CONTINUUM AND ATOMISTIC MODELS OF SURFACE ELASTICITY AND APPLICATIONS

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ABSTRACT OF THE DISSERTATION

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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 from atomistic models, which are compared with experimental data and prior simulation results.

This fundamental research is useful in a variety of applications. First, with the help of the proposed algorithm we quickly calculate the surface tension and determine the equilibrium shape of crystals. Secondly, in previous studies of wave propagation the impact of surface elasticity was not noticed. We find that when the surface/interface gains its own elasticity, the inhomogeneities between the bulk and the surface/interface result in nonlinearity for both interfacial and bulk wave propagation aspects. We study the interfacial wave between two half-spaces with surface elasticity taken into account. A sufficient condition for the existence and uniqueness of a subsonic interfacial wave is obtained for general anisotropic materials. In addition, from explicitly calculated dispersion relations of interfacial waves for interfaces between two solids and solid & fluid, we observe that the dispersion relations of interfacial waves are nonlinear at the presence of surface elasticity and depend on surface elasticity parameters. Further, we analyze the wave reflection and refraction with surface elasticity. We find that both the amplitude ratios and energy rates of reflected and refracted waves become dependent on the incident wave frequency. Also, the analysis of the existence of reflected and refracted waves shows that when the incident angle is above some critical angle, the corresponding reflected or refracted waves become typical interfacial waves. Finally, from Landau phenomenological theory we propose a model for size dependence of phase transformation temperature of ferroelectric nano-particles. We postulate that the surface effect plays an important role of such size effect. Our model shows the size dependence and predicts the critical size for certain ferroelectric particles.

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Chapter 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 [8, 9].

In this dissertation we focus on understanding mesoscopic effects and atomistic origin of surface elasticity [10, 11]. Surface elasticity of liquid is conventionally modeled by postulating a surface energy that is proportional to surface area; the proportional 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 [12]. On the other hand, modern technologies allow for fabrication and 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 nanostructures. This is evident from the experimental observations of size-dependent properties of nanostructures including the increase of strength [13, 14, 15, 16] and variation of the modulus of nanostructures [17, 18, 19, 20, 21, 22, 23]. Also, surfaces may induce phase transitions as shown in molecular dynamic (MD) simulations [24, 25, 26] and have been used to explain the size-dependent phase transition temperature of ferroelectric and ferromagnetic nanoparticles [5, 6, 7].

From a continuum viewpoint, the seminal works of Gurtin and Murdoch [27, 28] 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. 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 the best of our 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 reveal surface elastic stiffness tensor [29]. Therefore, a number of authors have turned to atomistic models for assessing surface elasticity properties and their effects on the overall properties of nanostructures [2, 30, 31].

From an atomistic viewpoint, surface elasticity arises from (i) interatomic bondbreaking when new surfaces are created, (ii) surface relaxation or reconstruction [11, 32], and (iii) interatomic bond stretching and reorientation under applications of macroscopic strains. The Cauchy-Born rule [33, 34, 35] 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 $E_{tot}(\mathbf{H})$ to the total strain energy of the continuum model $U_{strain}(\mathbf{H})$:

$$E_{\text{tot}}(\mathbf{H}) = U_{\text{strain}}(\mathbf{H}), \tag{1.1}$$

where $\mathbf{H} \in \mathbb{R}^{3 \times 3}$ is the unsymmetrized applied strain. This strategy has been used to investigate surface/interface elasticity properties of metallic crystals [2, 36], thermoelastic properties [37], coupling of surface and bulk elasticity of nanostructures [30], noncoherent metallic interfaces [31], nanowires [22, 23], nano-multilayers/plates [38, 39] and nanocrystal superlattices [40]. 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 [41, 42].

In spite of recent intensive study, 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 fullscale MD simulation.

The dissertation is organized as follows: in Chapter 2 we briefly review the Gurtin-Murdoch theory as a continuum theory for surface elasticity. We derive an atomistic formulation of surface elasticity and propose an algorithm for speedy calculation of surface elasticity parameters in Chapter 3. Chapter 4 is an application of the algorithm in calculation of surface tension and determination of equilibrium shape of crystals. Chapter 5 is a complete study of the impact of surface elasticity on elastic wave propagation. Section 5.1 shows an example of wave propagation in inhomogeneous domains. In Section 5.2 we analyze the existence and uniqueness condition of interfacial wave with surface elasticity at the interface. We study the impact of surface elasticity on both reflection and refraction of bulk waves at the interface of two solids in Section 5.3. Chapter 6 is an model for size effect of phase transition temperature of ferroelectric nano-particles, in which the surface stress plays an important role. We conclude in Chapter 7.

Chapter 2

Continuum surface elasticity: Gurtin-Murdoch theory

In this chapter we revisit the continuum theory for surface elasticity of solids that has been established by Gurtin and Murdoch [27, 28]. 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 $\mathscr{P}_{\mathbf{n}} : \mathbb{R}^{3 \times 3} \to \mathbb{S}_{\mathbf{n}}$ be the projection operator. Assume that the body undergoes a C^2 -deformation $\mathbf{y} : \Omega \to \mathbf{y}(\Omega)$. The Gurtin-Murdoch theory postulates that the surface elastic energy is given by

$$U_{\rm surf}[\mathbf{y}] = \int_{\Gamma} W_s(\nabla \mathbf{y}, \mathbf{n}) dS, \qquad (2.1)$$

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 , $W_s : \mathbb{R}^{3\times3} \times \mathbb{R}^3 \to \mathbb{R}$ is the surface energy density function that determines the surface stress-strain relation, and the explicit \mathbf{n} -dependence of W_s reflects 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 deformation gradient $\mathbf{F} \in \mathbb{R}^{3\times3}$,

(i)
$$W_s(\mathbf{F}, \mathbf{n}) = W_s(\mathscr{P}_{\mathbf{n}}\mathbf{F}, \mathbf{n}),$$

(ii) $W_s(\mathbf{QF}, \mathbf{n}) = W_s(\mathbf{F}, \mathbf{n}) \quad \forall \mathbf{Q} \in So(3), \text{ and}$ (2.2)
(iii) $W_s(\mathbf{FR}, \mathbf{n}) = W_s(\mathbf{F}, \mathbf{n}) \quad \forall \mathbf{R} \in \mathscr{G}_{\mathbf{n}},$

where the first equation reflects 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 $\mathscr{G}_{\mathbf{n}}$ 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 $\varepsilon_{\mathbf{n}}^{0} = \frac{1}{2}(\mathbf{F}_{\mathbf{n}}^{0T} + \mathbf{F}_{\mathbf{n}}^{0}) - \mathbf{I}$ be the linearized residual strain on the free surface. For a linearized theory, we assume that $|\varepsilon_{\mathbf{n}}^{0}| \ll 1$ 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 the neighborhood of $\mathbf{F}_{\mathbf{n}}^{0}$, we rewrite the surface elastic energy (2.1) as a functional of displacement:

$$U_{\rm surf}[\mathbf{u}] = \int_{\Gamma} \left[\gamma(\mathbf{n}) - \nabla \mathbf{u} \cdot \tau_0(\mathbf{n}) + \frac{1}{2} \nabla \mathbf{u} \cdot \mathbf{C}_s(\mathbf{n}) \nabla \mathbf{u} \right], \qquad (2.3)$$

where the terms beyond $O(\delta^2)$ are neglected, $\gamma(\mathbf{n}) := W_s^*(\mathbf{n}) + \frac{1}{2}\varepsilon_{\mathbf{n}}^0 \cdot \mathbf{C}_s(\mathbf{n})\varepsilon_{\mathbf{n}}^0$ is the surface tension (of the undeformed surface), $\tau_0(\mathbf{n}) = \mathbf{C}_s(\mathbf{n})\varepsilon_{\mathbf{n}}^0$ is the residual surface stress, and $\mathbf{C}_s(\mathbf{n})$ is the forth-order surface elasticity (or stiffness) tensor:

$$[\mathbf{C}_{s}(\mathbf{n})]_{piqj} = \frac{\partial^{2}W_{s}(\mathbf{F},\mathbf{n})}{\partial(\mathbf{F})_{pi}\partial(\mathbf{F})_{qj}}\Big|_{\mathbf{F}=\mathbf{F}_{\mathbf{n}}^{0}}$$

In addition to the major symmetry, the second of (2.2) 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 (2.2) implies that $W_s(\mathbf{F}, \mathbf{n}) = W_s(\mathbf{F}_{\mathbf{n}}^0, \mathbf{n})$ if $\mathscr{P}_{\mathbf{n}}(\mathbf{F} - \mathbf{F}_{\mathbf{n}}^0) = 0$, and hence

$$\mathbf{C}_{s}(\mathbf{n}) = \mathscr{P}_{\mathbf{n}}\mathbf{C}_{s}(\mathbf{n})\mathscr{P}_{\mathbf{n}}.$$

Further restrictions on the surface elasticity tensor C_s can be obtained by the last of (2.2) upon specifying the symmetry group \mathcal{G}_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 [43, 44, 42, 45].

Chapter 3

Determination of surface elastic properties from atomistic models

3.1 An atomistic model of a finite crystal

Though the continuum theory of surface elasticity has been well established, the surface elasticity properties, i.e., $\gamma(\mathbf{n})$, $\tau_0(\mathbf{n})$ and $\mathbf{C}_s(\mathbf{n})$ defined in (2.3), appear to be elusive to experimental investigations. Microscopically speaking, surface energy and surface elasticity arise from bond breaking between two half-space bodies. Besides probable 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.

3.1.1 Model description

We begin with an infinite body that, in the equilibrium state, would have its atomic positions at lattice points $\mathscr{L} \subset \mathbb{R}^3$. 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 $\Omega \cap \mathscr{L}$. 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. We denote the new position of the atom by \mathbf{x}_{v} with a reference position $\mathbf{x}_{v}^{0} \in \Omega \cap \mathscr{L}$, where $v \in \{1, \dots, M\}$ labels the atoms and M is the total number of atoms in the finite crystal. We assume the displacements of all atoms \mathbf{u}_{v} are small, i.e, $\mathbf{u}_{v} = \mathbf{x}_{v} - \mathbf{x}_{v}^{0} \sim \delta \ll a$.

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:

$$E_{\text{tot}} = E_{\text{tot}}(\mathbf{x}_1, \cdots, \mathbf{x}_M), \qquad (3.1)$$

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

$$E_{\text{tot}}(\mathbf{Q}\mathbf{x}_1 + \mathbf{c}, \cdots, \mathbf{Q}\mathbf{x}_M + \mathbf{c}) = E_{\text{tot}}(\mathbf{x}_1, \cdots, \mathbf{x}_M) \qquad \forall \mathbf{c} \in \mathbb{R}^3, \ \mathbf{Q} \in So(3).$$
(3.2)

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

$$E_{\text{tot}}(\mathbf{x}_{1},\cdots,\mathbf{x}_{M}) = E_{\text{tot}}(\mathbf{x}_{1}^{0},\cdots,\mathbf{x}_{M}^{0}) + \sum_{\nu=1}^{M} \mathbf{f}_{\nu} \cdot \mathbf{u}_{\nu} + \frac{1}{2} \sum_{\nu,\mu=1}^{M} \mathbf{u}_{\nu} \cdot \mathbf{K}_{\nu\mu} \mathbf{u}_{\mu} + o(\delta^{2}), \quad (3.3)$$

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

$$\mathbf{f}_{\nu} = \frac{\partial E_{\text{tot}}}{\partial \mathbf{x}_{\nu}} \bigg|_{(\mathbf{x}_{1}^{0}, \cdots, \mathbf{x}_{M}^{0})}, \qquad \mathbf{K}_{\nu\mu} = \frac{\partial^{2} E_{\text{tot}}}{\partial \mathbf{x}_{\nu} \partial \mathbf{x}_{\mu}} \bigg|_{(\mathbf{x}_{1}^{0}, \cdots, \mathbf{x}_{M}^{0})}.$$
(3.4)

Physically, the vectors \mathbf{f}_{v} can be interpreted as the force acting on the atom at \mathbf{x}_{v}^{0} and $\mathbf{K}_{v\mu} \in \mathbb{R}^{3\times3}_{sym}$ can be interpreted as the 'spring constants' between atoms at \mathbf{x}_{v}^{0} and \mathbf{x}_{μ}^{0} in the reference configuration $\Omega \cap \mathscr{L}$. We note that the general form of energy (3.3) can account for the angular and nonlocal dependence of atoms' energy. From (3.2) we infer that for any skew-symmetric tensor $\mathbf{W} = -\mathbf{W}^{T} \in \mathbb{R}^{3\times3}$ and $\mathbf{c} \in \mathbb{R}^{3}$,

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



Figure 3.1: Surface atoms and bulk atoms

Therefore,

$$\sum_{\nu=1}^{M} \mathbf{f}_{\nu} = 0, \qquad \sum_{\nu=1}^{M} \mathbf{K}_{\nu\mu} = \sum_{\mu=1}^{M} \mathbf{K}_{\nu\mu} = 0,$$

$$\sum_{\nu=1}^{M} \mathbf{f}_{\nu} \cdot \mathbf{W} \mathbf{x}_{\nu}^{0} = 0, \qquad \sum_{\mu=1}^{M} \mathbf{K}_{\nu\mu} \mathbf{W} \mathbf{x}_{\mu}^{0} = 0.$$
(3.5)

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. 3.1, for the vth atom in the reference state its "*neighboring atoms*" are defined as $\mathcal{N}_{v} = {\mathbf{x}_{\mu}^{0} \in \Omega : |\mathbf{x}_{v}^{0} - \mathbf{x}_{\mu}^{0}| \leq R}$. By the distance to the surface $\partial\Omega$, we refer to $\mathcal{B} = {\mathbf{x}_{v}^{0} \in \Omega : \operatorname{dist}(\partial\Omega, \mathbf{x}_{v}^{0}) > R}$ as the *bulk atoms* and $\mathcal{S} = {\mathbf{x}_{v}^{0} \in \Omega : \operatorname{dist}(\partial\Omega, \mathbf{x}_{v}^{0}) \leq R}$ as the *surface atoms*. The *cut-off radius R* is such that

$$\begin{cases} \mathbf{K}_{\nu\mu} = 0 & \text{if } |\mathbf{x}_{\nu}^{0} - \mathbf{x}_{\mu}^{0}| > R, \\ \mathbf{f}_{\nu} = 0 & \forall \mathbf{x}_{\nu}^{0} \in \mathscr{B}, \end{cases}$$
(3.6)

where the first reflects the physical intuition that two-atoms do not interact if they are far away, 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 \mathscr{L} , the coefficients $\mathbf{K}_{\nu\mu}$ and \mathbf{f}_{ν} defined by (3.4) are the only atomistic parameters needed for our subsequent calculations of bulk and surface elasticity properties for small strains. Also, equations (3.5) impose fundamental restrictions on an atomistic model that may be relevant to some fundamental conceptual problems [46]. If the cut-off radius *R* is small enough such that only the nearest neighbors interact, the total energy (3.3) 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 (3.3) can be regarded as the total energy in a discretized model for the linearized peridynamics with *R* being the *peridynamic horizon* [47]. Also, the energy (3.3) 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 [35, 48]. 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:

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

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

$$\mathbf{x}_{\boldsymbol{\nu}} = \mathbf{x}_{\boldsymbol{\nu}}^0 + \mathbf{H}\mathbf{x}_{\boldsymbol{\nu}}^0 \qquad (\boldsymbol{\nu} = 1, \cdots, M)$$

are the new positions of the atoms that follow from the Cauchy-Born rule. Assuming $\mathbf{H}\mathbf{x}_{v}^{0} \sim \delta \ll a \ (v = 1, \dots M)$, by (3.3) we have

$$\frac{1}{2}\mathbf{H}\cdot\mathbf{C}\mathbf{H} = \frac{1}{V} \left[\sum_{\mathbf{x}_{\nu}^{0} \in \mathscr{S}} \mathbf{f}_{\nu} \cdot \mathbf{H}\mathbf{x}_{\nu}^{0} + \frac{1}{2} \sum_{\mu,\nu=1}^{M} (\mathbf{H}\mathbf{x}_{\nu}^{0}) \cdot \mathbf{K}_{\nu\mu} (\mathbf{H}\mathbf{x}_{\mu}^{0}) \right].$$
(3.7)

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

bulk atoms:

$$\mathbf{K}_{\nu_{1}\mu_{1}} = \mathbf{K}_{\nu_{2}\mu_{2}} \qquad \text{if } \mathbf{x}_{\nu_{1}}^{0} - \mathbf{x}_{\mu_{1}}^{0} = \mathbf{x}_{\nu_{2}}^{0} - \mathbf{x}_{\mu_{2}}^{0}, \, \mathbf{x}_{\nu_{1}}^{0}, \mathbf{x}_{\nu_{2}}^{0}, \mathbf{x}_{\mu_{1}}^{0}, \mathbf{x}_{\mu_{2}}^{0} \in \mathscr{B}.$$
(3.8)

By (3.6) and (3.7), we find that

$$\frac{1}{2}\mathbf{H} \cdot \mathbf{C}\mathbf{H} = \frac{1}{V} \sum_{\mathbf{x}_{\nu}^{0} \in \mathscr{S}} \mathbf{f}_{\nu} \cdot \mathbf{H}\mathbf{x}_{\nu}^{0} + \frac{1}{2V} \sum_{\mu,\nu=1}^{M} (\mathbf{H}\mathbf{x}_{\nu}^{0}) \cdot \mathbf{K}_{\nu\mu} (\mathbf{H}\mathbf{x}_{\mu}^{0})$$

$$\rightarrow \frac{M}{2V} \sum_{\mathbf{x}_{\mu}^{0} \in \mathscr{N}_{\nu}} (\mathbf{H}\mathbf{x}_{\nu}^{0}) \cdot \mathbf{K}_{\nu\mu} (\mathbf{H}\mathbf{x}_{\mu}^{0}) \quad \text{as } V \to +\infty.$$
(3.9)

Moreover, by (3.9) the bulk elasticity tensor of the crystal is given by

$$[\mathbf{C}]_{piqj} = n_0 \sum_{\mathbf{x}_{\mu}^0 \in \mathscr{N}_{\nu}} (\mathbf{x}_{\nu}^0)_i [\mathbf{K}_{\nu\mu}]_{pq} (\mathbf{x}_{\mu}^0)_j \qquad \forall \nu \in \mathscr{B},$$
(3.10)

where the crystal constant $n_0 = M/V$ is the number of atoms per unit volume, and by (3.8) the value $[\mathbf{C}]_{piqj}$ is independent of the index v. Also, we remark that the properties in (3.5) guarantee that the bulk elasticity tensor satisfies the usual symmetries: $[\mathbf{C}]_{piqj} = [\mathbf{C}]_{qjpi} = [\mathbf{C}]_{pijq}$.

