1, \dots, w_\Theta) &= \gamma^0 + \frac{1}{2L^2} \left\{ \sum_{l=1}^{\Theta} \sum_{\nu \in \theta^{-1}(l)} \mathbf{f}_\nu \cdot (\mathbf{H} \mathbf{x}_\nu^0 + w_l \mathbf{e}_3) \right. \\ &\quad \left. + \frac{1}{2} \sum_{l, l'=1}^{\Theta} \sum_{\nu \in \theta^{-1}(l), \mu \in \theta^{-1}(l')} (\mathbf{H} \mathbf{x}_\nu^0 + w_l \mathbf{e}_3) \cdot \mathbf{K}_{\nu\mu} (\mathbf{H} \mathbf{x}_\mu^0 + w_{l'} \mathbf{e}_3) \right\} \\ &=: \gamma^0 + \boldsymbol{\sigma} \cdot \mathbf{H} + \frac{1}{2} \mathbf{H} \cdot \mathbf{SH} + \frac{1}{2} \left[\sum_{l=1}^{\Theta} (g_l w_l + w_l \mathbf{B}_l \cdot \mathbf{H}) + \frac{1}{2} \sum_{l, l'=1}^{\Theta} (\tilde{\mathbf{K}})_{ll'} w_l w_{l'} \right], \end{aligned} \quad (20)$$

where (recall that $\mathbf{C}$ is given by (14))

$$\begin{aligned} \boldsymbol{\sigma} &= \frac{1}{2L^2} \sum_{\nu=1}^M \mathbf{f}_\nu \otimes \mathbf{x}_\nu^0, & [\mathbf{S}]_{piqj} &= \frac{1}{2L^2} \left[\sum_{\nu, \mu=1}^M (\mathbf{x}_\nu^0)_i [\mathbf{K}_{\nu\mu}]_{pq} (\mathbf{x}_\mu^0)_j - V \mathbf{C} \right], \\ g_l &= \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l)} \mathbf{f}_\nu \cdot \mathbf{e}_3, & \mathbf{B}_l &= \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l)} \sum_{\mu=1}^M (\mathbf{K}_{\nu\mu} \mathbf{e}_3) \otimes \mathbf{x}_\mu^0, & \text{and} \\ (\tilde{\mathbf{K}})_{ll'} &= \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l), \mu \in \theta^{-1}(l')} \mathbf{e}_3 \cdot \mathbf{K}_{\nu\mu} \mathbf{e}_3. \end{aligned} \quad (21)$$

As implied by the concept 'cut-off' radius, we define the *cut-off layer number* N as

$$N = \left\lceil \frac{R}{d_0} \right\rceil := \max\{|l - l'| : \exists \nu \in \theta^{-1}(l), \mu \in \theta^{-1}(l') \text{ such that } |\mathbf{x}_\nu^0 - \mathbf{x}_\mu^0| \leq R\}. \quad (22)$$

Physically speaking, two layers will not interact at all if their layer number difference is greater than N . Because of periodicity and finite cut-off radius, the interior atoms in each crystal plane interact exactly in the same manner as all other interior atoms. Let $\nu_l \in \theta^{-1}(l)$ be a representative interior atom in the l th crystal plane. Then in the limit $L \rightarrow +\infty$, we can rewrite the quantities in (21) as

$$\begin{aligned}\boldsymbol{\sigma} &= n_0 d_0 \sum_{l \in [1, N]} l d_0 \mathbf{f}_{\nu_l} \otimes \mathbf{e}_3, & [\mathbf{S}]_{piqj} &= n_0 d_0 \sum_{l=1 \in [1, N]} \left[\sum_{\mathbf{x}_\mu^0 \in \mathcal{N}_{\nu_l} \cap \Omega} (\mathbf{x}_{\nu_l}^0)_i [\mathbf{K}_{\nu_l \mu}]_{pq} (\mathbf{x}_\mu^0)_j - \mathbf{C} \right], \\ g_l &= n_0 d_0 \mathbf{f}_{\nu_l} \cdot \mathbf{e}_3, & \mathbf{B}_l &= n_0 d_0 \sum_{\mu \in \mathcal{N}_{\nu_l} \cap \Omega} (\mathbf{K}_{\nu_l \mu} \mathbf{e}_3) \otimes \mathbf{x}_\mu^0, \\ (\tilde{\mathbf{K}})_{ll'} &= n_0 d_0 \sum_{\mu \in \theta^{-1}(l'), \mathbf{x}_\mu^0 \in \mathcal{N}_{\nu_l} \cap \Omega} \mathbf{e}_3 \cdot \mathbf{K}_{\nu_l \mu} \mathbf{e}_3.\end{aligned}\tag{23}$$

Moreover, by (9), (10) and (21) we immediately see that $\tilde{\mathbf{K}}, g_l$ and $\mathbf{B}_l$ defined in (20) satisfy that $\tilde{\mathbf{K}}^T = \tilde{\mathbf{K}}, \sum_{l'=1}^\Theta (\tilde{\mathbf{K}})_{ll'} = 0$ for any l , and

$$\begin{cases} (\tilde{\mathbf{K}})_{ll'} = (\tilde{\mathbf{K}})_{mm'} & \text{if } l, l', m, m' \in [N+1, \Theta-N] \text{ \& } |l-l'| = |m-m'|, \\ g_l = 0, \quad \mathbf{B}_l \cdot \mathbf{H} = 0 & \forall l \in [N+1, \Theta-N]. \end{cases}\tag{24}$$