3.1.2 Surface elasticity properties



Figure 3.2: Layer number $l \in \{1, 2, \dots, \Theta\}$ labels crystal planes parallel to the free surfaces.

We now derive the surface elasticity properties in terms of atomistic parameters as for the bulk stiffness tensor. In addition to the assumption that the reference crystal \mathscr{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, we assume the 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. 3.2. 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:

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

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

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

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

$$\mathbf{x}_{\nu} = \mathbf{x}_{\nu}^{0} + \mathbf{H}\mathbf{x}_{\nu}^{0} + w_{\theta(\nu)}\mathbf{e}_{3}, \qquad (3.11)$$

where the first two terms follow from the Cauchy-Born rule, and $w : \{1, \dots, \Theta\} \to \mathbb{R}$ 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

$$\mathbf{t} = (\mathbf{C}\mathbf{H})\mathbf{n},\tag{3.12}$$

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 strains such that (3.12) vanishes,

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

Then the surface energy density in the atomistic model as a function of the strain tensor **H** and relaxations (w_1, \dots, w_{Θ}) can be identified as (c.f., (3.14) and (3.10))

$$E_{\text{surf}}(\mathbf{H}, w_1, \cdots, w_{\Theta}) = \frac{1}{2L^2} \Big[E_{\text{tot}}(\mathbf{x}_1, \cdots, \mathbf{x}_M) - \frac{1}{2} V \mathbf{H} \cdot \mathbf{C} \mathbf{H} - V \varphi_0 \Big], \qquad (3.13)$$

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

$$\frac{1}{V}E_{\text{tot}}(\mathbf{x}_1^0,\cdots,\mathbf{x}_M^0) \to \varphi_0 \qquad \text{as } V \to +\infty.$$
(3.14)

Let

$$\gamma^{0} = \frac{1}{2L^{2}} [E_{\text{tot}}(\mathbf{x}_{1}^{0}, \cdots, \mathbf{x}_{M}^{0}) - V \varphi_{0}].$$
(3.15)

By (3.3), (3.11) and neglecting higher order terms, we rewirte the surface energy density (3.13) as

$$E_{\text{surf}}(\mathbf{H}, w_1, \cdots, w_{\Theta}) = \gamma^0 + \frac{1}{2L^2} \left\{ \sum_{l=1}^{\Theta} \sum_{\mathbf{v} \in \theta^{-1}(l)} \mathbf{f}_{\mathbf{v}} \cdot (\mathbf{H} \mathbf{x}_{\mathbf{v}}^0 + w_l \mathbf{e}_3) + \frac{1}{2} \sum_{l,l'=1}^{\Theta} \sum_{\mathbf{v} \in \theta^{-1}(l), \mu \in \theta^{-1}(l')} (\mathbf{H} \mathbf{x}_{\mathbf{v}}^0 + w_l \mathbf{e}_3) \cdot \mathbf{K}_{\nu\mu} (\mathbf{H} \mathbf{x}_{\mu}^0 + w_{l'} \mathbf{e}_3) \right\}$$
(3.16)
$$=: \gamma^0 + \boldsymbol{\sigma} \cdot \mathbf{H} + \frac{1}{2} \mathbf{H} \cdot \mathbf{S} \mathbf{H} + \frac{1}{2} \left[\sum_{l=1}^{\Theta} (g_l w_l + w_l \mathbf{B}_l \cdot \mathbf{H}) + \frac{1}{2} \sum_{l,l'=1}^{\Theta} (\tilde{\mathbf{K}})_{ll'} w_l w_{l'} \right],$$

where (recall that C is given by (3.10))

$$\sigma = \frac{1}{2L^2} \sum_{\nu=1}^{M} \mathbf{f}_{\nu} \otimes \mathbf{x}_{\nu}^{0}, \qquad [\mathbf{S}]_{piqj} = \frac{1}{2L^2} \left\{ \sum_{\nu,\mu=1}^{M} (\mathbf{x}_{\nu}^{0})_{i} [\mathbf{K}_{\nu\mu}]_{pq} (\mathbf{x}_{\mu}^{0})_{j} - V[\mathbf{C}]_{piqj} \right\},$$

$$g_{l} = \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l)} \mathbf{f}_{\nu} \cdot \mathbf{e}_{3}, \qquad \mathbf{B}_{l} = \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l)} \sum_{\mu=1}^{M} (\mathbf{K}_{\nu\mu} \mathbf{e}_{3}) \otimes \mathbf{x}_{\mu}^{0}, \qquad \text{and} \qquad (3.17)$$

$$(\tilde{\mathbf{K}})_{ll'} = \frac{1}{L^2} \sum_{\nu \in \theta^{-1}(l), \mu \in \theta^{-1}(l')} \mathbf{e}_{3} \cdot \mathbf{K}_{\nu\mu} \mathbf{e}_{3}.$$

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

$$N = \left[\frac{R}{d_0}\right] := \max\{|l - l'| : \exists v \in \theta^{-1}(l), \mu \in \theta^{-1}(l') \text{ such that } |\mathbf{x}_v^0 - \mathbf{x}_\mu^0| \le R\} (3.18)$$

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 $v_l \in \theta^{-1}(l)$ be a representative interior atom in the *l*th crystal plane. Then in the limit $L \to +\infty$, we can rewrite the quantities in (3.17) as

$$\sigma = n_0 d_0 \sum_{l \in [1,N]} l d_0 \mathbf{f}_{v_l} \otimes \mathbf{e}_3,$$

$$[\mathbf{S}]_{piqj} = n_0 d_0 \sum_{l=1 \in [1,N]} \left[\sum_{\mathbf{x}_{\mu}^0 \in \mathscr{N}_{v_l} \cap \Omega} (\mathbf{x}_{v_l}^0)_i [\mathbf{K}_{v_l \mu}]_{pq} (\mathbf{x}_{\mu}^0)_j - \mathbf{C} \right],$$

$$g_l = n_0 d_0 \mathbf{f}_{v_l} \cdot \mathbf{e}_3, \qquad \mathbf{B}_l = n_0 d_0 \sum_{\mu \in \mathscr{N}_{v_l} \cap \Omega} (\mathbf{K}_{v_l \mu} \mathbf{e}_3) \otimes \mathbf{x}_{\mu}^0,$$

$$(\tilde{\mathbf{K}})_{ll'} = n_0 d_0 \sum_{\mu \in \theta^{-1}(l'), \ \mathbf{x}_{\mu}^0 \in \mathscr{N}_{v_l} \cap \Omega} \mathbf{e}_3 \cdot \mathbf{K}_{v_l \mu} \mathbf{e}_3.$$

$$(3.19)$$

Moreover, by (3.5), (3.6) and (3.17) we immediately see that $\tilde{\mathbf{K}}, g_l$ and \mathbf{B}_l defined in (3.16) satisfy that $\tilde{\mathbf{K}}^T = \tilde{\mathbf{K}}, \sum_{l'=1}^{\Theta} (\tilde{\mathbf{K}})_{ll'} = 0$ for any *l*, and

$$\begin{cases} (\tilde{\mathbf{K}})_{ll'} = (\tilde{\mathbf{K}})_{mm'} & \text{if } l, l', m, m' \in [N+1, \Theta - N] \& |l-l'| = |m-m'|, \\ g_l = 0, & \mathbf{B}_l \cdot \mathbf{H} = 0 & \forall \, l \in [N+1, \Theta - N]. \end{cases}$$
(3.20)

To see the last of the above equation, inserting (3.10) into (3.12) and setting the traction equal to zero we have

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

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

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

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:

$$\begin{cases} (\mathbf{M}_{0})_{ij} = (\tilde{\mathbf{K}})_{ij} & i, j = 1, \cdots, N, \\ (\mathbf{M}_{1})_{ij} = (\tilde{\mathbf{K}})_{ij} & i, j = N + 1, \cdots, 2N, \\ (\mathbf{M}_{2})_{ij} = (\tilde{\mathbf{K}})_{ij} & i = 1, \cdots, N; j = N + 1, \cdots, 2N. \end{cases}$$
(3.21)

and *N*-vectors:

$$\mathbf{w}_{i} = (w_{iN+1}, w_{iN+2}, \cdots, w_{iN+N}), \qquad i = 0, 1, 2, \cdots, P,$$

$$\tilde{\mathbf{f}} = \mathbf{g} + (\mathbf{B}_{1} \cdot \mathbf{H}, \cdots, \mathbf{B}_{N} \cdot \mathbf{H}), \qquad \mathbf{g} = (g_{1}, \cdots, g_{N}).$$
(3.22)

It is clear that M_1, M_0 are symmetric and M_2 is nonsingular.

From (3.16) we observe that the surface energy density of the finite crystal $\mathscr{L} \cap \Omega$ 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 (3.16), (3.20), (3.21) and (3.22) we can write the relaxation-dependent (i.e., w_l -dependent) part of the surface energy density as

$$R(\mathbf{H};\mathbf{w}_0,\cdots,\mathbf{w}_{P-1}) := \tilde{\mathbf{f}} \cdot \mathbf{w}_0 + Q(\mathbf{w}_0,\cdots,\mathbf{w}_{P-1}), \qquad (3.23)$$

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

$$Q(\mathbf{w}_{0}, \cdots, \mathbf{w}_{P-1}) = \frac{1}{2} \sum_{l,l'=1}^{\Theta-N} (\tilde{\mathbf{K}})_{ll'} w_{l} w_{l'}$$

$$= \frac{1}{2} \begin{bmatrix} \mathbf{w}_{0} \\ \mathbf{w}_{1} \\ \mathbf{w}_{2} \\ \vdots \\ \mathbf{w}_{P-1} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{M}_{0} & \mathbf{M}_{2} & 0 & \cdots & 0 & 0 \\ \mathbf{M}_{2}^{T} & \mathbf{M}_{1} & \mathbf{M}_{2} & \cdots & 0 & 0 \\ 0 & \mathbf{M}_{2}^{T} & \mathbf{M}_{1} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & \mathbf{M}_{2}^{T} & \mathbf{M}_{1} \end{bmatrix} \begin{bmatrix} \mathbf{w}_{0} \\ \mathbf{w}_{1} \\ \mathbf{w}_{2} \\ \vdots \\ \mathbf{w}_{P-1} \end{bmatrix}$$
(3.24)
$$= \frac{1}{2} \mathbf{w}_{0} \cdot \mathbf{M}_{0} \mathbf{w}_{0} + \sum_{i=1}^{P-1} (\frac{1}{2} \mathbf{w}_{i} \cdot \mathbf{M}_{1} \mathbf{w}_{i} + \mathbf{w}_{i} \cdot \mathbf{M}_{2} \mathbf{w}_{i+1}).$$

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

$$\boldsymbol{R}^{*}(\mathbf{H}) := \min_{\mathbf{w}_{0}, \mathbf{w}_{1}, \cdots, \mathbf{w}_{P-1}} \boldsymbol{R}(\mathbf{H}; \mathbf{w}_{0}, \cdots, \mathbf{w}_{P-1}, \mathbf{w}_{P} = 0).$$
(3.25)

We are therefore motivated to consider the algebraic minimization problem

$$Q_{P}^{*}(\mathbf{w}_{0}) := \frac{1}{2} \mathbf{w}_{0} \cdot \mathbf{M}_{0} \mathbf{w}_{0} + \min_{\mathbf{w}_{1}, \cdots, \mathbf{w}_{P-1}} \left\{ \sum_{i=1}^{P-1} \left(\frac{1}{2} \mathbf{w}_{i} \cdot \mathbf{M}_{1} \mathbf{w}_{i} + \mathbf{w}_{i} \cdot \mathbf{M}_{2} \mathbf{w}_{i+1} \right) \right\}$$

$$= \frac{1}{2} \mathbf{w}_{0} \cdot \mathbf{M}_{0} \mathbf{w}_{0} + \min_{\mathbf{w}_{1}} \left\{ \frac{1}{2} \mathbf{w}_{1} \cdot \mathbf{M}_{1} \mathbf{w}_{1} + \mathbf{w}_{0} \cdot \mathbf{M}_{2} \mathbf{w}_{1} + \cdots + \min_{\mathbf{w}_{P-2}} \left[\frac{1}{2} \mathbf{w}_{P-2} \cdot \mathbf{M}_{1} \mathbf{w}_{P-2} + \mathbf{w}_{P-3} \cdot \mathbf{M}_{2} \mathbf{w}_{P-2} + \min_{\mathbf{w}_{P-1}} \left(\frac{1}{2} \mathbf{w}_{P-1} \cdot \mathbf{M}_{1} \mathbf{w}_{P-1} + \mathbf{w}_{P-2} \cdot \mathbf{M}_{2} \mathbf{w}_{P-1} \right) \right] \right\}.$$
(3.26)

To represent the solution to the minimization problem (3.25), it will be convenient to introduce a *nonlinear* mapping $\mathbb{T} : \mathbb{R}^{N \times N}_{sym} \to \mathbb{R}^{N \times N}_{sym}$ as

$$\mathbb{T}(\mathbf{A}) = \mathbf{M}_1 - \mathbf{M}_2 \mathbf{A}^{-1} \mathbf{M}_2^T.$$
(3.27)

By successively solving the algebraic minimization problem for $\mathbf{w}_{P-1}, \mathbf{w}_{P-2}, \cdots \mathbf{w}_1$, we find that the minimizers of (3.26) satisfy that

$$\mathbf{w}_i = -[\mathbb{T}^{P-1-i}(\mathbf{M}_1)]^{-1}\mathbf{M}_2^T\mathbf{w}_{i-1} \qquad \forall i = 1, \cdots, P-2,$$
(3.28)

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 (3.23) the minimum is given by

$$R^*(\mathbf{H}) = \min_{\mathbf{w}_0} [\mathbf{Q}_P^*(\mathbf{w}_0) + \tilde{\mathbf{f}} \cdot \mathbf{w}_0], \qquad (3.29)$$

and the relaxations \boldsymbol{w}_0^* are given by

$$\mathbf{w}_0^* = -\left\{\mathbf{M}_0 - \mathbf{M}_2[\mathbb{T}^{P-2}(\mathbf{M}_1)]^{-1}\mathbf{M}_2^T\right\}^{-1}\tilde{\mathbf{f}}.$$
(3.30)

We observe that the above solutions (3.28), (3.29) and (3.30) 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

$$c^{-1}|\mathbf{w}|^2 \le \mathbf{w} \cdot \mathbb{T}^i(\mathbf{M}_1)\mathbf{w} \le c|\mathbf{w}|^2 \qquad \forall i = 1, \cdots, P-2 \& \mathbf{w} \in \mathbb{R}^N.$$
(3.31)

(ii) For an infinite crystal, the above inequalities shall hold for $P \to \infty$ 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 $\Lambda \in \mathbb{R}^{N \times N}_{sym}$ and the limit Λ can be determined by