To see the last of the above equation, inserting (14) into (16) and setting the traction equal to zero we have

$$n_0 \sum_{\mathbf{x}_\mu^0 \in \mathcal{N}_\nu} (\mathbf{x}_\nu^0 \cdot \mathbf{e}_3) \mathbf{K}_{\nu \mu} (\mathbf{H} \mathbf{x}_\mu^0) = 0 \quad \forall \mathbf{x}_\nu^0 \in \mathcal{B},$$

which implies that $\sum_{\mathbf{x}_\mu^0 \in \mathcal{N}_\nu} \mathbf{K}_{\nu \mu} (\mathbf{H} \mathbf{x}_\mu^0) = 0 \quad \forall \mathbf{x}_\nu^0 \in \mathcal{B}$, and particularly that

$$\mathbf{B}_l \cdot \mathbf{H} = \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l)} \sum_{\mu \in \mathcal{N}_\nu} \mathbf{e}_3 \cdot \mathbf{K}_{\nu \mu} (\mathbf{H} \mathbf{x}_\mu^0) \rightarrow 0 \quad \text{as } L \rightarrow \infty \quad \forall l \in [N, \Theta - N + 1].$$

Without loss of generality assume that there are in total $\Theta = N \times (P+1)$ crystal planes. For brevity we introduce $N \times N$ matrices:

$$\begin{cases} (\mathbf{M}_0)_{ij} = (\tilde{\mathbf{K}})_{ij} & i, j = 1, \dots, N, \\ (\mathbf{M}_1)_{ij} = (\tilde{\mathbf{K}})_{ij} & i, j = N+1, \dots, 2N, \\ (\mathbf{M}_2)_{ij} = (\tilde{\mathbf{K}})_{ij} & i = 1, \dots, N; j = N+1, \dots, 2N. \end{cases}\tag{25}$$

and N -vectors:

$$\begin{aligned}\mathbf{w}_i &= (w_{iN+1}, w_{iN+2}, \dots, w_{iN+N}), & i &= 0, 1, 2, \dots, P, \\ \tilde{\mathbf{f}} &= \mathbf{g} + (\mathbf{B}_1 \cdot \mathbf{H}, \dots, \mathbf{B}_N \cdot \mathbf{H}), & \mathbf{g} &= (g_1, \dots, g_N).\end{aligned}\tag{26}$$

It is clear that $\mathbf{M}_1, \mathbf{M}_0$ are symmetric and $\mathbf{M}_2$ is nonsingular.

From (20) we observe that the surface energy density of the finite crystal $\mathcal{L} \cap \Omega$ is a

quadratic function of layer relaxations w_l . By symmetry we focus on the bottom free surface by setting $\mathbf{w}_P = 0$, i.e., the ‘top surface’ is constrained and not free to relax. Then by (20), (24), (25) and (26) we can write the relaxation-dependent (i.e., w_l -dependent) part of the surface energy density as

$$R(\mathbf{H}; \mathbf{w}_0, \dots, \mathbf{w}_{P-1}) := \tilde{\mathbf{f}} \cdot \mathbf{w}_0 + Q(\mathbf{w}_0, \dots, \mathbf{w}_{P-1}), \quad (27)$$

where the quadratic form $Q : \mathbb{R}^{\Theta-N} \rightarrow \mathbb{R}$ is given by

$$\begin{aligned} Q(\mathbf{w}_0, \dots, \mathbf{w}_{P-1}) &= \frac{1}{2} \sum_{l, l'=1}^{\Theta-N} (\tilde{\mathbf{K}})_{ll'} w_l w_{l'} \\ &= \frac{1}{2} \begin{bmatrix} \mathbf{w}_0 \\ \mathbf{w}_1 \\ \mathbf{w}_2 \\ \vdots \\ \mathbf{w}_{P-1} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{M}_0 & \mathbf{M}_2 & 0 & \cdots & 0 & 0 \\ \mathbf{M}_2^T & \mathbf{M}_1 & \mathbf{M}_2 & \cdots & 0 & 0 \\ 0 & \mathbf{M}_2^T & \mathbf{M}_1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & \mathbf{M}_2^T & \mathbf{M}_1 \end{bmatrix} \begin{bmatrix} \mathbf{w}_0 \\ \mathbf{w}_1 \\ \mathbf{w}_2 \\ \vdots \\ \mathbf{w}_{P-1} \end{bmatrix} \\ &= \frac{1}{2} \mathbf{w}_0 \cdot \mathbf{M}_0 \mathbf{w}_0 + \sum_{i=1}^{P-1} \left(\frac{1}{2} \mathbf{w}_i \cdot \mathbf{M}_1 \mathbf{w}_i + \mathbf{w}_i \cdot \mathbf{M}_2 \mathbf{w}_{i+1} \right). \end{aligned} \quad (28)$$

For a strain tensor $\mathbf{H} \in \mathbb{H}_0$, the layer relaxations $\mathbf{w}_i$ ($i = 0, \dots, P-1$) shall be such that the total energy is minimized:

$$R^*(\mathbf{H}) := \min_{\mathbf{w}_0, \mathbf{w}_1, \dots, \mathbf{w}_{P-1}} R(\mathbf{H}; \mathbf{w}_0, \dots, \mathbf{w}_{P-1}, \mathbf{w}_P = 0). \quad (29)$$

We are therefore motivated to consider the algebraic minimization problem

$$\begin{aligned} Q_P^*(\mathbf{w}_0) &:= \frac{1}{2} \mathbf{w}_0 \cdot \mathbf{M}_0 \mathbf{w}_0 + \min_{\mathbf{w}_1, \dots, \mathbf{w}_{P-1}} \left\{ \sum_{i=1}^{P-1} \left(\frac{1}{2} \mathbf{w}_i \cdot \mathbf{M}_1 \mathbf{w}_i + \mathbf{w}_i \cdot \mathbf{M}_2 \mathbf{w}_{i+1} \right) \right\} \\ &= \frac{1}{2} \mathbf{w}_0 \cdot \mathbf{M}_0 \mathbf{w}_0 + \min_{\mathbf{w}_1} \left\{ \frac{1}{2} \mathbf{w}_1 \cdot \mathbf{M}_1 \mathbf{w}_1 + \mathbf{w}_0 \cdot \mathbf{M}_2 \mathbf{w}_1 + \cdots + \min_{\mathbf{w}_{P-2}} \left[\frac{1}{2} \mathbf{w}_{P-2} \cdot \mathbf{M}_1 \mathbf{w}_{P-2} \right. \right. \\ &\quad \left. \left. + \mathbf{w}_{P-3} \cdot \mathbf{M}_2 \mathbf{w}_{P-2} + \min_{\mathbf{w}_{P-1}} \left(\frac{1}{2} \mathbf{w}_{P-1} \cdot \mathbf{M}_1 \mathbf{w}_{P-1} + \mathbf{w}_{P-2} \cdot \mathbf{M}_2 \mathbf{w}_{P-1} \right) \right] \right\}. \end{aligned} \quad (30)$$

To represent the solution to the minimization problem (29), it will be convenient to introduce a *nonlinear* mapping $\mathbb{T} : \mathbb{R}_{\text{sym}}^{N \times N} \rightarrow \mathbb{R}_{\text{sym}}^{N \times N}$ as

$$\mathbb{T}(\mathbf{A}) = \mathbf{M}_1 - \mathbf{M}_2 \mathbf{A}^{-1} \mathbf{M}_2^T. \quad (31)$$

By successively solving the algebraic minimization problem for $\mathbf{w}_{P-1}, \mathbf{w}_{P-2}, \dots, \mathbf{w}_1$, we find that the minimizers of (30) satisfy the following relations

$$\mathbf{w}_i = -[\mathbb{T}^{P-1-i}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T \mathbf{w}_{i-1} \quad \forall i = 1, \dots, P-2, \quad (32)$$

and the minimum is given by

$$Q_P^*(\mathbf{w}_0) = \frac{1}{2} \mathbf{w}_0 \cdot \left\{ \mathbf{M}_0 - \mathbf{M}_2 [\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T \right\} \mathbf{w}_0.$$

Therefore, by (27) the minimum is given by

$$R^*(\mathbf{H}) = \min_{\mathbf{w}_0} [\mathbf{Q}_P^*(\mathbf{w}_0) + \tilde{\mathbf{f}} \cdot \mathbf{w}_0], \quad (33)$$

and the minimizing relaxations $\mathbf{w}_0^*$ are given by

$$\mathbf{w}_0^* = - \left\{ \mathbf{M}_0 - \mathbf{M}_2 [\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T \right\}^{-1} \tilde{\mathbf{f}}. \quad (34)$$

We observe that the above solutions (32), (33) and (34) represent relaxations in equilibrium or energy minimizing configuration of the crystal planes only if

- (i) $\mathbb{T}^i(\mathbf{M}_1)$ is positive definite and bounded, i.e., there exists $c > 1$ such that

$$c^{-1} |\mathbf{w}|^2 \leq \mathbf{w} \cdot \mathbb{T}^i(\mathbf{M}_1) \mathbf{w} \leq c |\mathbf{w}|^2 \quad \forall i = 1, \dots, P-2 \text{ \& } \mathbf{w} \in \mathbb{R}^N. \quad (35)$$

- (ii) For an infinite crystal, the above inequalities shall hold for $P \rightarrow \infty$ to guarantee a stable crystal. Therefore, up to a subsequence and without relabeling the sequence $\{\mathbb{T}^i(\mathbf{M}_1)\}$ converges to a limit $\mathbf{\Lambda} \in \mathbb{R}_{\text{sym}}^{N \times N}$ and the limit $\mathbf{\Lambda}$ can be determined by

$$\mathbb{T}(\mathbf{\Lambda}) = \mathbf{\Lambda}, \quad \text{i.e.,} \quad \mathbf{\Lambda} \mathbf{M}_2^{-T} \mathbf{\Lambda} - \mathbf{M}_1 \mathbf{M}_2^{-T} \mathbf{\Lambda} + \mathbf{M}_2 = 0.$$

Since $\mathbf{\Lambda} = \mathbf{\Lambda}^T$, the above algebraic equation can be rewritten as a standard *algebraic Riccati equation*:

$$\mathbf{\Lambda} (\mathbf{M}_2^{-T} + \mathbf{M}_2^{-1}) \mathbf{\Lambda} - \mathbf{M}_1 \mathbf{M}_2^{-T} \mathbf{\Lambda} - \mathbf{\Lambda} \mathbf{M}_2^{-1} \mathbf{M}_1 + \mathbf{M}_2 + \mathbf{M}_2^T = 0. \quad (36)$$

- (iii) The matrix $\mathbf{M}_0 - \mathbf{M}_2 [\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T$ is positive definite. Moreover, for a macroscopic crystal $\Omega \cap \mathcal{L}$, the number of crystal planes, $N \times (P+1)$, is an extremely large number and the surface properties shall be *insensitive* to the precise number of crystal planes, and henceforth

$$\begin{aligned} \mathbf{M}_0 - \mathbf{M}_2 [\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T &= \mathbf{M}_0 - \mathbf{M}_1 + \mathbf{M}_1 - \mathbf{M}_2 [\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1} \mathbf{M}_2^T \\ &= \mathbf{M}_0 - \mathbf{M}_1 + \mathbb{T}^{P-1}(\mathbf{M}_1) \rightarrow \mathbf{M}_0 - \mathbf{M}_1 + \mathbf{\Lambda} =: \mathbf{Y}^{-1}. \end{aligned} \quad (37)$$