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

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

$$\Lambda(\mathbf{M}_{2}^{-T} + \mathbf{M}_{2}^{-1})\Lambda - \mathbf{M}_{1}\mathbf{M}_{2}^{-T}\Lambda - \Lambda\mathbf{M}_{2}^{-1}\mathbf{M}_{1} + \mathbf{M}_{2} + \mathbf{M}_{2}^{T} = 0.$$
(3.32)

(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 $\Omega \cap \mathscr{L}$, 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

$$\mathbf{M}_{0} - \mathbf{M}_{2} [\mathbb{T}^{P-2}(\mathbf{M}_{1})]^{-1} \mathbf{M}_{2}^{T} = \mathbf{M}_{0} - \mathbf{M}_{1} + \mathbf{M}_{1} - \mathbf{M}_{2} [\mathbb{T}^{P-2}(\mathbf{M}_{1})]^{-1} \mathbf{M}_{2}^{T}$$

$$= \mathbf{M}_{0} - \mathbf{M}_{1} + \mathbb{T}^{P-1}(\mathbf{M}_{1}) \rightarrow \mathbf{M}_{0} - \mathbf{M}_{1} + \Lambda =: \mathbf{Y}^{-1}.$$
(3.33)

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

$$\mathbf{Y}^{-1} = \mathbf{M}_0 - \mathbf{M}_1 + \Lambda \quad \text{is positive definite.} \tag{3.34}$$

(iv) The minimum of the right hand side of (3.29) shall be independent of *P* and is given by

$$R^*(\mathbf{H}) = \min_{\mathbf{w}_0} [\mathbf{Q}_P^*(\mathbf{w}_0) + \tilde{\mathbf{f}} \cdot \mathbf{w}_0] = -\frac{1}{2} \tilde{\mathbf{f}} \cdot (\mathbf{M}_0 - \mathbf{M}_1 + \Lambda)^{-1} \tilde{\mathbf{f}} = -\frac{1}{2} \tilde{\mathbf{f}} \cdot \mathbf{Y} \tilde{\mathbf{f}}, (3.35)$$

and by (3.28) and (3.30) the relaxations satisfies

$$\mathbf{w}_0^* = -\mathbf{Y}\tilde{\mathbf{f}}$$

$$\mathbf{w}_i^* = -\Lambda^{-1}\mathbf{M}_2\mathbf{w}_{i-1}^* = \dots = (-\Lambda^{-1}\mathbf{M}_2)^i\mathbf{w}_0^* \qquad \forall i = 1, 2, \dots.$$
(3.36)

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

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

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

We now employ the basic principle (1.1) to identify the surface elasticity properties in the continuum model. By (2.3), (3.16), (3.13), (3.35) and in account of relaxations of both bottom and top surfaces, we have that for any $\mathbf{H} \in \mathbb{H}_0$,

$$\gamma(\mathbf{n}) - \mathbf{H} \cdot \tau_0(\mathbf{n}) + \frac{1}{2} \mathbf{H} \cdot \mathbf{C}_s(\mathbf{n}) \mathbf{H} = \gamma^0 + \boldsymbol{\sigma} \cdot \mathbf{H} + \frac{1}{2} \mathbf{H} \cdot \mathbf{S} \mathbf{H} + R^*(\mathbf{H}).$$

By $(3.22)_2$, we identify the surface elasticity properties in the continuum theory from the atomistic model as (c.f., (3.15), (3.17), (3.32) and (3.33))

$$\gamma(\mathbf{n}) = \gamma^{0} - \frac{1}{2} \mathbf{g} \cdot \mathbf{Y} \mathbf{g},$$

$$[\tau_{0}(\mathbf{n})]_{ij} = -(\sigma)_{ij} + \sum_{l,l'=1}^{N} g_{l}(\mathbf{Y})_{ll'}(\mathbf{B}_{l'})_{ij},$$

$$[\mathbf{C}_{s}(\mathbf{n})]_{piqj} = (\mathbf{S})_{piqj} - \sum_{l,l'=1}^{N} (\mathbf{Y})_{ll'}(\mathbf{B}_{l})_{pi}(\mathbf{B}_{l'})_{qj},$$

(3.37)

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 Λ , can be determined by solving a low-rank $N \times N$ algebraic Riccati equation (3.32). No molecular dynamic simulation per

se is necessary to compute the surface relaxations and surface elasticity properties; the algorithm implied by our analysis would be orders of magnitude more efficient than a full-scale MD simulation.

3.2 Examples

We now present a few examples concerning computation of surface relaxations and surface elasticity parameters from atomistic models. Though our framework is valid for general atomistic models, for simplicity we consider two-body potentials (pair potentials) and embedded atom model (EAM) potentials [1]. 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.

3.2.1 Pair potentials

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

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

and therefore the total energy of the finite crystal (3.1) is given by

$$E_{\text{tot}}(\mathbf{x}_{1},\cdots,\mathbf{x}_{M}) = \frac{1}{2} \sum_{\nu,\mu=1}^{M} V(r_{\nu\mu}).$$
(3.38)

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 \mathscr{L} . Then, by (3.4) we immediately have that

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

By (3.17), we calculate the matrices $(\tilde{\mathbf{K}})_{ll'}$, \mathbf{B}_l and vector \mathbf{g} as follows:

$$\begin{split} (\tilde{\mathbf{K}})_{ll'} = & N_0 d_0 \sum_{\mu \in \mathscr{N}_{\nu_l} \cap \theta^{-1}(l')} \left[-\frac{(l-l')^2 d_0^2}{(r_{\nu_l \mu}^0)^2} V''(r_{\nu \mu}^0) \\& -\frac{(r_{\nu_l \mu}^0)^2 - (l-l')^2 d_0^2}{(r_{\nu_l \mu}^0)^3} V'(r_{\nu_l \mu}^0) \right] \quad |l-l'| \in [1,N], \\ (\tilde{\mathbf{K}})_{ll} = & N_0 d_0 \sum_{l' \in \mathscr{M}_l} \sum_{\mu \in \mathscr{N}_{\nu_l} \cap \theta^{-1}(l')} \left[\frac{(l-l')^2 d_0^2}{(r_{\nu_l \mu}^0)^2} V''(r_{\nu_l \mu}^0) \\& + \frac{(r_{\nu_l \mu}^0)^2 - (l-l')^2 d_0^2}{(r_{\nu_l \mu}^0)^3} V'(r_{\nu_l \mu}^0) \right], \end{split}$$
(3.39)
$$g_l = & N_0 d_0 \sum_{l'=2l}^{N+l} \sum_{\mu \in \mathscr{N}_{\nu} \cap \theta^{-1}(l')} \frac{(l-l') d_0}{r_{\nu \mu}^0} V'(r_{\nu \mu}^0), \\ \mathbf{B}_l = & N_0 d_0 \sum_{l'=2l}^{N+l} \left\{ \frac{(l-l') d_0 \mathbf{r}_{\nu \mu}^0 \otimes \mathbf{r}_{\nu \mu}^0}{(r_{\nu \mu}^0)^2} V''(r_{\nu \mu}^0) - \frac{(l-l') d_0 \mathbf{r}_{\nu \mu}^0 \otimes \mathbf{r}_{\nu \mu}^0}{(r_{\nu \mu}^0)^3} V'(r_{\nu \mu}^0) \\& + \frac{\mathbf{e}_3 \otimes (\mathbf{x}_{\nu}^0 - \mathbf{x}_{\mu}^0)}{r_{\nu \mu}^0} V'(r_{\nu \mu}^0) \right\} \quad l \in [1, N]. \end{split}$$

where $\mathcal{M}_l := [\max\{1, l-N\}, l) \cup (l, l+N]$. If we denote by

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

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:

$$\mathbf{M}_{0} = \begin{bmatrix} \sum_{i=1}^{N} m_{i} & -m_{1} & -m_{2} & \cdots & -m_{N-1} \\ -m_{1} & m_{1} + \sum_{i=1}^{N} m_{i} & -m_{1} & \cdots & -m_{N-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_{N-1} & -m_{N-2} & -m_{N-3} & \cdots & \sum_{i=1}^{N-1} m_{i} + \sum_{i=1}^{N} m_{i} \end{bmatrix}, \\ \mathbf{M}_{1} = \begin{bmatrix} 2\sum_{i=1}^{N} & -m_{1} & -m_{2} & \cdots & -m_{N-1} \\ -m_{1} & 2\sum_{i=1}^{N} m_{i} & -m_{1} & \cdots & -m_{N-2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_{N-1} & -m_{N-2} & -m_{N-3} & \cdots & 2\sum_{i=1}^{N} m_{i} \end{bmatrix}, \quad (3.40)$$
$$\mathbf{M}_{2} = \begin{bmatrix} -m_{N} & 0 & 0 & \cdots & 0 \\ -m_{N-1} & -m_{N} & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ -m_{1} & -m_{2} & -m_{3} & \cdots & -m_{N} \end{bmatrix}.$$

The explicit expressions of the matrices \mathbf{M}_i (i = 0, 1, 2) in (3.40) will be convenient for verifying if the pair potential is physically reasonable, i.e., if (3.31) and (3.34) are satisfied, and computing the surface relaxations (3.36) and surface elasticity properties (3.37) by solving the algebraic Riccati equation (3.32) with explicitly calculated parameters in (3.39).

Percentage of		Cu	Ag		Au			Ni
relaxation		$EXP^{[49]}$		EXP ^[50]		$MD^{[51]}$		EXP ^[52]
$\Delta_{12}(\%)$	-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]	Pt			
			$MD^{[51]}$		$MD^{[51]}$			
		-2.80	-3.21	-3.52	-4.82			
		0.12	0.27	0.37	0.75			

Table 3.1: Normalized relaxations Δ_{12} and Δ_{23} for (111) surfaces of FCC crystals with Johnson EAM potentials [1] and comparison with experimental data (EXP) and prior MD simulations (MD).

3.2.2 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 $\rho_v(r_{\nu\mu})$ 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 (3.4) and (3.19) and then numerically solving the algeraic Riccati equation (3.32). Further, we calculate the surface elasticity properties by (3.37). All the calculations are performed by using Johnson EAM potentials [1].

The results of our calculations are shown in Table 3.1 - 3.3 in comparison with experimental data or prior MD simulations. Table 3.1 shows normalized relaxations between neighboring layers $(\Delta_{\alpha \alpha+1} = (w_{\alpha+1} - w_{\alpha})/d_0, \ \alpha = 1,2)$ at zero applied strain $(\mathbf{H} = 0)$. Due to lack of experimental data, results of Au, Pd and Pt are compared only with prior MD simulations based on similar EAM potentials [51]. 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 3.2 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 $(\tau_0)_{12}$ vanishes for all studied crystals, as implied by in-plane symmetry of the free surface. The surface elastic stiffness tensor is shown in Table 3.3. 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 [53], $[\mathbf{C}_s]_{1111} = [\mathbf{C}_s]_{2222}, (\tau_0)_{11} = (\tau_0)_{22}$ are verified by our calculations.

Element	γ	γ^*	γ^{\star}	$(au_0)_{11}$	$(au_0)_{11}^*$	$(au_0)_{22}$	$(au_0)^*_{22}$	$(au_0)_{12}$	$(au_0)_{12}^*$
Cu	1.15	1.24	$1.49^{[54]}$	-0.33	0.55	-0.33	0.55	0.00	0.00
Ag	0.80	0.80	$1.20^{[55]}$	0.10	0.65	0.10	0.65	0.00	0.00
Au	0.70	0.70	$1.18^{[55]}$	0.94	1.64	0.94	1.64	0.00	0.00
Ni	1.47	1.43	$1.94^{[55]}$	-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 ^[55]	1.32	2.54	1.31	2.54	0.00	0.00

Table 3.2: Surface tension γ , residual surface stress $(\tau_0)_{\alpha\beta}$ for (111) surfaces of FCC metals with Johnson EAM potentials [1]. Results are compared with prior MD simulations (*, Shenoy, 2005[2]) and experimental data (*). All entries are in J/m^2 .

Element	$(C_s)_{1111}$	$(\mathbf{C}_{s})_{1111}^{*}$	$(C_s)_{2222}$	$(C_s)_{2222}^*$	$(C_s)_{1212}$	$(\mathbf{C}_{s})_{1212}^{*}$
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

Table 3.3: Surface elastic stiffness tensor $(\mathbf{C}_s)_{\alpha\beta\alpha'\beta'}$ for (111) surfaces of FCC metals with Johnson EAM potentials [1]. Results are compared with prior MD simulations results (*, Shenoy, 2005[2]). All entries are in J/m^2 .

Chapter 4 Application: equilibrium shape of crystals

In order to understand the microscopic crystal structures, the equilibrium shape of crystal is a topic which has drawn lots of interest for more than a century. It not only provides evidences in fundamental studies of nano-structure properties, but also gives guidance in fabricating nano-materials. In this chapter we study the equilibrium shape with Wulff construction, which is a classic and most widely used theorem in characterizing crystal shapes. In order to perform the Wulff Construction on a given material, one needs to first find the surface tension for surfaces of all directions in 3D-space. Since experimental data of surface tension is limited to low index directions, determining the equilibrium shape is usually carried out by MD simulations. However, with help of the algorithm developed in Chapter. 3 we find a more efficient numerical way. Below in the first section we introduce the Wulff construction and the standard procedure of doing so. In the second section we first numerically calculate the surface tensions for various directions by solely solving the *algebraic Riccati equation* (3.32), and then perform the Wulff construction followed by detailed discussions.

4.1 The Wulff construction of crystals

The Wulff construction was proposed by Wulff [56] a century ago and later proved by Von Laue [57] and Dinghas [58]. It has also been verified by some experimental results [59, 60, 61] later on. The Wulff construction has been extended to be applicable on a variety of crystal structures including free particles, particles attached to solid substrates [62], twinned particles [63], and recently alloys [64]. In addition to predicting the shape of stabilized crystals, the Wulff construction can also help to study the dynamic progress of facet growth in during nano particle synthesis [65], controlling the nanocrystal shapes in synthesis [66], understanding the adsorption progress [67], and so on. Besides, the crystal shape given by the Wulff construction is scale invariant, except for only a few case where some large strain effects are included [68, 69] or the effects of edge and corner atoms are taken into account [70, 71, 72]. However even in those particular scenarios the deviations are still relatively small. Therefore, in general the Wulff construction can potentially be applied to crystals of almost all length scales, which as well broadens the potential applications.

The Wulff's theorem is stated as follows:

Theorem 1. For a crystal $B \subset \mathbb{R}^d$ with fixed volume V, The equilibrium shape of the crystal \mathcal{W} is that which minimizes the value ΔG defined as

$$\Delta G = \int_{\mathbf{y} \in \partial B} \gamma(\mathbf{n}(\mathbf{y})) ds_{\mathbf{y}}, \tag{4.1}$$

where $\gamma(\mathbf{n})$ is the surface tension (cf. (2.3)), \mathbf{n} is the unit normal of ∂B at \mathbf{y} , $ds_{\mathbf{y}}$ is an element of area at \mathbf{y} . The solution \mathcal{W} of the minimization problem, the Wulff shape, is written as

$$\mathscr{W} = \bigcap_{\mathbf{n} \in S^{d-1}} \{ \mathbf{x} \in \mathbb{R}^d : \mathbf{x} \cdot \mathbf{n} \le \gamma(\mathbf{n}) \},$$
(4.2)

where S^{d-1} denotes the surface of the shape formed by $\gamma(\mathbf{n})$.

We remark that equation (4.2) describes the equilibrium shape of the crystal, while the actual domain occupied by the equilibrium crystal can be obtained by a shift of the corresponding dilatation:

$$\mathscr{W}_V := rac{V^{rac{1}{d}}}{|\mathscr{W}|^{rac{1}{d}}} \mathscr{W}.$$

In practice for a 3-D case, the key step to perform Wulff construction is to find the surface tension $\gamma(\mathbf{n})$ for all directions **n** in space so that they form a 3-D shape with

$$\Gamma_{\gamma} = \{ \mathbf{x} : \mathbf{x} = \gamma(\mathbf{n})\mathbf{n}, \quad \forall \ |\mathbf{n}| = 1 \ \& \ \mathbf{n} \in \mathbb{R}^3 \}.$$



Figure 4.1: A 2-D Wulff construction

being its surface. By drawing planes passing trough **x** with unit normal **n** for all $\mathbf{x} \in \Gamma_{\gamma}$, the equilibrium shape of crystal is the domain bounded by all such planes. The reader is also referred to Figure 4.1 for a simple 2*D* example of Wulff construction.

4.2 **Results and discussions**

With the help of the algorithm determining surface elasticity parameters provided in Chapter 3, we develop a numerical method (see Appendix A) to quickly calculate the surface tension of various directions by only solving the *algebraic Riccati equation* (3.32), which can be order of magnitudes more efficient than a full-scale MD simulation.