We therefore find the following necessary condition for a free surface without reconstruction of in-plane lattice structure:

$$\mathbf{Y}^{-1} = \mathbf{M}_0 - \mathbf{M}_1 + \mathbf{\Lambda} \quad \text{is positive definite.} \quad (38)$$

- (iv) The minimum of the right hand side of (33) shall be independent of P and is given by

$$R^*(\mathbf{H}) = \min_{\mathbf{w}_0} [\mathbf{Q}_P^*(\mathbf{w}_0) + \tilde{\mathbf{f}} \cdot \mathbf{w}_0] = -\frac{1}{2} \tilde{\mathbf{f}} \cdot (\mathbf{M}_0 - \mathbf{M}_1 + \mathbf{\Lambda})^{-1} \tilde{\mathbf{f}} = -\frac{1}{2} \tilde{\mathbf{f}} \cdot \mathbf{Y} \tilde{\mathbf{f}}, \quad (39)$$

and by (32) and (34) the relaxations satisfies

$$\mathbf{w}_0^* = -\mathbf{Y}\tilde{\mathbf{f}}, \quad \mathbf{w}_i^* = -\mathbf{\Lambda}^{-1}\mathbf{M}_2\mathbf{w}_{i-1}^* = \cdots = (-\mathbf{\Lambda}^{-1}\mathbf{M}_2)^i\mathbf{w}_0^* \quad \forall i = 1, 2, \dots \quad (40)$$

Since $|\mathbf{w}_i| \rightarrow 0$ as $i \rightarrow +\infty$, we conclude that $\mathbf{w}_0^*$ shall belong to the eigenspace of $\mathbf{\Lambda}^{-1}\mathbf{M}_2$ associated with eigenvalues that are strictly less than one (absolute value), i.e.,

$$\mathbf{w}_0^* \in \{\mathbf{w} \in \mathbb{R}^N : |\mathbf{\Lambda}^{-1}\mathbf{M}_2\mathbf{w}| < |\mathbf{w}|\}.$$

Therefore, the magnitude of relaxations shall decay exponentially away from the free surface.

We now employ the basic principle (1) to identify the surface elasticity properties in the continuum model. By (4), (20), (17), (39) and in account of relaxations of both bottom and top surfaces, we have that for any $\mathbf{H} \in \mathbb{H}_0$,

$$\gamma(\mathbf{n}) - \mathbf{H} \cdot \boldsymbol{\tau}_0(\mathbf{n}) + \frac{1}{2}\mathbf{H} \cdot \mathbf{C}_s(\mathbf{n})\mathbf{H} = \gamma^0 + \boldsymbol{\sigma} \cdot \mathbf{H} + \frac{1}{2}\mathbf{H} \cdot \mathbf{S}\mathbf{H} + R^*(\mathbf{H}).$$

By (26)₂, we identify the surface elasticity properties in the continuum theory from the atomistic model as (c.f., (19), (21), (36) and (37))

$$\begin{aligned} \gamma(\mathbf{n}) &= \gamma^0 - \frac{1}{2}\mathbf{g} \cdot \mathbf{Y}\mathbf{g}, \\ [\boldsymbol{\tau}_0(\mathbf{n})]_{ij} &= -(\boldsymbol{\sigma})_{ij} + \sum_{l,l'=1}^N g_l(\mathbf{Y})_{ll'}(\mathbf{B}_{l'})_{ij}, \\ [\mathbf{C}_s(\mathbf{n})]_{piqj} &= (\mathbf{S})_{piqj} - \sum_{l,l'=1}^N (\mathbf{Y})_{ll'}(\mathbf{B}_l)_{pi}(\mathbf{B}_{l'})_{qj}, \end{aligned} \quad (41)$$

where the first terms on the right hand sides are independent of the relaxations and the second terms arise from surface relaxations. Upon specifying the atomistic model, the first terms depend only on the reference perfect lattice and can be quickly computed. Also, the relaxations, i.e., the unknown matrix $\mathbf{\Lambda}$, can be determined by solving a low-rank $N \times N$ *algebraic Riccati equation* (36). No molecular dynamics simulation *per se* is necessary to compute the surface relaxations and surface elasticity properties; the algorithm derived from our analysis would be orders of magnitude more efficient than a full-scale MD simulation.

4. Examples

We now present a few examples concerning computation of surface relaxations and surface elasticity properties from atomistic models. Although our framework is valid for general atomistic models, for simplicity we consider two-body potentials (pair potentials) and embedded atom model (EAM) potentials [35]. For pair potentials we obtain explicit formulas of relevant atomistic parameters which will be convenient for computing surface elasticity properties; for EAM potentials we numerically determine surface relaxations and surface

elasticity properties of a few FCC metallic crystals. Our results in general agree well with experimental data or prior simulations.

4.1. Pair potential

For a pair potential model, the interaction energy between two atoms depends only on their distance:

$$V(r_{\nu\mu}) = V(|\mathbf{x}_\nu - \mathbf{x}_\mu|), \quad r_{\nu\mu} = |\mathbf{x}_\nu - \mathbf{x}_\mu|,$$

and therefore the total energy of the finite crystal (5) is given by

$$E_{\text{tot}}(\mathbf{x}_1, \dots, \mathbf{x}_M) = \frac{1}{2} \sum_{\nu, \mu=1}^M V(r_{\nu\mu}). \quad (42)$$

Assuming the atoms in the perfect infinite crystal form a simple Bravais lattice, we can determine lattice vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ by minimizing the total energy per unit cell and obtain the reference Bravais lattice $\mathcal{L}$. Then, by (8) we immediately have that $(\mathbf{r}_{\nu\mu}^0 := \mathbf{x}_\nu^0 - \mathbf{x}_\mu^0)$

$$\begin{aligned} \mathbf{f}_\nu &= \sum_{\mu \in \mathcal{N}_\nu} \frac{\mathbf{r}_{\nu\mu}^0}{r_{\nu\mu}^0} V'(r_{\nu\mu}^0), \\ \mathbf{K}_{\nu\mu} &= -\frac{\mathbf{r}_{\nu\mu}^0 \otimes \mathbf{r}_{\nu\mu}^0}{(r_{\nu\mu}^0)^2} V''(r_{\nu\mu}^0) - \frac{(r_{\nu\mu}^0)^2 \mathbf{I} - \mathbf{r}_{\nu\mu}^0 \otimes \mathbf{r}_{\nu\mu}^0}{(r_{\nu\mu}^0)^3} V'(r_{\nu\mu}^0) \quad \nu \neq \mu, \\ \mathbf{K}_{\nu\nu} &= \sum_{\mu \in \mathcal{N}_\nu} \frac{\mathbf{r}_{\nu\mu}^0 \otimes \mathbf{r}_{\nu\mu}^0}{(r_{\nu\mu}^0)^2} V''(r_{\nu\mu}^0) + \frac{(r_{\nu\mu}^0)^2 \mathbf{I} - \mathbf{r}_{\nu\mu}^0 \otimes \mathbf{r}_{\nu\mu}^0}{(r_{\nu\mu}^0)^3} V'(r_{\nu\mu}^0). \end{aligned}$$

By (21), we can calculate the matrices $(\tilde{\mathbf{K}})_{ll'}$, $\mathbf{B}_l$ and vector $\mathbf{g}$. For example, if we denote by

$$m_j = \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l), \mu \in \mathcal{N}_\nu \cap \theta^{-1}(l')} \left[\frac{j^2 d_0^2}{(r_{\nu\mu}^0)^2} V''(r_{\nu\mu}^0) + \frac{(r_{\nu\mu}^0)^2 - j^2 d_0^2}{(r_{\nu\mu}^0)^3} V'(r_{\nu\mu}^0) \right]$$

for l, l' with $|l - l'| = j$, then the matrices $\mathbf{M}_0, \mathbf{M}_1, \mathbf{M}_2$ that govern surface relaxations are given as below:

$$\begin{aligned}\mathbf{M}_0 &= \begin{bmatrix} \sum_{i=1}^N m_i & -m_1 & -m_2 & \cdots & -m_{N-1} \\ -m_1 & m_1 + \sum_{i=1}^N m_i & -m_1 & \cdots & -m_{N-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_{N-1} & -m_{N-2} & -m_{N-3} & \cdots & \sum_{i=1}^{N-1} m_i + \sum_{i=1}^N m_i \end{bmatrix}, \\ \mathbf{M}_1 &= \begin{bmatrix} 2 \sum_{i=1}^N m_i & -m_1 & -m_2 & \cdots & -m_{N-1} \\ -m_1 & 2 \sum_{i=1}^N m_i & -m_1 & \cdots & -m_{N-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_{N-1} & -m_{N-2} & -m_{N-3} & \cdots & 2 \sum_{i=1}^N m_i \end{bmatrix}, \\ \mathbf{M}_2 &= \begin{bmatrix} -m_N & 0 & 0 & \cdots & 0 \\ -m_{N-1} & -m_N & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_1 & -m_2 & -m_3 & \cdots & -m_N \end{bmatrix}.\end{aligned}$$

The above explicit expressions of the matrices $\mathbf{M}_i$ ($i = 0, 1, 2$) will be convenient for verifying if the pair potential is physically reasonable, i.e., if (35) and (38) are satisfied, and computing the surface relaxations (40) and surface elasticity properties (41) by solving the algebraic Riccati equation (36).

Table I. Normalized relaxations Δ_{12} and Δ_{23} for (111) surfaces of FCC crystals with Johnson EAM potentials [35] and comparison with experimental data (EXP) and prior MD simulations (MD).

Percentage of relaxation	Cu EXP[26]		Ag EXP[42]		Au MD[15]		Ni EXP[9]	
$\Delta_{12}(\%)$	-1.24	-0.7 ± 0.5	-2.06	-2.5	-4.53	-4.25	-0.34	-1.2 ± 1.2
$\Delta_{23}(\%)$	-0.03		0.03		0.65	0.64	-0.02	

Pd MD[15]		Pt MD[15]	
-2.80	-3.21	-3.52	-4.82
0.12	0.27	0.37	0.75

4.2. EAM potentials

The EAM potentials modify the pair potentials by accounting for the effect of electron cloud on the total energy:

$$E_{\text{tot}}(\mathbf{x}_1, \cdots, \mathbf{x}_M) = \frac{1}{2} \sum_{\nu=1}^M \left[\sum_{\mu=1}^M V_{\nu\mu}(r_{\nu\mu}) + F \left(\sum_{\mu=1}^M \rho_{\nu}(r_{\nu\mu}) \right) \right],$$

where $\rho_{\nu}(r_{\nu\mu})$ is the contribution to the electron density from atom μ at the location of atom ν , and F is the embedding function representing the energy required to place atom

ν into the electron cloud. We find the surface relaxations for (111) surface of several FCC metals by calculating the atomistic model parameters defined in (8) and (23) and then numerically solving the *algebraic Riccati equation* (36). Further, we calculate the surface elasticity properties by (41). All the calculations are performed by using Johnson EAM potentials [35].