As an example, Figure 4.2 shows the calculated surface tensions of Au with directions in (110) plane. The calculation agrees very well with prior MD simulations. Both our calculation and MD simulation agree that the surface tension γ in (111) direction is a global minimizer. In addition to the (111) direction, we find that surface tensions of (110) and (001) orientations are local minimizers, which is also verified by the Wulff


Figure 4.2: Surface tension of Au of directions in (1,1,0) plane compared with MD simulations (× [3], \cdot [4])

construction of Au below. Figure 4.3 shows the Wulff construction of gold. The equilibrium shape consists of the corresponding surfaces of the three local minimizers, and our figure is in good agreement with previous studies of FCC crystals. Also from the equilibrium shape we see that the largest areas are those of (111) surfaces, while the smallest area are those of (110) surfaces. This is physically reasonable because (111) surfaces have smallest surface tension so that in order to minimize the surface energy it is favorable in most of other directions, and vice versa.



Figure 4.3: Wulff construction of Au Crystals

Chapter 5

Application: wave propagations at the material surface/interface

The study of wave propagation at material surfaces and interfaces dates back to a century ago. For homogeneous media, Lord Rayleigh (1885) [73] first derived the wave speed for free surface wave, and later Stoneley (1924) [74] gave the analytic expression for interfacial waves. In both cases the wave speeds are constants for given material properties, i.e., the dispersion relation is linear. Recently, it is believed that in inhomogeneous media the dispersion relation becomes nonlinear [75]. In this chapter we find such effect of inhomogeneity is not limited to bulk elastic properties, but also appears in inhomogeneity between bulk and surface/interface (when the surface/interface is considered to be elastic). Since the definition of surface can also be extended to ultrathin membranes or structures that one of the dimensions is much smaller than the other two, this fundamental study is expected to have many applications in both research and practice. In the following we start with a numerical example for surface waves in an inhomogeneous half-space without considering surface elasticity. In the second section we show that when surface elasticity is included, the dispersion relation becomes nonlinear even though both the bulk and the interface are assumed to be homogeneous. Finally we discuss the impact of surface elasticity on reflection and refraction of bulk waves.



Figure 5.1: A two-material periodic half-space in the numerical example

5.1 Numerical example: free surface wave in periodic inhomogeneous half-space

As an example, by finite element method we numerically calculate the dispersion relation of the surface waves in an elastic half-space and demonstrate the existence of band gaps, which has been pointed out by Djafari-Rouhani et al. [76] based on the Fourier analysis. The half-space consists of alternating slabs of two materials as shown in Figure 5.1. The periodic half-space consists of alternating slabs of two materials. The slabs are perpendicular to the surface Γ_0 and the period in e_1 -direction is one. We further assume that the slabs are either made of copper (isotropic, Young's modulus $E_{Cu} = 115Gpa$, Poisson's ratio $v_{Cu} = 0.355$, Density $\rho_{Cu} = 8.92g/cm^3$) or aluminum (isotropic, Young's modulus $E_{Al} = 69Gpa$, Poisson's ratio $v_{Al} = 0.334$, Density $\rho_{Al} = 2.7g/cm^3$). We are interested in the dispersion relations of surface waves propagating in e_1 -direction.

In numerical simulations we consider a truncated finite two dimensional tube $T_{truc} = (0,1) \times (0,10)$. For a given wave number $t_1 \in (0,2\pi)$, by the standard finite element

method we find the eigenfrequencies ω such that

$$\begin{cases} -\operatorname{div}(\mathbf{C}(x_1, x_2)\nabla\mathbf{u}(x_1, x_2)) = \boldsymbol{\omega}^2 \boldsymbol{\rho}(x_1, x_2)\mathbf{u}(x_1, x_2) & \text{on } T_{truc} \\ (\mathbf{C}(x_1, x_2)\mathbf{u}(x_1, x_2))\mathbf{e}_2 = 0 & \text{if } x_2 = 0, \\ \mathbf{u} = 0 & \text{if } x_2 = 10, \\ \mathbf{u}(1, x_2) = \mathbf{u}(0, x_2)\exp(-it_1) & \forall x_2 \in (0, 10), \end{cases}$$
(5.1)

admits a nontrivial solution, where $\mathbf{u}(x_1, x_2)$ is the displacement vector. Here, $\mathbf{C}(x_1, x_2)$ $(\boldsymbol{\rho}(x_1, x_2))$ takes the value of the bulk stiffness tensor (density) of copper if $x_1 \in (0, \theta)$ and the elasticity tensor (density) of aluminum if $x_1 \in (\theta, 1)$. From the spectrum theory, we see that the above eigenvalue problem in general has infinite many eigenfrequencies, including those do not correspond to surface waves. To eliminate these eigenfrequencies, we use the criterion

$$U_b \ge 5U_t \tag{5.2}$$

where $U_b(U_t)$ is the strain energy in bottom (top) half of the T_{truc} , i.e., $(0,1) \times (0,5)$ $((0,1) \times (5,10))$. Upon eliminating the eigenfrequencies violating (5.2), we are left with eigenfrequencies $\omega_1(t_1) < \omega_2(t_1) < \omega_3(t_1) < \cdots$, which are presumably eigenfrequencies of surface waves in different bands. We hereby obtain the dispersion relation of the surface wave (Fig. 5.2). From the dispersion relation we see the band gaps appear when the wave number $k = n\pi$, $(n \in \mathbb{Z})$. We also compare the dispersion relation of the surface waves with that of the bulk waves propagating in the \mathbf{e}_1 direction. The results are shown in Figure 5.3, where the solid line "—" shows that of the surface wave and the cross signs "×" are data points from the simulations.

From Figure 5.3, we observe a few interesting features of the dispersion curves. First, band gaps are present for both curves. Also, the bulk waves has a higher frequency than the surface waves for the same wave number. These features of the dispersion curves provide a potential method to manipulate elastic waves. For example, for excitations at frequencies at the band gaps of the bulk waves, surface waves are preferably excited and propagate along the free surface, instead of radiating into the half-space, whereas excitations at frequencies at the band gaps of surface waves tend to propagate into the half-space instead of along the surface. Also, at the long wave-length limit, i.e., $t_1 \rightarrow 0$, it is anticipated the dispersion relation should be predicted by the homogenization theory. Indeed we numerically verify that the phase speed of the surface waves coincides with the surface waves of a homogeneous half-space with the effective elasticity tensor and the effective density. However, we are not aware of a rigorous proof of this fact for surface waves, though the homogenization theory has been well established for bulk waves in the long wave length limit (see, e.g., [77, 78])



Figure 5.2: Dispersion relation of surface wave in two-material periodic half space. Without loss of generality, two materials are set as aluminum and copper. Their material constants are as follows: $E_{Al} = 69Gpa$, $E_{Cu} = 115Gpa$, $v_{Al} = 0.334$, $v_{Cu} = 0.355$, $\rho_{Al} = 2.7g/cm^3$, $\rho_{Cu} = 8.92g/cm^3$



Figure 5.3: Dispersion relations of the bulk waves and surface waves propagating in \mathbf{e}_1 -direction. The dashed curve "--" shows the dispersion curve of the bulk waves; the solid line "--" shows that of the surface wave. The cross signs "×" denote the data points from the simulation

5.2 Interfacial waves with surface elasticity

5.2.1 Introduction

Interfacial waves refer to localized wave modes that propagate along the interface of two materials and decay away from the interface. The dispersion relations of interfacial waves are important for probing material properties and designing wave guides for a number of applications. For two isotropic elastic materials, Stoneley [74] first derived explicit solutions of interfacial waves that are subsequently named as *Stoneley waves*. Barnett *et al.* [79] explored interfacial waves between general anisotropic solids and found sufficient conditions for the existence and uniqueness of *subsonic* interfacial waves in terms of surface impedance tensor.

At the advent of modern nanotechnology, it is widely speculated that elastic energy associated with a surface, or surface elasticity, will play an important role in determining the size-dependent behaviors at the length scale of submicron and below[43, 80].

A widely used model of surface elasticity has been established by Gurtin and Murdoch [27, 81] (cf. (2.3)). For a homogeneous continuum body the above surface elastic energy may be regarded as the next order of approximation of total internal energy beyond the bulk elastic energy. This is to some extent justified from the fundamental atomistic models in [82] and the elastic properties of surface have been calculated according to this viewpoint [2, 31]. From this standing point, it is anticipated that surface elasticity is particularly important for small bodies.

Surface elasticity may emerge from other considerations. First of all, as noticed in [83], an elastic surface may arise solely from the roughness of surfaces/interfaces and bulk elasticity even if the pristine flat surface is assumed to be free of surface elasticity. Also, for some heterogeneous structures, e.g., a sandwich structure with soft thick core and stiff thin face plates [84], the overall structure may be well modeled by a single elastic body with elastic surfaces. For these problems, it is worth noticing that the significance of "surface elasticity" prevails at all length scales instead of being limited to small bodies, which, consequently, broadens the applications of the model of surface elasticity and the results presented in this paper.

The ramifications of surface elasticity have been examined in several contexts, e.g., the *effective* bulk stress-strain relation due to nano-inclusions [43, 44], the sensing and vibration of nano-beams and plates [80, 85], wave in thin film attached on substrate [86], and the free surface waves [87]. The interested reader is also referred to [88] for a generalization of surface elasticity incorporating curvature dependence of energy, [45] for further clarification of the formulation, and [89] for a mathematical proof of existence and uniqueness theorem of boundary value problems with surface elasticity.

In this section we study interfacial waves at the presence of surface elasticity. Since the energy of interfacial waves concentrates around the interface, we anticipate surface elasticity may have a significant effect on the dispersion relation of interfacial waves. In addition, it is of fundamental interest to prove whether an interfacial wave exists, and if so, is unique for a given frequency. These problems will be addressed by techniques



Figure 5.4: An elastic interface between two half spaces.

developed in the study of classic free surface waves and interfacial waves in the absence of surface elasticity [73, 74, 90, 91]. In particular, we obtain a similar existence and uniqueness theorem for *subsonic* interfacial waves between general anisotropic solids and interfaces. In addition, we explicitly calculate the dispersion relations of interfacial waves at the presence of surface elasticity for isotropic materials. A critical observation lies in that the interfacial wave is now dispersive and depends on the surface elastic properties. This distinguishing characteristics may be used to probe both the bulk and surface properties by acoustic measurements [92, 93, 94, 95]. Further, upon specializing the bulk properties to various limits, the results of this paper can recover the classic interfacial waves in the absence of surface elasticity and be used to calculate the interfacial waves between fluid and solid.

5.2.2 Problem formulation

Consider an infinite elastic medium with an interface $\Gamma = \{(x_1, x_2, x_3) : x_3 = 0\}$ between two half spaces: $\Omega_1 = \{(x_1, x_2, x_3) | x_3 > 0\}$ and $\Omega_2 = \{(x_1, x_2, x_3) | x_3 < 0\}$ (see Fig. 5.4). The bulk elastic properties of the two half spaces are described by the *bulk* stiffness tensors:

$$\mathbf{C}(\mathbf{x}) = \mathbf{C}_{\boldsymbol{\alpha}}$$
 if $\mathbf{x} \in \Omega_{\boldsymbol{\alpha}}, \ \boldsymbol{\alpha} = 1, 2,$

where the fourth-order tensor C_{α} ($\alpha = 1, 2$) satisfies the usual major and minor symmetries:

$$(\mathbf{C}_{\alpha})_{piqj} = (\mathbf{C}_{\alpha})_{pijq} = (\mathbf{C}_{\alpha})_{qjpi}$$
(5.3)

and the convexity condition:

$$\mathbf{A} \cdot \mathbf{C}_{\alpha} \mathbf{A} > 0, \quad \forall 0 \neq \mathbf{A} \in \mathbb{R}^{3 \times 3}_{\text{sym}}.$$
(5.4)

To account for the elastic effects of the interface Γ , we model the interface as an elastic massless membrane bonded with the two half spaces without slip. Starting from the postulation (2.1) and following the paradigm of classic nonlinear elasticity, upon linearization one can show that the above postulation implies the following *surface stress-strain relation*:

$$\boldsymbol{\sigma}_s = \mathbf{C}_s \nabla \mathbf{u} + \boldsymbol{\sigma}_s^0, \tag{5.5}$$

where $\mathbf{C}_s : \mathbb{R}^{3 \times 3} \to \mathbb{R}^{3 \times 3}$ is the fourth-order surface stiffness tensor satisfying the similar major and minor symmetries in (5.3) as a bulk stiffness tensor, **u** is the displacement, and σ_s^0 is the residual surface stress. We remark that since interfaces are of two dimensions, the surface elastic energy shall depend only on the stretching within the interface. Therefore, surface strain, residual surface stress and surface elastic stiffness tensor "live only on the surface" in the sense that

$$oldsymbol{\sigma}_s, \ oldsymbol{\sigma}_s^0 \in \mathbb{M} \quad ext{ and } \quad \mathbf{C}_s \mathbf{M}^\perp = 0 \quad \forall \, \mathbf{M}^\perp \in \mathbb{M}^\perp,$$

where $\mathbb{M} = \{ \mathbf{M} \in \mathbb{R}^{3 \times 3} : \mathbf{Mn} = 0, \ \mathbf{M}^T \mathbf{n} = 0 \}$, **n** is the unit normal on the surface Γ , and $\mathbb{M}^{\perp} = \{ \mathbf{M}^{\perp} \in \mathbb{R}^{3 \times 3} : \mathbf{M}^{\perp} \cdot \mathbf{M} = 0, \ \forall \mathbf{M} \in \mathbb{M} \}.$

The elastodynamic equations for small deformation in the two bulk half spaces are standard and given by

$$\begin{cases} \operatorname{div}[\mathbf{C}_{1}\nabla\mathbf{u}(\mathbf{x},t)] = \rho_{1}\frac{\partial^{2}}{\partial t^{2}}\mathbf{u}(\mathbf{x},t) & \text{for } x_{3} > 0, \\ \operatorname{div}[\mathbf{C}_{2}\nabla\mathbf{u}(\mathbf{x},t)] = \rho_{2}\frac{\partial^{2}}{\partial t^{2}}\mathbf{u}(\mathbf{x},t) & \text{for } x_{3} < 0, \end{cases}$$
(5.6)

where ρ_{α} ($\alpha = 1,2$) denote the mass densities. Further, the balance of linear momentum for any subsurface on Γ implies

$$\operatorname{div}_{s}[\mathbf{C}_{s}\nabla\mathbf{u}(\mathbf{x},t)+\boldsymbol{\sigma}_{0}]+[\mathbf{C}_{1}\nabla\mathbf{u}(\mathbf{x}^{+},t)-\mathbf{C}_{2}\nabla\mathbf{u}(\mathbf{x}^{-},t)]\mathbf{e}_{3}=0\quad\text{for }\mathbf{x}\in\Gamma,\qquad(5.7)$$

where div_s denotes the surface divergence [27], and \mathbf{x}^+ (\mathbf{x}^-) denotes the boundary value approached from the top (bottom) of the interface. We remark that the above equation (5.7) can be regarded as the generalized Young-Laplace equation for the solid elastic surface Γ .

We define localized *interfacial waves* as solutions to (5.6) and (5.7) satisfying the boundary conditions:

$$\mathbf{u}(\mathbf{x},t) \to 0$$
 as $x_3 \to \pm \infty$. (5.8)

The presence of heterogeneity and the elastic interface Γ may give rise to interfacial waves that are important for interface characterization and the overall dynamic behaviors of the body. Below we explore the properties of interfacial waves propagating along interface between two half-spaces including the existence, uniqueness and dispersion relations of interfacial waves.