The results of our calculations are shown in Table I - III in comparison with experimental data or prior MD simulations. Table I shows normalized relaxations between neighboring layers ($\Delta_{\alpha\alpha+1} = (w_{\alpha+1} - w_{\alpha})/d_0$, $\alpha = 1, 2$) at zero strain tensor $\mathbf{H} = 0$). Due to lack of experimental data, results of Au, Pd and Pt are compared only with prior MD simulations based on similar EAM potentials [15]. Our results are generally in good agreement with experimental data or prior MD simulations. The relaxation between the 1st and 2nd layer is much larger than that between the 2nd and 3rd layer, and the relaxations between higher layer numbers are negligible, which agrees with our prediction of exponential decay of relaxations away from the free surface. The relaxation of different metals can differ a lot. For example, the relaxation of gold is over ten times larger than relaxation of nickel. Table II gives the surface tension and residual surface stress. The results of surface tension and residual stress agree qualitatively well with experimental data or prior MD simulations. The component $(\boldsymbol{\tau}_0)_{12}$ vanishes for all studied crystals, as implied by in-plane symmetry of the free surface. The surface elastic stiffness tensor is shown in table III. In these calculations we notice that values of stiffness is sensitive to the parameter of EAM potentials. Nevertheless, our results are still comparable with prior MD simulations. For surface with three fold or more symmetry [5], $[\mathbf{C}_s]_{1111} = [\mathbf{C}_s]_{2222}$, $(\boldsymbol{\tau}_0)_{11} = (\boldsymbol{\tau}_0)_{22}$ is verified by our calculations.

Table II. Surface tension γ , residual surface stress $(\boldsymbol{\tau}_0)_{\alpha\beta}$ for (111) surfaces of FCC metals with Johnson EAM potentials [35]. Results are compared with prior MD simulations (*, Shenoy, 2005[46]) and experimental data ($\star$). All entries are in J/m^2 .

Element	γ	γ^*	$\gamma^\star$	$(\boldsymbol{\tau}_0)_{11}$	$(\boldsymbol{\tau}_0)_{11}^*$	$(\boldsymbol{\tau}_0)_{22}$	$(\boldsymbol{\tau}_0)_{22}^*$	$(\boldsymbol{\tau}_0)_{12}$	$(\boldsymbol{\tau}_0)_{12}^*$
Cu	1.15	1.24	1.49 ^[3]	-0.33	0.55	-0.33	0.55	0.00	0.00
Ag	0.80	0.80	1.20 ^[24]	0.10	0.65	0.10	0.65	0.00	0.00
Au	0.70	0.70	1.18 ^[24]	0.94	1.64	0.94	1.64	0.00	0.00
Ni	1.47	1.43	1.94 ^[24]	-1.15	-0.12	-1.15	-0.12	0.00	0.00
Pd	1.27	1.16		0.56	1.63	0.55	1.63	0.00	0.00
Pt	1.30	1.24	1.95 ^[24]	1.32	2.54	1.31	2.54	0.00	0.00

5. Conclusion

In this paper we have developed a framework to determine surface relaxations and surface elasticity properties of monatomic crystals with a simple Bravais lattice from atomistic models. Similar results may be obtained for a multiatomic multi-lattice system. Besides explicit formula (41) of surface elasticity properties, our analysis shows that (i) Surface relaxations always lower surface tension and surface elasticity tensor. (ii) The stability of bulk crystal implies that the matrices $\mathbf{M}_1$ and $\mathbf{M}_2$ defined by (23) and (25) necessarily satisfies (35) and

Table III. Surface elastic stiffness tensor $(\mathbf{C}_s)_{\alpha\beta\alpha'\beta'}$ for (111) surfaces of FCC metals with Johnson EAM potentials [35]. Results are compared with prior MD simulations results (*, Shenoy, 2005[46]). All entries are in J/m^2 .

Element	$(\mathbf{C}_s)_{1111}$	$(\mathbf{C}_s)_{1111}^*$	$(\mathbf{C}_s)_{2222}$	$(\mathbf{C}_s)_{2222}^*$	$(\mathbf{C}_s)_{1212}$	$(\mathbf{C}_s)_{1212}^*$
Cu	0.85	-1.97	0.85	-1.97	0.11	0.14
Ag	-1.74	-3.04	-1.73	-3.04	0.18	-0.50
Au	-6.17	-7.98	-6.13	7.98	0.98	-2.63
Ni	6.80	2.18	6.77	2.18	0.04	1.78
Pd	-5.36	-7.82	-5.31	-7.82	0.45	2.00
Pt	-9.07	-12.67	-9.02	-12.67	1.20	-3.89

be such that the *algebraic Riccati equation* (36) admits a positive definite solution for every rational crystal planes. This places non-obvious restrictions on the underlying atomistic model that appear to be unnoticed before. (iii) A simple surface reconstruction criterion is obtained, i.e., if $\mathbf{M}_0 - \mathbf{M}_1 + \mathbf{A}$ is not positive definite, by (39) the relaxations alone may lower the total energy indefinitely, meaning that surface reconstructions necessarily occur. (iv) The magnitude of relaxations decays exponentially away from the free surface.