5.2.3 Existence and uniqueness of the interfacial waves

Without loss of generality we assume the wave propagates in e_1 -direction. By translational invariance we seek a solution to (5.6)-(5.7) that can be written as

$$\mathbf{u}(\mathbf{x},t) = \hat{\mathbf{u}}(kx_3)e^{i(kx_1 - \omega t)},\tag{5.9}$$

where $\hat{\mathbf{u}} : \mathbb{R} \to \mathbb{C}^3$ describes the mode shape along \mathbf{e}_3 -axis, k > 0 is the wave number along \mathbf{e}_1 -axis, and $\omega > 0$ is the frequency. Let $y = kx_3$. Inserting the above equation into (5.6) and (5.7) we obtain

$$\begin{cases} (\rho_1 v^2 \mathbf{I} - \mathbf{Q}_1) \hat{\mathbf{u}}(y) + i(\mathbf{R}_1 + (\mathbf{R}_1)^T) \hat{\mathbf{u}}'(y) + \mathbf{T}_1 \hat{\mathbf{u}}''(y) = 0 & \text{for } x_3 > 0, \\ (\rho_2 v^2 \mathbf{I} - \mathbf{Q}_2) \hat{\mathbf{u}}(y) + i(\mathbf{R}_2 + (\mathbf{R}_2)^T) \hat{\mathbf{u}}'(y) + \mathbf{T}_2 \hat{\mathbf{u}}''(y) = 0 & \text{for } x_3 < 0, \\ -k \mathbf{Q}_s \hat{\mathbf{u}}(0) + i(\mathbf{R}_1^T - \mathbf{R}_2^T) \hat{\mathbf{u}}(0) + \mathbf{T}_1 \hat{\mathbf{u}}'(0^+) - \mathbf{T}_2 \hat{\mathbf{u}}'(0^-) = 0, \end{cases}$$
(5.10)

where $v = \omega/k$ is the wave speed, ()' = $\frac{d}{dy}$, and ($\alpha = 1, 2$)

$$(\mathbf{R}_{\alpha})_{pq} = (\mathbf{C}_{\alpha})_{p1q3}, \quad (\mathbf{T}_{\alpha})_{pq} = (\mathbf{C}_{\alpha})_{p3q3},$$
$$(\mathbf{Q}_{\alpha})_{pq} = (\mathbf{C}_{\alpha})_{p1q1}, \quad (\mathbf{Q}_{s})_{pq} = (\mathbf{C}_{s})_{p1q1}.$$

From symmetry condition (5.3) and convexity condition (5.4), it is clear that \mathbf{Q}_{α} , \mathbf{T}_{α} , and \mathbf{Q}_s are all 3 × 3 symmetric matrices and that \mathbf{Q}_{α} and \mathbf{T}_{α} are all positive definite and invertible for $\alpha = 1, 2$. By the theory of ordinary differential equations [96], a general solution to (5.10)_{1,2} is given by

$$\hat{\mathbf{u}}(kx_3) = \begin{cases} e^{-x_3 k \mathbf{E}_1} \hat{\mathbf{u}}_1 & \text{for } x_3 > 0, \\ e^{x_3 k \mathbf{E}_2} \hat{\mathbf{u}}_2 & \text{for } x_3 < 0 \end{cases}$$
(5.11)

for some $\mathbf{E}_1, \mathbf{E}_2 \in \mathbb{C}^{3 \times 3}$ and vector $\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2 \in \mathbb{C}^3$. From the displacement continuity at $x_3 = 0$, we clearly have $\hat{\mathbf{u}}_1 = \hat{\mathbf{u}}_2$. To satisfy $(5.10)_{1,2}$, it is sufficient to have

$$\begin{cases} \mathbf{T}_{1}\mathbf{E}_{1}^{2} - i[\mathbf{R}_{1} + (\mathbf{R}_{1})^{T})]\mathbf{E}_{1} + \rho_{1}v^{2}\mathbf{I} - \mathbf{Q}_{1} = 0, \\ \mathbf{T}_{2}\mathbf{E}_{2}^{2} + i[\mathbf{R}_{2} + (\mathbf{R}_{2})^{T})]\mathbf{E}_{2} + \rho_{2}v^{2}\mathbf{I} - \mathbf{Q}_{2} = 0. \end{cases}$$
(5.12)

Moreover, by (5.11) equation $(5.10)_3$ can be rewritten as

$$[-k\mathbf{Q}_s + i(\mathbf{R}_1^T - \mathbf{R}_2^T) - (\mathbf{T}_1\mathbf{E}_1 + \mathbf{T}_2\mathbf{E}_2)]\hat{\mathbf{u}}_1 = 0.$$
(5.13)

Further, in account of (5.8) we shall require that

$$\operatorname{eig}(\mathbf{E}_1), \operatorname{eig}(\mathbf{E}_2) \subset \mathbb{C}_+, \tag{5.14}$$

where $eig(\cdot)$ denotes the set of eigenvalues, and \mathbb{C}_+ is the set of all complex numbers with positive real parts.

We remark that equations in (5.12) can be identified as *algebraic Riccati equations*. To solve for \mathbf{E}_{α} , we assume that $\lambda_{\alpha} \in \mathbb{C}$ and $\mathbf{a}_{\alpha} \in \mathbb{C}^{3}$ are a pair of eigenvalue and eigenvector of \mathbf{E}_{α} :

$$\mathbf{E}_{\alpha}\mathbf{a}_{\alpha} = \lambda_{\alpha}\mathbf{a}_{\alpha}, \qquad \mathbf{a}_{\alpha} \neq 0$$

Operating the left hand sides of (5.12) on the eigenvector **a** we find that

$$[\mathbf{T}_{\alpha}\lambda_{\alpha}^{2} + (-1)^{\alpha}i(\mathbf{R}_{\alpha} + \mathbf{R}_{\alpha}^{T})\lambda_{\alpha} + \rho v^{2}\mathbf{I} - \mathbf{Q}_{\alpha}]\mathbf{a}_{\alpha} = 0.$$
(5.15)

Taking complex conjugate of (5.15), we observe that if $(\lambda_{\alpha}, \mathbf{a}_{\alpha})$ satisfy (5.15), so do $(-\bar{\lambda}_{\alpha}, \bar{\mathbf{a}}_{\alpha})$.

The above equation (5.15) can be identified as a generalized eigenvalue-eigenvector problem. Clearly, the eigenvalues λ_{α} can be determined as the roots of the polynomial:

$$P_{\alpha}(\lambda, \nu) := \det[\mathbf{T}_{\alpha}\lambda^{2} + (-1)^{\alpha}i(\mathbf{R}_{\alpha} + \mathbf{R}_{\alpha}^{T})\lambda + \rho\nu^{2}\mathbf{I} - \mathbf{Q}_{\alpha}]$$
(5.16)

whereas the associated eigenvectors \mathbf{a}_{α} can be obtained as nonzero solutions to (5.15). In a generic case, we shall be able to find six eigenvalue-eigenvector pairs $(\lambda_{\alpha}^{i}, \mathbf{a}_{\alpha}^{i})$ $(i = 1, \dots, 6)$ for a given v > 0. Let $\mathbf{A}_{\alpha} = [\mathbf{a}_{\alpha}^{i_{1}}; \mathbf{a}_{\alpha}^{i_{2}}; \mathbf{a}_{\alpha}^{i_{3}}] \in \mathbb{C}^{3 \times 3}$ be the matrix formed by three of the (column) eigenvectors and $\mathbf{D}_{\alpha} = \text{diag}[\lambda_{\alpha}^{i_{1}}, \lambda_{\alpha}^{i_{2}}, \lambda_{\alpha}^{i_{3}}]$ be the diagonal matrix formed by the corresponding eigenvalues. If det $\mathbf{A}_{\alpha} \neq 0$, then a solution to (5.12)_{α} is given by

$$\mathbf{E}_{\alpha} = \mathbf{A}_{\alpha} \mathbf{D}_{\alpha} \mathbf{A}_{\alpha}^{-1}.$$

For interfacial waves, we shall focus on solutions to (5.12) that satisfy (5.14). Since the eigenvalues of (5.15) are symmetric about the imaginary axis, a solution $\mathbf{E}_{\alpha} \in \mathbb{C}^{3\times 3}$ to (5.12) satisfying (5.14) cannot be constructed by the above procedure if $P_{\alpha}(\lambda, v)$ has a pure imaginary solution. This motivates us to introduce the *limiting speed* [75]:

$$\hat{v}_{\alpha} := \inf\{v > 0 : P_{\alpha}(\lambda, v) \text{ has a pure imaginary root}\}$$

The reader is referred to [90] for a neat geometrical interpretation of the limiting speed \hat{v}_{α} on the slowness section on the plane spanned by $\{\mathbf{e}_1, \mathbf{e}_3\}$. Let

$$\hat{v} = \min\{\hat{v}_1, \hat{v}_2\}.$$

In analogy with free surface waves, we refer to interfacial waves as *subsonic* if the phase speed $v < \hat{v}$, and *supersonic* if otherwise. Following [91] and [97], it can be shown that if $0 \le v < \hat{v}$, both equations in (5.12) admit unique solutions $\mathbf{E}_{\alpha}(v)$ ($\alpha = 1,2$) satisfying (5.14). We can therefore define two new quantities

$$\begin{cases} \mathbf{M}_{1}(v) = \mathbf{T}_{1}\mathbf{E}_{1}(v) - i\mathbf{R}_{1}^{T}, \\ \mathbf{M}_{2}(v) = \mathbf{T}_{2}\mathbf{E}_{2}(v) + i\mathbf{R}_{2}^{T}, \end{cases}$$
(5.17)

which are known as *surface impedance matrices*. Replacing \mathbf{E}_{α} by \mathbf{M}_{α} in (5.12), we find that \mathbf{M}_{α} ($\alpha = 1, 2$) satisfy the standard algebraic Riccati equations:

$$\begin{cases} (\mathbf{M}_{1} - i\mathbf{R}_{1}^{T})\mathbf{T}_{1}^{-1}(\mathbf{M}_{1} + i\mathbf{R}_{1}^{T}) - \mathbf{Q}_{1} + \rho_{1}v^{2}\mathbf{I} = 0, \\ (\mathbf{M}_{2} + i\mathbf{R}_{2}^{T})\mathbf{T}_{2}^{-1}(\mathbf{M}_{2} - i\mathbf{R}_{2}^{T}) - \mathbf{Q}_{2} + \rho_{2}v^{2}\mathbf{I} = 0. \end{cases}$$
(5.18)

We define the *interface impedance matrix* as

$$\mathbf{Z}(v) = \mathbf{M}_1(v) + \mathbf{M}_2(v) + k\mathbf{Q}_s.$$
(5.19)

Then equation (5.13) admits a nonzero solution $\hat{\mathbf{u}}_1$ if and only if

$$\det \mathbf{Z}(v) = 0. \tag{5.20}$$

We now derive a few useful properties of the interface impedance matrix that follow from [91, 97].

Lemma 2. Assume that \mathbf{Q}_s is positive semi-definite. Then the interface impedance matrix $\mathbf{Z}(v)$ defined by (5.19) satisfies that

(*i*) $\mathbf{Z}(v)$ is Hermitian for $v \in (0, \hat{v})$;

- (ii) $\mathbf{Z}(0)$ is positive definite;
- (iii) $\frac{d}{dv}\mathbf{Z}(v)$ is negative definite for $v \in (0, \hat{v})$, i.e., every eigenvalue of $\mathbf{Z}(v)$ is monotonically decreasing as a function of v;
- (*iv*) $\mathbf{a} \cdot \mathbf{Z}(v) \mathbf{a} \ge 0$, $\forall \mathbf{a} \in \mathbb{R}^3 \text{ and } v \in (0, \hat{v})$.

Proof. To show (*i*) and (ii), following Fu & Mielke (2002) we define the following quantity for a trial $\mathbf{u}(\mathbf{x}, t)$ satisfying (5.9), (5.6) and (5.8):

$$\mathscr{P} = \frac{1}{2} \frac{k}{2\pi} \int_0^{2\pi/k} (-(\mathbf{C}_1)_{p3qj} u_{q,j} \bar{u}_p + (\mathbf{C}_2)_{p3qj} u_{q,j} \bar{u}_p + ((\mathbf{C}_s)_{piqj} u_{q,j} + (\boldsymbol{\sigma}_s^0)_{pi}) \bar{u}_{p,i}) \mathrm{d}x_1.$$

From (5.9) and (5.8) it is clear that \mathscr{P} can be rewritten as

$$\mathcal{P} = \frac{k}{4\pi} \left[\int_{\partial T_1} (\mathbf{C}_1)_{piqj} u_{q,j} n_i \bar{u}_p dS + \int_{\partial T_2} (\mathbf{C}_2)_{piqj} u_{q,j} n_i \bar{u}_p dS \right] + \frac{k}{4\pi} \int_0^{2\pi/k} \left[(\mathbf{C}_s)_{piqj} u_{q,j} + (\boldsymbol{\sigma}_s^0)_{pi}) \bar{u}_{p,i} dx_1 \right],$$
(5.21)

where ∂T_1 and ∂T_2 are the boundary of the semi-infinite tubes $T_1 = \{(x_1, x_2, x_3) | 0 < x_1 < 2\pi/k, 0 < x_2 < 1, x_3 > 0\}$ and $T_2 = \{(x_1, x_2, x_3) | 0 < x_1 < 2\pi/k, 0 < x_2 < 1, x_3 < 0\}$, respectively, and **n** represents the unit outward normal of ∂T_1 and ∂T_2 . By (5.6), (5.9), (5.11) and the divergence theorem, \mathscr{P} can be further expressed as

$$\mathscr{P} = \frac{k}{4\pi} \left\{ \int_0^\infty \int_0^{2\pi/k} P_1 dx_1 dx_3 + \int_{-\infty}^0 \int_0^{2\pi/k} P_2 dx_1 dx_3 + \int_0^{2\pi/k} \left[(\mathbf{C}_s)_{piqj} u_{q,j} + (\boldsymbol{\sigma}_s^0)_{pi} \right] \bar{u}_{p,i} dx_1 \right\},$$
(5.22)

where

$$P_{\alpha} = (\mathbf{C}_{\alpha})_{piqj} u_{q,j} \bar{u}_{p,i} + \rho_{\alpha} \ddot{u}_{i} \bar{u}_{i}$$

$$= (\mathbf{Q}_{\alpha})_{pq} u_{q,1} \bar{u}_{p,1} + (\mathbf{R}_{\alpha})_{qp} u_{q,1} \bar{u}_{p,3} + (\mathbf{R}_{\alpha})_{pq} u_{q,3} \bar{u}_{p,1}$$

$$+ (\mathbf{T}_{\alpha})_{pq} u_{p,3} \bar{u}_{q,3} - \rho_{\alpha} v^{2} u_{i} \bar{u}_{i}$$

$$= k^{2} (\hat{\mathbf{u}} \cdot \mathbf{Q}_{\alpha} \hat{\mathbf{u}} + \hat{\mathbf{u}}' \cdot i \mathbf{R}_{\alpha}^{T} \hat{\mathbf{u}} - \hat{\mathbf{u}} \cdot i \mathbf{R}_{\alpha} \hat{\mathbf{u}}' + \hat{\mathbf{u}}' \cdot \mathbf{T}_{\alpha} \hat{\mathbf{u}}' - \rho_{\alpha} v^{2} \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}).$$
(5.23)

Noticing that P_{α} are independent of x_1 , we have

$$\mathcal{P} = \frac{1}{2}k \int_0^\infty (\hat{\mathbf{u}} \cdot \mathbf{Q}_1 \hat{\mathbf{u}} + \hat{\mathbf{u}}' \cdot i\mathbf{R}_1^T \hat{\mathbf{u}} - \hat{\mathbf{u}} \cdot i\mathbf{R}_1 \hat{\mathbf{u}}' + \hat{\mathbf{u}}' \cdot \mathbf{T}_1 \hat{\mathbf{u}}' - \rho_1 v^2 \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}) dy + \frac{1}{2}k \int_{-\infty}^0 (\hat{\mathbf{u}} \cdot \mathbf{Q}_2 \hat{\mathbf{u}} + \hat{\mathbf{u}}' \cdot i\mathbf{R}_2^T \hat{\mathbf{u}} - \hat{\mathbf{u}} \cdot i\mathbf{R}_2 \hat{\mathbf{u}}' + \hat{\mathbf{u}}' \cdot \mathbf{T}_2 \hat{\mathbf{u}}' - \rho_2 v^2 \hat{\mathbf{u}} \cdot \hat{\mathbf{u}}) dy$$
(5.24)
+ $\frac{1}{2}k^2 \hat{\mathbf{u}}_0 \cdot \mathbf{Q}_s \hat{\mathbf{u}}_0,$

where $\hat{\mathbf{u}}_0 = \hat{\mathbf{u}}(0)$. Integrating by parts we have

•

$$\int_0^\infty [\hat{\mathbf{u}}' \cdot i\mathbf{R}_1^T \hat{\mathbf{u}} + \hat{\mathbf{u}}' \cdot \mathbf{T}_1 \hat{\mathbf{u}}'] dy = \hat{\mathbf{u}} \cdot (i\mathbf{R}_1^T \hat{\mathbf{u}} + \mathbf{T}_1 \hat{\mathbf{u}}') \Big|_0^\infty - \int_0^\infty \hat{\mathbf{u}} \cdot (i\mathbf{R}_1^T \hat{\mathbf{u}}' + \mathbf{T}_1 \hat{\mathbf{u}}'') dy$$
$$\int_{-\infty}^0 [\hat{\mathbf{u}}' \cdot i\mathbf{R}_2^T \hat{\mathbf{u}} + \hat{\mathbf{u}}' \cdot \mathbf{T}_2 \hat{\mathbf{u}}'] dy = \hat{\mathbf{u}} \cdot (i\mathbf{R}_2^T \hat{\mathbf{u}} + \mathbf{T}_2 \hat{\mathbf{u}}') \Big|_{-\infty}^0 - \int_{-\infty}^0 \hat{\mathbf{u}} \cdot (i\mathbf{R}_2^T \hat{\mathbf{u}}' + \mathbf{T}_2 \hat{\mathbf{u}}'') dy$$