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- [1] N. C. Admal and E. B. Tadmor. A unified interpretation of stress in molecular systems. *Journal of Elasticity*, 100:63 – 143, 2010.
- [2] N. W. Ashcroft and N. D. Mermin. *Solid State Physics*. Brooks/Cole, Cengage Learning, 1976.
- [3] C. E. Bauer, R. Speiser, and J. P. Hirth. Surface energy of copper as a function of oxygen activity. *Metall. Trans. A*, 7(1):75–709, 1976.
- [4] R. Berger, E. Delamarche, H.P. Lang, C. Gerber, J.K. Gimzewski, E. Meyer, and H.J. Guntherodt. Surface stress in the self-assembly of alkanethiols on gold. *Science*, 276:2021–2024, 1997.
- [5] M. J. Buerger. *Elementary Crystallography*. New York : Wiley, 1963.
- [6] G. Y. Chen, T. Thundat, E. A. Wachter, and R. J. Warmack. Adsorption-induced surface stress and its effects on resonance frequency of microcantilevers. *J. Appl. Phys.*, 77(8):3618–3622, 1995.
- [7] C.Mi, S.Jun, and D.A.Kouris. Atomistic calculations of interface elastic properties in noncoherent metallic bilayers. *Phys. Rev. B*, 77(7):075425, 2008.
- [8] S. Cuenot, C. Fretigny, S. Demoustier-Champagne, and B. Nysten. Surface tension effect on the mechanical properties of nanomaterials measured by atomic force microscopy. *Phys. Rev. B*, 69:165410, 2004.

- [9] J. E. Demuth, P. M. Marcus, and D. W. Jepsen. Analysis of low-energy-electron-diffraction intensity spectra for (001), (110), and (111) nickel. *Phys. Rev. B*, 11(4):1460–1474, 1975.
- [10] J. Diao, K. Gall, and M. L. Dunn. Surface-stress-induced phase transformation in metal nanowires. *Nat. Mater.*, 2:656–660, 2003.
- [11] Remi Dingreville, Jianmin Qu, and Mohammed Cherkaoui. Surface free energy and its effect on the elastic behavior of nano-sized particles, wires and films. *Journal of the Mechanics and Physics of Solids*, 53(8):1827 – 1854, 2005.
- [12] H.L. Duan, J. Wang, Z.P. Huang, and B.L. Karimhaloo. Size-dependant effective elastic constants of solids containing nano-inhomogeneities with interface stress. *J. Mech. Phys. Solids*, 53:1574–1596, 2005.
- [13] Tadmor E., Ortiz M., and Phillips R. Quasicontinuum analysis of defects in solids. *Philosophical Magazine A*, 73:1529–1563, 1996.
- [14] W. E and P. Ming. Cauchy-born rule and the stability of crystalline solids: Static problems. *Arch. Rational Mech. Anal.*, 183:241–297, 2007.
- [15] S. M. Foiles, M. I. Baskes, and M. S. Daw. Embedded-atom-method functions for the fcc metals cu, ag, au, ni, pd, pt, and their alloys. *Phys. Rev. B*, 33(12):7983–7991, 1986.
- [16] P. Goudeau, P. O. Renault, P. Villain, C. Coupeau, V. Pelosin, B. Boubeker, K.F. Badawi, D. Thiaudiere, and M. Gailhanou. Characterization of thin film elastic properties using x-ray diffraction and mechanical methods: application to polycrystalline stainless steel. *Thin Solid Films*, 398:496–500, 2001.
- [17] J. R. Greer and W. D. Nix. Nanoscale gold pillars strengthened through dislocation starvation. *Phys. Rev. B*, 73:245410, Jun 2006.
- [18] L.X. Hu and L.P. Liu. Interfacial waves with surface elasticity. *J. Appl. Mech*, 81:081007, 2014.
- [19] Z.P. Huang and L. Sun. Size-dependent effective properties of a heterogeneous material with interface energy effect: from finite deformation theory to infinitesimal strain analysis. *Acta Mech.*, 190:151–163, 2007.
- [20] D. C. Hurley, V. K. Tewarya, and A. J. Richards. Thin-film elastic-property measurements with laser-ultrasonic saw spectrometry. *Thin Solid Films*, 398:326–330, 2001.
- [21] K. Ishikawa, K. Yoshikawa, and N. Okada. Size effect on the ferroelectric phase transition in PbTiO_3 ultrafine particles. *Phys. Rev. B*, 37(10):5852–5855, 1988.
- [22] G. Y. Jing, H. L. Duan, X. M. Sun, Z. S. Zhang, J. Xu, Y. D. Li, J. X. Wang, and D. P. Yu. Surface effects on elastic properties of silver nanowires: Contact atomic-force microscopy. *Phys. Rev. B*, 73:235409, 2006.