Inserting the above equations into (5.24), by (5.10) and (5.11) we obtain

$$\mathcal{P}(v, \hat{\mathbf{u}}_{0}) = \frac{1}{2}k\hat{\mathbf{u}} \cdot (\mathbf{T}_{1}\hat{\mathbf{u}}' + i\mathbf{R}_{1}^{T}\hat{\mathbf{u}})\Big|_{0}^{\infty} + \frac{1}{2}k\hat{\mathbf{u}} \cdot (\mathbf{T}_{2}\hat{\mathbf{u}}' + i\mathbf{R}_{2}^{T}\hat{\mathbf{u}})\Big|_{-\infty}^{0} + \frac{1}{2}k^{2}\hat{\mathbf{u}}_{0} \cdot \mathbf{Q}_{s}\hat{\mathbf{u}}_{0}$$
$$= \frac{1}{2}k\hat{\mathbf{u}}_{0} \cdot [(\mathbf{T}_{1}\mathbf{E}_{1} - i\mathbf{R}_{1}^{T}) + (\mathbf{T}_{2}\mathbf{E}_{2} + i\mathbf{R}_{2}^{T}) + k\mathbf{Q}_{s}]\hat{\mathbf{u}}_{0}$$
$$= \frac{1}{2}k\hat{\mathbf{u}}_{0} \cdot (\mathbf{M}_{1} + \mathbf{M}_{2} + k\mathbf{Q}_{s})\hat{\mathbf{u}}_{0}$$
$$= \frac{1}{2}k\hat{\mathbf{u}}_{0} \cdot \mathbf{Z}(v)\hat{\mathbf{u}}_{0}.$$
(5.25)

From (5.22), we see that \mathscr{P} is always real, and hence $\mathbf{Z}(v)$ is hermitian. In addition, differentiating both (5.24) and (5.25) with respect to *v* we have

$$\hat{\mathbf{u}}_0 \cdot \frac{\mathrm{d}\mathbf{Z}(v)}{\mathrm{d}v} \hat{\mathbf{u}}_0 = -2\rho_1 v \int_0^\infty \hat{\mathbf{u}} \cdot \hat{\mathbf{u}} \mathrm{d}y - 2\rho_2 v \int_{-\infty}^0 \hat{\mathbf{u}} \cdot \hat{\mathbf{u}} \mathrm{d}y < 0$$

Therefore, $\frac{d\mathbf{Z}(v)}{dv}$ is negative definite, meaning all eigenvalues of $\mathbf{Z}(v)$ are monotonically decreasing functions of v in $(0, \hat{v})$.

Further, if v = 0, i.e., $\omega = 0$, by (5.22) and (5.23) we recognize \mathscr{P} as the strain energy (density) of the displacement defined by (5.9) and (5.11). The solid being statically stable requires that

$$\mathscr{P}(0, \hat{\mathbf{u}}_0) > 0 \qquad \forall \ \hat{\mathbf{u}}_0 \in \mathbb{C}^3 \text{ with } |\hat{\mathbf{u}}_0| = 1.$$
(5.26)

Due to property (ii) and (iii), the existence of an interfacial wave with phase speed $v_0 < \hat{v}$ satisfying (5.20) requires that $\mathbf{Z}(\hat{v}-)$ has at least one negative eigenvalue. In addition, the matrix $\mathbf{Z}(\hat{v}-)$ can have at most one negative eigenvalue since one could always find a vector $\mathbf{a} \in \mathbb{R}^3$ violating property (iv) if otherwise [91]. So in order for the interfacial wave to exist, eigenvalues of $\mathbf{Z}(\hat{v}-)$ should meet either of these two situations: (1) two positive and a negative eigenvalues; (2) one positive, one negative and one zero eigenvalues. In conclusion, we have the following existence theorem for subsonic interfacial waves:

Theorem 3. Assume that the matrix \mathbf{Q}_s is positive semi-definite. If det $\mathbf{Z}(\hat{v}-) < 0$ or $(tr \mathbf{Z}(\hat{v}-))^2 - tr \mathbf{Z}^2(\hat{v}-) < 0$, there exist a unique subsonic interfacial wave. The phase speed $v = \omega/k \in (0, \hat{v})$ is determined by

$$\det \mathbf{Z}(v) = 0$$

We remark that the positive semi-definiteness of \mathbf{Q}_s in the above theorem is a strong assumption. In fact, the above theorem stands as long as \mathbf{Q}_s is such that $\mathbf{Z}(0)$ is positive definite. Therefore, the subsonic interfacial wave is unique for small k since $\mathbf{M}_1(0)$ and $\mathbf{M}_2(0)$ are both positive definite [97].

5.2.4 Explicit solutions of the interfacial waves

An explicit solution (if exist) can be found when the interfacial wave is polarized in a symmetry plane (x_1 - x_3 plane say) of both solids. A trial solution for this problem can be written as

$$\mathbf{u}(x_1, x_3, t) = \begin{cases} \hat{\mathbf{u}}_1 \exp(-ikp_1 x_3) \exp(ikx_1 - \omega t) & \text{for } x_3 > 0, \\ \hat{\mathbf{u}}_2 \exp(ikp_2 x_3) \exp(ikx_1 - \omega t) & \text{for } x_3 < 0. \end{cases}$$

Inserting the above trial solution into (5.6) one can find a quartic equation for p_{α} ($\alpha = 1$ or 2). For each half-space two pairs of complex conjugate solutions can be found from the quartic equation. Destrade and Fu [98] have obtained analytic solutions of the

quartic equations in terms of v and implemented a numerical method for calculating the interfacial wave speed from the condition at the interface without surface elasticity.

In particular, if both half-spaces are isotropic, by symmetry we observe that $\hat{\mathbf{u}}_1 \cdot \mathbf{e}_2 = \hat{\mathbf{u}}_2 \cdot \mathbf{e}_2 = 0$, and subsequently, omit components associated with \mathbf{e}_2 -direction in matrices of (5.12) and (5.13). Removing trivial components associated \mathbf{e}_2 -direction and with an abuse of notation, we find the material tensors defined by (5.11) as

$$\mathbf{Q}_{\alpha} = \begin{bmatrix} 2\mu_{\alpha} + \lambda_{\alpha} & 0\\ 0 & \mu_{\alpha} \end{bmatrix}, \quad \mathbf{R}_{\alpha} = \begin{bmatrix} 0 & \lambda_{\alpha}\\ \mu_{\alpha} & 0 \end{bmatrix},$$
$$\mathbf{T}_{\alpha} = \begin{bmatrix} \mu_{\alpha} & 0\\ 0 & 2\mu_{\alpha} + \lambda_{\alpha} \end{bmatrix}, \quad \mathbf{Q}_{s} = \begin{bmatrix} Q_{s} & 0\\ 0 & 0 \end{bmatrix},$$
(5.27)

where $Q_s = (\mathbf{Q}_s)_{11} = (\mathbf{C}_s)_{1111}$ is the surface elastic modulus. Since the surface impedance matrices are Hermitian, we can write them as

$$\mathbf{M}_{1} = \begin{bmatrix} {}^{1}m_{1} & {}^{1}m_{3} + i \, {}^{1}m_{4} \\ {}^{1}m_{3} - i \, {}^{1}m_{4} & {}^{1}m_{2} \end{bmatrix},$$

$$\mathbf{M}_{2} = \begin{bmatrix} {}^{2}m_{1} & {}^{2}m_{3} - i \, {}^{2}m_{4} \\ {}^{2}m_{3} + i \, {}^{2}m_{4} & {}^{2}m_{2} \end{bmatrix},$$
(5.28)

where $\alpha m_j (\alpha = 1, 2; j = 1, \dots, 4) \in \mathbb{R}$. Solving (5.18) for \mathbf{M}_{α} , we find that [97]

$$^{lpha}m_1 = \sqrt{\mu_{lpha}(2\mu_{lpha} + \lambda_{lpha} -
ho_{lpha}v^2) - rac{\mu_{lpha}}{2\mu_{lpha} + \lambda_{lpha}}(rac{\lambda_{lpha} + \mu_{lpha}}{1 + \gamma_{lpha}})^2,} \ ^{lpha}m_2 = \gamma_{lpha}rac{2\mu_{lpha} + \lambda_{lpha}}{\mu_{lpha}} m_1, \quad ^{lpha}m_3 = 0, \quad ^{lpha}m_4 = rac{\gamma_{lpha}\lambda_{lpha} - \mu_{lpha}}{1 + \gamma_{lpha}},$$

where

$$\gamma_{\alpha} = \sqrt{rac{\mu_{lpha}(\mu_{lpha} -
ho_{lpha}v^2)}{(2\mu_{lpha} + \lambda_{lpha})(2\mu_{lpha} + \lambda_{lpha} -
ho_{lpha}v^2)}}, \qquad lpha = 1,2$$

Then equation (5.20) implies that

$$({}^{1}m_{1} + {}^{2}m_{1} + kQ_{s})({}^{1}m_{2} + {}^{2}m_{2}) - ({}^{1}m_{3} + {}^{2}m_{3})^{2} - ({}^{1}m_{4} + {}^{2}m_{4})^{2} = 0.$$
(5.29)

Now let

$$v_{\alpha l} = \left(\frac{\lambda_{\alpha} + 2\mu_{\alpha}}{\rho_{\alpha}}\right)^{\frac{1}{2}}, \qquad v_{\alpha t} = \left(\frac{\mu_{\alpha}}{\rho_{\alpha}}\right)^{\frac{1}{2}}$$
 (5.30)

be the longitudinal bulk wave speeds and transverse bulk wave (shear wave) speeds $(\alpha = 1, 2)$, respectively, and

$$q_{\alpha l} = \sqrt{1 - \left(\frac{v}{v_{\alpha l}}\right)^2}, \qquad q_{\alpha t} = \sqrt{1 - \left(\frac{v}{v_{\alpha t}}\right)^2}.$$
 (5.31)

By some tedious algebraic manipulation, equation (5.29) can be rewritten as

$$((1 - q_{2l}q_{2l})\rho_1^2 - (q_{1t}q_{2l} + q_{1l}q_{2t} + 2)\rho_2\rho_1 + (1 - q_{1l}q_{1t})\rho_2^2)v^4 + 4((q_{2l}q_{2t} - 1)\rho_1 + (1 - q_{1l}q_{1t})\rho_2)(\rho_1v_{1t}^2 - \rho_2v_{2t}^2)v^2 + 4(q_{1l}q_{1t} - 1)(q_{2l}q_{2t} - 1)(\rho_1v_{1t}^2 - \rho_2v_{2t}^2)^2 + kQ_s((q_{2l}q_{2t} - 1)\rho_1 + (q_{1l}q_{1t} - 1)\rho_2)v^2 = 0,$$
(5.32)

which determines the interfacial wave speed. Upon inspection it is clear that if the surface elasticity is ignored ($Q_s = 0$), the solution of v to the above equation is the wave speed of the classic Stoneley wave [74] and independent of the wave number k. At the presence of surface elasticity ($Q_s > 0$), a generic solution to the above equation clearly depends on k, meaning that the interfacial wave is dispersive. We also notice that the solution to equation (5.32) may not exist.

We now solve (5.32) numerically and results of interfacial wave speed versus frequency are shown in Fig. 5.5-5.7. In Fig. 5.5 the impact of surface elastic modulus is studied for two bulk materials with $\rho_1 = 500Kg/m^3$, $\rho_2 = 10000Kg/m^3$, $v_{1t} = v_{2t} =$ 1000m/s, $v_{1l} = v_{2l} = 1450m/s$ (cf., (5.30)). Figure 5.5 shows that the wave speed v monotonically increases (resp. decreases) with respect to frequency ω for positive (resp. negative) Q_s . However, interfacial wave speed v becomes independent of Q_s at long wavelength limit ($\omega \rightarrow 0$). In Fig. 5.6 we show the dependence of interfacial waves on bulk densities for given surface elastic modulus of $Q_s = 10000J/m^2$ whereas



Figure 5.5: Dependence of interfacial wave speed on surface elastic modulus $Q_s(J/m^2)$. v is normalized by the corresponding wave speed v_0 for $Q_s = 0$. ($\rho_1 = 500 kg/m^3$, $\rho_2 = 10000 kg/m^3$, $v_{1t} = v_{2t} = 1000 m/s$, and $v_{1l} = v_{2l} = 1450 m/s$)



Figure 5.6: Dependence of interfacial wave speed on densities ρ_1 and $\rho_2(kg/m^3)$. v is normalized by limiting wave speed \hat{v} . ($Q_s = 10000J/m^2$, $v_{1t} = v_{2t} = 1000m/s$, and $v_{1l} = v_{2l} = 1450m/s$)



Figure 5.7: Dependence of interfacial wave speed on bulk wave speeds for given limiting speed $\hat{v} = 2000m/s$. v is normalized by \hat{v} . $(Q_s = 10000J/m^2, \rho_1 = 500kg/m^3, \rho_2 = 10000kg/m^3, v_{1t} = v_{2t} = 1000m/s$, and $v_{1l} = v_{2l}$)



Figure 5.8: Dispersion relation of interfacial wave at the interface of Aluminum $(\rho_1 = 2700 kg/m^3, v_{1t} = 3040m/s, \text{ and } v_{1l} = 6420m/s)$ and water $(\rho_2 = 1000 kg/m^3$ and $v_{water} = 1484m/s$). Here surface elastic parameter is $Q_s = 100000J/m^2$ and interfacial wave speed v is normalized by speed of sound in water v_{water} .

the bulk wave speeds are specified as $v_{1t} = v_{2t} = 1000m/s$, $v_{1l} = v_{2l} = 1450m/s$. We remark that the surface elastic modulus $Q_s = 10000J/m^2$, though orders of magnitude larger than pristine surface of typical solid crystals, is realistic and physical for composite structures, e.g., a sandwich plate with thick soft core and stiff thin face plates. Curves with the same density ratio $\rho_1 : \rho_2 = 1 : 20$ intersects at $\omega = 0$, indicating that the wave speed at long wave length limit depends only on the ratio rather than the values of densities. This is in fact a property of the classic Stoneley waves. On the other hand, at any nonzero frequency larger densities correspond to greater interfacial wave speed. We also observe that interfacial waves are less likely to exist as the ratio gets closer to 1. Figure 5.7 shows the dependence of interfacial wave speed on bulk wave speeds for $Q_s = 10000J/m^2$, $\rho_1 = 500Kg/m^3$, $\rho_2 = 10000Kg/m^3$, $v_{1t} = v_{2t} = 1000m/s$, $v_{1l} = v_{2l}$. We observe that smaller difference between bulk longitudinal speeds and bulk shear speeds results in lower interfacial wave speed at the long wavelength limit, and also makes the interfacial wave speed depend more sensitively on frequency.

Further, we can study interfacial waves propagating along solid/fluid and two fluids interfaces in present framework. Assume that medium 2 is an inviscid fluid. Since the fluid cannot sustain shear force, we set the shear modulus to zero ($\mu_2 = 0$) for fluid phase. Then the condition at the interface shall be written as

$$\begin{cases} \hat{\mathbf{u}}_2 \cdot \mathbf{n} - \hat{\mathbf{u}}_1 \cdot \mathbf{n} = 0, \\ [\mathbf{M}_1(\mathbf{v}) + k\mathbf{Q}_s] \hat{\mathbf{u}}_1 = -\mathbf{M}_2(\mathbf{v}) \hat{\mathbf{u}}_2 = p\mathbf{n}, \end{cases}$$
(5.33)

where p is the pressure. By (5.28) components of $M_2(v)$ are given by

$${}^{2}m_{1} = {}^{2}m_{3} = {}^{2}m_{4} = 0, \quad {}^{2}m_{2} = \rho_{2}v^{2}\sqrt{\frac{\lambda_{2}}{\lambda_{2} - \rho_{2}v^{2}}}.$$
 (5.34)

Inserting (5.28) and (5.34) into (5.33) we have

$$({}^{1}m_{1}+kQ_{s})({}^{1}m_{2}+{}^{2}m_{2})-{}^{1}m_{4}^{2}=0.$$
 (5.35)

Substituting (5.30) and (5.31) into above equation (5.35) we have the following equation in terms of bulk wave speeds:

$$-2\rho_{1}v_{1t}^{2}v_{1l}^{2}[\rho_{2}(q_{1l}+q_{1t})+\rho_{1}q_{2l}]v^{4}$$

$$+\rho_{1}v_{1t}^{2}v_{1l}^{2}(v_{1t}^{2}+v_{1l}^{2})[\rho_{1}q_{2l}-\rho_{1}q_{1t}q_{1l}q_{2l}+\rho_{2}(q_{1l}+q_{1t})]v^{2}$$

$$+4\rho_{1}^{2}v_{1t}^{4}v_{1l}^{2}(v_{1l}^{2}-v_{1t}^{2}+v_{1t}^{2}q_{1t}q_{1l})q_{2l}$$

$$+kQ_{s}(v_{1t}^{2}q_{qt}+v_{1l}^{2}q_{1l})(\rho_{1}v_{1t}^{2}v_{1l}^{2}(q_{1l}+q_{1t})q_{1t}q_{2l}$$

$$+\rho_{2}v^{2}(v_{1t}^{2}q_{1t}+v_{1l}^{2}q_{1l})) = 0.$$
(5.36)

By equation (5.36) we calculate the interfacial wave speed versus frequency for Aluminum/Water interface with surface elasticity ($\rho_1 = 2700kg/m^3$, $v_{1t} = 3040m/s$, $v_{1l} = 6420m/s$, $\rho_2 = 1000kg/m^3$, $v_{water} = 1484m/s$ and $Q_s = 100000J/m^2$). From Fig. 5.8, we observe that at the presence of surface elasticity the interfacial wave speed decreases as frequency increases. Also, we remark that interfacial wave speed is lower than the acoustic wave speed in water v_{water} and that the interfacial waves implied by (5.35) decay only in the solid but not the fluid phase (since we have ignored the viscosity).