- [23] Ju-Young Kim and Julia R. Greer. Tensile and compressive behavior of gold and molybdenum single crystals at the nano-scale. *Acta Materialia*, 57(17):5245 – 5253, 2009.
- [24] V. K. Kumikov and Kh. B. Khokonov. On the measurement of surface free energy and surface tension of solid metals. *J. Appl. Phys.*, 54:1346–1350, 1983.
- [25] Wuwei Liang, Min Zhou, and Fujiu Ke. Shape memory effect in cu nanowires. *Nano Letters*, 5(10):2039–2043, 2005.
- [26] S. A. Lindgren, L. Wallden, J. Rundgren, and P. Westrin. Low-energy electron diffraction from cu(111): Subthreshold effect and energy-dependent inner potential; surface relaxation and metric distances between spectra. *Phys. Rev. B*, 29(2):576–588, 1984.
- [27] R. Maranganti and P. Sharma. Length scales at which classical elasticity breaks down for various materials. *Phys. Rev. Lett.*, 98:195504, 2007.
- [28] M.E.Gurtin and A.I.Murdoch. A continuum theory of elastic material surfaces. *Arch. Rat. Mech. Anal.*, 57(4):291–323, 1975.
- [29] M.E.Gurtin and A.I.Murdoch. Surface stress in solids. *Int. J. Solids Struct.*, 14:431–440, 1978.
- [30] F. Ojaghnezhad and H. M. Shodja. A combined first principles and analytical treatment for determination of the surface elastic constants: application to si(001) ideal and reconstructed surfaces. *Philosophical Magazine Letters*, 92(1):7–19, 2012.
- [31] H. S. Park and P. A. Klein. Surface cauchy-born analysis of surface stress effects on metallic nanowires. 75:085408, *Phys. Rev. B*.
- [32] H. S. Park, P. A. Klein, and G. J. Wagner. A surface cauchy?born model for nanoscale materials. *Int. J. Numer. Meth. Engng*, 68:1072–1095, 2006.
- [33] S. Pathak and V. B. Shenoy. Size dependence of thermal expansion of nanostructures. *Phys. Rev. B*, 72:113404, Sep 2005.
- [34] C.W. Price and J. P. Hirth. Surface energy and surface stress tensor in an atomistic model. *Surface Science*, 57:509–522, 1976.
- [35] R.A.Johnson. Alloy models with the embedded-atom method. *Phys. Rev. B*, 39(17):12554–12559, 1989.
- [36] P. O. Renault, E. Le Bourhis, P. Villain, Ph. Goudeau, K. F. Badawi, and D. Faure. Measurement of the elastic constants of textured anisotropic thin films from x-ray diffraction data. *Appl. Phys. Lett.*, 83(3):473–475, 2003.
- [37] P. Sharma and S. Ganti. Size-dependent eshelby’s tensor for embedded nano-inclusions incorporating surface/interface energies. *J. Appl. Mech*, 71:663–671, 2004.
- [38] P. Sharma, S. Ganti, and N. Bhate. Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities. *Appl. Phys. Lett.*, 82:535–537, 2003.

- [39] S. A. Silling. Reformulation of elasticity theory for discontinuities and long-range forces. *Journal of the Mechanics and Physics of Solids*, 48:175–209, 2000.
- [40] D. J. Steigmann, and R. W. Ogden. Plane deformations of elastic solids with intrinsic boundary elasticity *P. Roy. Soc. A-Math. Phy.*, 453:853–877, 1997.
- [41] D. J. Steigmann, and R. W. Ogden. Elastic surface-substrate interactions *P. Roy. Soc. A-Math. Phy.*, 455:437–474, 1999.
- [42] P. Statiris, H. C. Lu, and T. Gustafsson. Temperature dependent sign reversal of the surface contraction of ag(111). *Phys. Rev. Lett.*, 72(22):3574–3577, 1994.
- [43] F. H. Streitz, R. C. Cammarata, and K. Sieradzki. Surface-stress effects on elastic properties. i. thin metal films. *Phys. Rev. B*, 49(15):10699–10706, 1994.
- [44] C. T. Sun and H. Zhang. Size-dependent elastic moduli of platelike nanomaterials. *J. Appl. Phys.*, 93(2):1212–1218, 2003.
- [45] K. Uchino, E. Sadanaga, and T. Hirose. Dependence of the crystal structure on particle size in barium titanate. *J. Am. Ceram. Soc.*, 72(8):1555–1558, 1989.
- [46] V.B.Shenoy. Atomistic calculations of elastic properties of metallic fcc crystal surfaces. *Phys. Rev. B*, 71(9):094104, 2005.
- [47] P. Villain, Ph. Goudeau, P. O. Renault, and K. F. Badawi. Size effect on intragranular elastic constants in thin tungsten films. *Appl. Phys. Lett.*, 81(23):4365–4367, 2002.
- [48] L. Vitos, A. V. Ruban, H. L. Skriver, and J. Kollar. The surface energy of metals. *Surface Science*, 411:186 – 202, 1998.
- [49] J. Wan, Y. L. Fan, D. W. Gong, S. G. Shen, and X. Q. Fan. Surface relaxation and stress of fcc metals: Cu, ag, au, ni, pd, pt, al and pb. *Modelling Simul. Mater. Sci. Eng.*, 7:189–206, 1999.
- [50] J. Wang and H. Huang. Novel deformation mechanism of twinned nanowires. *Applied Physics Letters*, 88(20):203112, 2006.
- [51] D. Wolf. Surface-stress-induced structure and elastic behavior of thin films. *Appl. Phys. Lett.*, 58(19):2081–2083, 1991.
- [52] E. W. Wong, P. E. Sheehan, and C. M. Lieber. Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes. *Science*, 277:1971–1975, 1997.
- [53] B. Wu, A. Heidelberg, and J. J. Boland. Mechanical properties of ultrahigh-strength gold nanowires. *Nature Materials*, 4:525–529, 2005.
- [54] Mehdi B. Zanjani and Jennifer R. Lukes. Size dependent elastic moduli of cdse nanocrystal superlattices predicted from atomistic and coarse grained models. *The Journal of Chemical Physics*, 139(14):144702, 2013.

- [55] W. L. Zhong, B. Jiang, P. L. Zhang, J. M. Ma, H. M. Cheng, Z. H. Yang, and L. X. Li. Phase transition in pbtiO_3 ultrafine particles of different sizes. *J. Phys.: Condens. Matter*, 5:2619–2624, 1993.