5.3 Reflection and refraction of bulk elastic waves at material interface with surface elasticity

In this section we study the wave reflection and refraction of bulk waves at the interface of two media when the interface has surface elasticity. For the cases without surface elasticity, the topic has been completely studied [99] and analytic solutions have been found [100]. In these theories the amplitude ratios and energy rates of reflected and refracted waves are all real numbers and uniquely determined by the material properties and incident angle. In the analysis we studied three general case: (i) shear horizontal (SH) waves, (ii) pressure (P) waves, and (iii) shear vertical (SV) waves. Any bulk waves can be without loss of generalization written as linear combinations of these three waves. This analysis shows that the reflected and refracted waves gain some new properties as the surface elasticity is included.



Figure 5.9: Illustration of wave reflection and refraction of incident SH-wave at the interface of two solid half-spaces

5.3.1 Reflection and refraction of SH-waves

Consider an infinite elastic medium with an interface $\Gamma = \{(x_1, x_2, x_3) : x_3 = 0\}$ between two half spaces: $\Omega_1 = \{(x_1, x_2, x_3) | x_3 > 0\}$ and $\Omega_2 = \{(x_1, x_2, x_3) | x_3 < 0\}$. A plane SHwave (oscillating in \mathbf{e}_2 direction) propagates in $\mathbf{e}_1 - \mathbf{e}_3$ plane from Ω_2 to Ω_1 as shown in Figure 5.9. Notice that both its reflected and refracted waves are also SH-waves. Let

$$\mathbf{k}_{I} = (k_{I} \sin \theta_{I}, 0, k_{I} \cos \theta_{I})^{T},$$
$$\mathbf{k}_{R} = (k_{R} \sin \theta_{R}, 0, -k_{R} \cos \theta_{R})^{T},$$
$$\mathbf{k}_{T} = (k_{T} \sin \theta_{T}, 0, k_{T} \cos \theta_{T})^{T},$$

be wave vectors of indent, reflected and reflected waves, where $\theta_I, \theta_R, \theta_T \in (0, \pi/2)$ are the incident, reflect and refract angle, and $k_I = |\mathbf{k}_I|$, $k_R = |\mathbf{k}_R|$ and $k_T = |\mathbf{k}_T|$ are their corresponding wave numbers. Then the wave function will have the form

$$\mathbf{u}(\mathbf{x},t) = \begin{cases} \left[A_I e^{i(\mathbf{k}_I \cdot \mathbf{x} - \omega t)} + A_R e^{i(\mathbf{k}_R \cdot \mathbf{x} - \omega t)} \right] \mathbf{e}_2, & \mathbf{x} \in \Omega_2 \\ A_T e^{i(\mathbf{k}_T \cdot \mathbf{x} - \omega t)} \mathbf{e}_2, & \mathbf{x} \in \Omega_1 \end{cases}$$
(5.37)

where A_I , A_R and A_T are amplitudes of indent, reflected and reflected waves. Since the wave vector has to be continuous at the interface, we have

$$\mathbf{u}(\mathbf{x}^+, t) = \mathbf{u}(\mathbf{x}^-, t) \qquad \forall x_1, t \in \mathbb{R},$$
(5.38)

where \mathbf{x}^+ (\mathbf{x}^-) denotes the boundary value approached from the top (bottom) of the interface, i.e., $x_3 \rightarrow 0^+$ ($x_3 \rightarrow 0^-$). Equation (5.38) implies that

$$A_I e^{i(k_I \sin \theta_I x_1 - \omega t)} + A_R e^{i(k_R \sin \theta_R x_1 - \omega t)} = A_T e^{i(k_T \sin \theta_T x_1 - \omega t)} \quad \forall x_1, t \in \mathbb{R}.$$

Immediately we have

$$\begin{cases} k_I \sin \theta_I = k_R \sin \theta_R = k_T \sin \theta_T =: k_1, \\ A_I + A_R = A_T. \end{cases}$$
(5.39)

Since the frequency is an invariant during the reflection and refraction, we have

$$k_I v_{2t} = k_R v_{2t} = k_T v_{1t} = \omega, (5.40)$$

and therefore

$$k_R = \frac{v_{1t}}{v_{2t}} k_T = k_I.$$

where ω is the angular frequency of the incident wave and v_{1t} are v_{2t} are the shear wave speed of Ω_1 and Ω_2 (cf. (5.30)). Now by (5.39)₁ we explicitly write the reflect and refract angles for given incident angle as

$$\begin{cases} \theta_R = \theta_I, \\ \theta_T = \sin^{-1}(\frac{v_{1t}}{v_{2t}}\sin\theta_I). \end{cases}$$
(5.41)

Besides, balance of tractions at the interface should require

$$\operatorname{div}_{s}[\mathbf{C}_{s}\nabla\mathbf{u}(\mathbf{x},t)+\boldsymbol{\sigma}_{0}]+[\mathbf{C}_{1}\nabla\mathbf{u}(\mathbf{x}^{+},t)-\mathbf{C}_{2}\nabla\mathbf{u}(\mathbf{x}^{-},t)]\mathbf{e}_{3}=0, \quad \mathbf{x}\in\Gamma.$$
(5.42)

For simplicity of analytic expressions, we now assume that Ω_1 , Ω_2 and Γ are all isotropic bodies. Inserting the wave function (5.37) into (5.42) we have

$$[\mu_2(ik_I\cos\theta_I A_I - ik_R\cos\theta_R A_R) - \mu_1 ik_T\cos\theta_T A_T - \mu_s k_T^2\sin^2\theta_T A_T]e^{i(k_1x_1 - \omega t)}\mathbf{e}_2 = 0.$$
(5.43)

Amplitude ratios

In order to quantitatively study the amount of reflection and refraction, we now adopt the classic definition of *amplitude ratios* [99] of reflection and refraction: $R(\theta_I, k_1) := A_R/A_I$ and $T(\theta_I, k_1) := A_T/A_I$. By solving equations (5.39) and (5.43) we have

$$R(\theta_I, k_1) = \frac{ik_I \cos \theta_I \mu_2 - ik_T \cos \theta_T \mu_1 - k_I^2 \sin^2 \theta_I \mu_s}{ik_I \cos \theta_I \mu_2 + ik_T \cos \theta_T \mu_1 + k_I^2 \sin^2 \theta_I \mu_s},$$

$$T(\theta_I, k_1) = \frac{2ik_I \cos \theta_I \mu_2}{ik_I \cos \theta_I \mu_2 + ik_T \cos \theta_T \mu_1 + k_I^2 \sin^2 \theta_I \mu_s}.$$

Here θ_T is a function of θ_I from (5.41). By (5.40) we can simplify the above equation by writing k_T in terms of material properties only:

$$R(\theta_{I},k_{1}) = \frac{\cos \theta_{I} \mu_{2} - \cos \theta_{T} \mu_{1} v_{2t} / v_{1t} + i \sin^{2} \theta_{I} \mu_{s} k_{I}}{\cos \theta_{I} \mu_{2} + \cos \theta_{T} \mu_{1} v_{2t} / v_{1t} - i \sin^{2} \theta_{I} \mu_{s} k_{I}},$$

$$T(\theta_{I},k_{1}) = \frac{2 \cos \theta_{I} \mu_{2}}{\cos \theta_{I} \mu_{2} + \cos \theta_{T} \mu_{1} v_{t1} / v_{t2} - i \sin^{2} \theta_{I} \mu_{s} k_{I}}.$$
(5.44)

We remark that if the surface elasticity is not included, *R* and *T* are real constants for given incident angle θ_I . They are readily obtained from (5.44) by setting $\mu_s = 0$, which coincide with the theories of reflection and refraction in previous studies. When we consider the surface elasticity $R(\theta_I, k_1)$ and $T(\theta_I, k_1)$ gain a few new characteristics. First, these amplitude ratios now also depend on the incident wave number k_I . Secondly, we notice that $R(\theta_I, k_1)$ and $T(\theta_I, k_1)$ become complex numbers, meaning there exist phase shifts for both reflected and refracted waves. Therefore, the magnitudes of $R(\theta_I, k_1)$ and $T(\theta_I, k_1)$ become the aspects of amplitudes.

To see the impact of surface elasticity on the reflection and refraction of bulk waves, we numerically calculate the magnitudes of the amplitude ratios $|R(\theta_I, k_1)|$ and $|T(\theta_I, k_1)|$ at the interface of Cu ($v_{1t} = 2195$ m/s, $\mu_1 = 48$ Gpa) and Al ($v_{2t} = 3100$ m/s, $\mu_2 = 26$ Gpa). Figure 5.10 shows |R| and |T| for $\theta_I = 30^\circ$ and $\mu_s = 2 \times 10^5$ J/m². We observe that the surface elasticity at the interface tends to increase the amount of reflection while decrease the amount of refraction. Also, at the long wave length limit ($\omega \rightarrow 0$), the values of |R| and |T| coincide with the classic theory of reflection and refraction. Figure 5.11 shows the impact of surface elasticity at different incident angles.



Figure 5.10: Amplitude ratios of reflection and refraction with incident SH-wave at interface of Cu ($v_{1t} = 2195$ m/s, $\mu_1 = 48$ Gpa) and Al ($v_{2t} = 3100$ m/s, $\mu_2 = 26$ Gpa). ($\theta_I = 30^o$, $\mu_s = 2 \times 10^5$ J/m²)



Figure 5.11: Amplitude ratios of reflection *R* with incident SH-wave at interface of Cu $(v_{1t} = 2195 \text{ m/s}, \mu_1 = 48 \text{ Gpa})$ and Al $(v_{2t} = 3100 \text{ m/s}, \mu_2 = 26 \text{ Gpa})$. $(\mu_s = 2 \times 10^5 \text{ J/m}^2)$



Figure 5.12: Amplitude ratios of reflection *R* with incident SH-wave at interface of Cu $(v_{1t} = 2195 \text{ m/s}, \mu_1 = 48 \text{ Gpa})$ and Al $(v_{2t} = 3100 \text{ m/s}, \mu_2 = 26 \text{ Gpa})$. $(k = 1 \times 10^6 \text{ /m})$

We find that at low incident angles the the surface elasticity doesn't have appearant effect on the amplitudes, and in particular it has no effect at all when the incident angle $\theta_I = 0$. As the incident angle increases, the surface elasticity becomes a very important factor in determining the amplitudes of reflection and refraction. Figure 5.12 shows the dependence of |R| on incident angle θ_I for different surface elasticity constants at the interface. We observe that at extreme points $\theta_I = 0^o$ and $\theta_I = 90^o$, the values of |R| are invariant with the surface elasticity. For larger surface elasticity constant μ_s , the value of |R| tends to increase faster as the incident angle increases.

Energy rates of reflection and refraction

In order to determine the energy distribution of reflected and refracted waves, we introduce the density of total energy for solid waves:

$$\begin{aligned} \boldsymbol{\varepsilon}_{tot} &= \frac{1}{2} \boldsymbol{\rho} (\frac{\partial \mathbf{u}}{\partial t})^2 + \frac{1}{2} \nabla \mathbf{u} \cdot \mathbf{C} (\nabla \mathbf{u}) \\ &= \boldsymbol{\rho} \boldsymbol{\omega}^2 A^2, \end{aligned}$$

where *A* is the amplitude. Due to the conservation of energy, the energy flux into and out of the interface Γ should be balanced

$$\mathbf{j}_{\text{in}} = \mathbf{j}_{\text{out}} \qquad \text{at } \Gamma. \tag{5.45}$$

Equation (5.45) implies

$$\rho_2 \omega^2 |A_I|^2 v_{2t} (\mathbf{k}_I / |\mathbf{k}_I| \cdot \mathbf{e}_3) - \rho_2 \omega^2 |A_R|^2 v_{2t} (\mathbf{k}_R / |\mathbf{k}_R| \cdot \mathbf{e}_3)$$

= $\rho_1 \omega^2 |A_T|^2 v_{1t} (\mathbf{k}_T / |\mathbf{k}_T| \cdot \mathbf{e}_3)$ (5.46)

Now we define the *energy rate of reflection and refraction* $\hat{R}(\theta_I, k_I) \in (0, 1)$ and $\hat{T}(\theta_I, k_I) \in (0, 1)$ as

$$\hat{R}(\theta_{I},k_{I}) = \frac{\rho_{2}\omega^{2}|A_{R}|^{2}v_{2t}(\mathbf{k}_{R}/|\mathbf{k}_{R}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2t}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = |R|^{2},$$

$$\hat{T}(\theta_{I},k_{I}) = \frac{\rho_{1}\omega^{2}|A_{I}|^{2}v_{1t}(\mathbf{k}_{T}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2t}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{\rho_{1}v_{1t}\cos\theta_{T}}{\rho_{2}v_{2t}\cos\theta_{I}}|T|^{2}.$$
(5.47)

Physically, the energy rate of reflection and refraction is the percentage of incident wave propagation energy distributed in reflection and refraction, respectively. By substituting (5.44) into (5.47), one can verify the conservation of energy that

$$\hat{R} + \hat{T} = 1,$$

which is exactly the equation (5.46). From (5.47) we see that the energy rates also depend on the wave number k_I , in the sense that depend on incident wave frequency ω .

Existence of reflected and refracted waves and critical angles

From (5.39) we have

$$\sin \theta_T = \frac{k_I}{k_T} \sin \theta_I = \frac{v_{1t}}{v_{2t}} \sin \theta_I.$$
(5.48)

Particularly, when $v_{1t} > v_{2t}$, it is possible that $\frac{v_{1t}}{v_{2t}} \sin \theta_I \ge 1$. We hereby define the *critical incident angle* θ_c such that

$$\frac{v_{1t}}{v_{2t}}\sin\theta_c=1,$$

namely

$$\theta_c = \sin^{-1}(v_{2t}/v_{1t}). \tag{5.49}$$

For $\theta_I \ge \theta_c$, (5.48) implies that $|\theta_T| = \pi/2$ so that the there will be no refraction wave penetrating the interface. In this case the refracted wave doesn't exist, i.e., a total reflection occurs, where all the propagation energies are distributed into the reflected wave. Particularly, when $\theta_I > \theta_c$ we have $\sin \theta_I > 1$ in order for the equation (5.48) to hold. Therefore, θ_T has to be complex and can be expressed as $\theta_T = \pi/2 \pm i\beta$ $(\beta \in \mathbb{R}+)$. We find that

$$\sin \theta_T = \cosh \beta$$
, $\cos \theta_T = \mp i \sinh \beta$.

Hence, β is solved by (5.48) as

$$\beta = \cosh^{-1}(\sin\theta_I \frac{k_I}{k_T}).$$

The originally assumed refraction wave function is now written as

$$\mathbf{u}_T(\mathbf{x},t) = \begin{cases} A_T e^{k_T \sinh\beta x_3} e^{ik_T \cosh\beta x_1} \mathbf{e}_2, & x_3 < 0, \\ A_T e^{-k_T \sinh\beta x_3} e^{ik_T \cosh\beta x_1} \mathbf{e}_2, & x_3 > 0, \end{cases}$$

which is a typical interfacial wave studied in Section 5.2. From here we find that as long as either reflected or refracted waves vanish at the critical angle, the corresponding waves will become interfacial waves.

5.3.2 Reflection and refraction of P waves

Now consider propagation of P-waves in the same domains Ω_1 and Ω_2 . P-waves are bulk elastic waves that oscillate in the same the direction as its propagation in $\mathbf{e}_1 - \mathbf{e}_3$ plane (see Figure 5.13). Therefore, its reflected and refracted waves should also oscillate in the same plane, which could be either P-waves or SV-waves. Here SV-waves are bulk elastic waves that oscillate in the same plane as propagation but perpendicular



Figure 5.13: Illustration of wave reflection and refraction of incident P-wave at the interface of two solid half-spaces

to its propagation orientation. Hence, in general there can be two reflected waves and two refracted waves. Let

$$\mathbf{k}_{I} = (k_{I} \sin \theta_{I}, 0, k_{I} \cos \theta_{I})^{T},$$

$$\mathbf{k}_{RP} = (k_{RP} \sin \theta_{RP}, 0, -k_{RP} \cos \theta_{RP})^{T},$$

$$\mathbf{k}_{RS} = (k_{RS} \sin \theta_{RS}, 0, -k_{RS} \cos \theta_{RS})^{T},$$

$$\mathbf{k}_{TP} = (k_{TP} \sin \theta_{TP}, 0, k_{TP} \cos \theta_{TP})^{T},$$

$$\mathbf{k}_{TS} = (k_{TS} \sin \theta_{TS}, 0, k_{TS} \cos \theta_{TS})^{T}$$
(5.50)

be the wave vector of incident wave, reflected P-wave, reflected SV-wave, refracted P-wave and refracted SV-wave, respectively. We can hereby write the wave function as

$$\mathbf{u}(\mathbf{x},t) = \begin{cases} A_I \mathbf{p}_I e^{i(\mathbf{k}_I \cdot \mathbf{x} - \omega t)} + A_{RP} \mathbf{p}_{RP} e^{i(\mathbf{k}_{RP} \cdot \mathbf{x} - \omega t)} + A_{RS} \mathbf{p}_{RS} e^{i(\mathbf{k}_{RS} \cdot \mathbf{x} - \omega t)}, & \mathbf{x} \in \Omega_2 \\ A_{TP} \mathbf{p}_{TP} e^{i(\mathbf{k}_{TP} \cdot \mathbf{x} - \omega t)} + A_{TS} \mathbf{p}_{TS} e^{i(\mathbf{k}_{TS} \cdot \mathbf{x} - \omega t)}, & \mathbf{x} \in \Omega_1 \end{cases}$$
(5.51)

where

$$\mathbf{p}_{I} = \mathbf{k}_{I} / |\mathbf{k}_{I}| = (\sin \theta_{I}, 0, \cos \theta_{I}),$$

$$\mathbf{p}_{RP} = \mathbf{k}_{RP} / |\mathbf{k}_{RP}| = (\sin \theta_{RP}, 0, -\cos \theta_{RP}),$$

$$\mathbf{p}_{RS} = \mathbf{k}_{RS} / |\mathbf{k}_{RS}| \times \mathbf{e}_{2} = (\cos \theta_{RS}, 0, \sin \theta_{RS}),$$

$$\mathbf{p}_{TP} = \mathbf{k}_{TP} / |\mathbf{k}_{TP}| = (\sin \theta_{TP}, 0, \cos \theta_{TP}),$$

$$\mathbf{p}_{TS} = \mathbf{k}_{TS} / |\mathbf{k}_{TS}| \times \mathbf{e}_{2} = (-\cos \theta_{TS}, 0, \sin \theta_{TS})$$
(5.52)

denote the corresponding directions of oscillation. The continuity condition (5.38) at the interface Γ writes

$$A_{I}\mathbf{p}_{I}e^{i(k_{I}\sin\theta_{I}x_{1}-\omega t)} + A_{RP}\mathbf{p}_{RP}e^{i(k_{RP}\sin\theta_{RP}x_{1}-\omega t)} + A_{RS}\mathbf{p}_{RS}e^{i(k_{RS}\sin\theta_{RS}x_{1}-\omega t)}$$
$$=A_{TP}\mathbf{p}_{TP}e^{i(k_{TP}\sin\theta_{TP}x_{1}-\omega t)} + A_{TS}\mathbf{p}_{TS}e^{i(k_{TS}\sin\theta_{TS}x_{1}-\omega t)} \quad \forall x_{1}, t \in \mathbb{R}.$$

From the above equation we have

$$\begin{cases} k_I \sin \theta_I = k_{RP} \sin \theta_{RP} = k_{RS} \sin \theta_{RS} = k_{TP} \sin \theta_{TP} = k_{TS} \sin \theta_{TS} =: k_1, \\ A_I \sin \theta_I + A_{RP} \sin \theta_I + A_{RS} \cos \theta_{RS} = A_{TP} \sin \theta_{TP} - A_{TS} \cos \theta_{TS}, \\ A_I \cos \theta_I - A_{RP} \cos \theta_I + A_{RS} \sin \theta_{RS} = A_{TP} \cos \theta_{TP} + A_{TS} \sin \theta_{TS}, \end{cases}$$
(5.53)

Since the frequency is an invariant we have

$$k_I v_{2l} = k_{RP} v_{2l} = k_{RS} v_{2t} = k_{TP} v_{1l} = k_{TS} v_{1t} = \omega,$$
(5.54)

which implies

$$k_{RP} = k_I, \qquad k_{RS} = \frac{v_{2l}}{v_{2t}} k_I, \qquad k_{TP} = \frac{v_{2l}}{v_{1l}} k_I, \qquad k_{TS} = \frac{v_{2l}}{v_{1t}} k_I.$$
 (5.55)

Relating (5.53) and (5.68) one can solve θ_{RP} , θ_{RS} , θ_{TP} and θ_{TS} :

$$\theta_{RP} = \theta_I, \qquad \theta_{RS} = \sin^{-1} \left(\frac{v_{2t}}{v_{2l}} \sin \theta_I \right),$$

$$\theta_{TP} = \sin^{-1} \left(\frac{v_{1l}}{v_{2l}} \sin \theta_I \right), \qquad \theta_{TS} = \sin^{-1} \left(\frac{v_{1t}}{v_{2l}} \sin \theta_I \right).$$
(5.56)

Further, according to the balance of traction (5.42) at the interface Γ we have

$$[\mathbf{C}_{1}(iA_{TP}\mathbf{p}_{TP}\otimes\mathbf{k}_{TP}+iA_{TS}\mathbf{p}_{TS}\otimes\mathbf{k}_{TS})$$

$$-\mathbf{C}_{2}(iA_{I}\mathbf{p}_{I}\otimes\mathbf{k}_{I}+iA_{RP}\mathbf{p}_{RP}\otimes\mathbf{k}_{RP}+iA_{RS}\mathbf{p}_{RS}\otimes\mathbf{k}_{RS})]\mathbf{e}_{3}$$
(5.57)
$$-k_{1}^{2}Q_{s}[(A_{TP}\mathbf{p}_{TP}+A_{TS}\mathbf{p}_{TS})\cdot\mathbf{e}_{1}]\mathbf{e}_{1}=0.$$

For simplicity of analytic expression, without loss of generalization we assume Ω_1 , Ω_2 and *Gamma* are all isotropic. The equation above writes

$$iA_{TP}k_{TP}\begin{pmatrix}2\mu_{1}\sin\theta_{TP}\cos\theta_{TP}\\0\\\lambda_{1}+2\mu_{1}\cos^{2}\theta_{TP}\end{pmatrix}+iA_{TS}k_{TS}\begin{pmatrix}\mu_{1}(\sin^{2}\theta_{TS}-\cos^{2}\theta_{TS})\\0\\2\mu_{1}\sin\theta_{TS}\cos\theta_{TS}\end{pmatrix}$$
$$-iA_{RS}k_{RS}\begin{pmatrix}\mu_{2}(\sin^{2}\theta_{RS}-\cos^{2}\theta_{RS})\\0\\-2\mu_{2}\sin\theta_{RS}\cos\theta_{RS}\end{pmatrix}-iA_{RP}k_{RP}\begin{pmatrix}-2\mu_{2}\sin\theta_{RP}\cos\theta_{RP}\\0\\\lambda_{2}+2\mu_{2}\cos^{2}\theta_{RP}\end{pmatrix}$$
(5.58)
$$-iA_{I}k_{I}\begin{pmatrix}2\mu_{2}\sin\theta_{I}\cos\theta_{I}\\0\\\lambda_{2}+2\mu_{2}\cos^{2}\theta_{I}\end{pmatrix}-k_{1}^{2}Q_{s}\begin{pmatrix}A_{TP}\sin\theta_{TP}-A_{TS}\cos\theta_{TS}\\0\\0\end{pmatrix}=0.$$
$$0$$

where $Q_s = \lambda_s + 2\mu_s$ (cf. (5.27)).

Amplitude ratios

Now we define the amplitude ratios of reflected P-wave, reflected SV-wave, refracted P-wave and refracted SV-wave as

$$RP = A_{RP}/A_I$$
, $RS = A_{RS}/A_I$, $TP = A_{TP}/A_I$, $TS = A_{TS}/A_I$, (5.59)

which can be solved by the following linear equations with some simplifications of equation (5.53) and (5.58).

$$\begin{bmatrix} \sin \theta_{RP} & \cos \theta_{RS} & -\sin \theta_{TP} & \cos \theta_{TS} \\ -\cos \theta_{RP} & \sin \theta_{RS} & -\cos \theta_{TP} & -\sin \theta_{TS} \\ \sin 2\theta_{RP} & \frac{v_{2l}}{v_{2l}} \cos 2\theta_{RS} & \left(\frac{\mu_{1}v_{2l}}{\mu_{2}v_{1l}} \sin 2\theta_{TP} & \left(-\frac{\mu_{1}v_{2l}}{\mu_{2}v_{1l}} \cos 2\theta_{TS} \\ + ik_{1}\frac{Q_{s}v_{2l}}{\mu_{2}v_{1l}} \sin^{2} \theta_{TP}\right) & -ik_{1}\frac{Q_{s}v_{2l}}{2\mu_{2}v_{1l}} \sin 2\theta_{TS} \end{bmatrix} \begin{bmatrix} RP \\ RS \\ TP \\ TS \end{bmatrix} \\ (5.60)$$

In above simplification we also used the relation

E.

$$\frac{\lambda_2+2\mu_2\cos^2\theta_{RP}}{\mu_2}=\frac{v_{2l}^2}{v_{2t}^2}\cos 2\theta_{RS}.$$

We remark that though the explicit expressions of RP, RS, TP and TS may be tedious, the calculation are simple and straightforward for given incident angle and wave number. We numerically calculate the magnitudes of amplitude ratios for incident Pwave at Cu-Al interface shown in Figure 5.14. The amplitude ratios are also observed to be frequency dependent. Besides, it is worth mentioning that when the incident wave is perpendicular to the interface ($\theta_I = 0$), from equation (5.60) we immediately have RS = 0 and TS = 0. Therefore, we conclude that reflected and refracted waves of perpendicular incident P-wave are P-waves only.

Energy rates of reflection and refraction

According to the balance of energy flux at the interface Γ (cf. (5.45)), we have

$$\rho_2 \omega^2 |A_I|^2 v_{2l} (\mathbf{k}_I / |\mathbf{k}_I| \cdot \mathbf{e}_3)$$

$$-\rho_2 \omega^2 |A_{RP}|^2 v_{2l} (\mathbf{k}_{RP} / |\mathbf{k}_{RP}| \cdot \mathbf{e}_3) - \rho_2 \omega^2 |A_{RS}|^2 v_{2t} (\mathbf{k}_{RS} / |\mathbf{k}_{RS}| \cdot \mathbf{e}_3)$$
(5.61)
$$= \rho_1 \omega^2 |A_{TP}|^2 v_{1l} (\mathbf{k}_{TP} / |\mathbf{k}_{TP}| \cdot \mathbf{e}_3) + \rho_1 \omega^2 |A_{TS}|^2 v_{1t} (\mathbf{k}_{TS} / |\mathbf{k}_{TS}| \cdot \mathbf{e}_3)$$



Figure 5.14: Amplitude ratios of reflection and refraction with incident P-wave at interface of Cu ($v_{1t} = 2195$ m/s, $\mu_1 = 48$ Gpa) and Al ($v_{2t} = 3100$ m/s, $\mu_2 = 26$ Gpa). ($\theta_I = 30^o$, $\mu_s = 2 \times 10^5$ J/m², $\lambda_s = 6 \times 10^5$ J/m² and $Q_s = \lambda_s + 2\mu_s = 1 \times 10^6$ J/m²)

Now we define the *energy rates of reflection and refraction* of P-waves and SV-waves as $\hat{RP}(\theta_I, k_I), \hat{RS}(\theta_I, k_I), \hat{TP}(\theta_I, k_I), \hat{TS}(\theta_I, k_I) \in (0, 1)$. From (5.72) we have

$$\hat{RP}(\theta_{I},k_{I}) = \frac{\rho_{2}\omega^{2}|A_{RP}|^{2}v_{2l}(\mathbf{k}_{RP}/|\mathbf{k}_{RP}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2l}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = |RP|^{2}$$

$$\hat{RS}(\theta_{I},k_{I}) = \frac{\rho_{2}\omega^{2}|A_{RS}|^{2}v_{2l}(\mathbf{k}_{RS}/|\mathbf{k}_{RS}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2l}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{v_{2l}\cos\theta_{RS}}{v_{2l}\cos\theta_{I}}|RS|^{2}$$

$$\hat{TP}(\theta_{I},k_{I}) = \frac{\rho_{1}\omega^{2}|A_{TP}|^{2}v_{1l}(\mathbf{k}_{TP}/|\mathbf{k}_{TP}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2l}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{\rho_{1}v_{1l}\cos\theta_{TP}}{\rho_{2}v_{2l}\cos\theta_{I}}|TP|^{2}$$

$$\hat{TS}(\theta_{I},k_{I}) = \frac{\rho_{1}\omega^{2}|A_{TS}|^{2}v_{1l}(\mathbf{k}_{TS}/|\mathbf{k}_{TS}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2l}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{\rho_{1}v_{1l}\cos\theta_{TS}}{\rho_{2}v_{2l}\cos\theta_{I}}|TS|^{2}$$
(5.62)

Similarly, one can verify that

$$\hat{RP} + \hat{RS} + \hat{TP} + \hat{TS} = 1.$$
 (5.63)

Existence of reflected and refracted waves and critical angles

The analysis of wave existence for incident P-wave is not a single criterion. First, since $v_{2l} > v_{2t}$ we always have $\theta_I = \theta_{RP} > \theta_{RS}$. Therefore, the reflected P-wave and SV-wave

always exist. The existence conditions for the refracted waves include the following cases:

• $v_{2l} < v_{1t}$. In this case, we consider two critical angles:

$$\theta_{cp} = \sin^{-1}(v_{2l}/v_{1l}), \qquad \theta_{cs} = \sin^{-1}(v_{2l}/v_{1t}).$$
 (5.64)

To discuss the range of incident angle, we have

- $\theta_i < \theta_{cp}$. Since $\sin \theta_{TS} < \sin \theta_{TP} < 1$, both SV-wave and P-wave exist.
- $\theta_{cp} \leq \theta_i < \theta_{cs}$. Since $\sin \theta_{TS} < 1 \leq \sin \theta_{TP}$, only SV-wave exists and the original assumed refracted P-wave becomes an interfacial wave.
- $\theta_i \ge \theta_{cs}$. Since $1 \le \sin \theta_{TS} < \sin \theta_{TP}$, no refracted wave exists. Both the assumed refracted P-wave and SV-wave become interfacial waves. The total reflection occurs in this case.
- $v_{1t} < v_{2l} < v_{1l}$. Since $\sin \theta_{TS} < \sin \theta_l$, the refracted SV wave always exists. We only need to consider one critical angle:

$$\theta_{cp} = \sin^{-1}(v_{2l}/v_{1l}).$$

When $\theta_I \ge \theta_{cp}$, only SV-wave exists and refracted P-wave becomes an interfacial wave.

• $v_{2l} > v_{1l}$. $\sin \theta_{TS} < \sin \theta_{TP} < \sin \theta_l$, both refracted P-wave and SV-wave exist.

5.3.3 Reflection and refraction of SV-waves

The configuration of incident SV-wave is similar to the case of incident P-waves (see Figure 5.15). Since both waves oscillate in the same $\mathbf{e}_1 - \mathbf{e}_3$ plane, their reflected and refracted waves both consist of P-waves and SV-waves. Let \mathbf{k}_I , \mathbf{k}_{RP} , \mathbf{k}_{RS} , \mathbf{k}_{TP} and \mathbf{k}_{TS} (cf. (5.50)) be the wave vector of incident wave, reflected P-wave, reflected SV-wave, refracted P-wave and refracted SV-wave, respectively. Then the wave function


Figure 5.15: Illustration of wave reflection and refraction of incident SV-wave at the interface of two solid half-spaces

is written as

$$\mathbf{u}(\mathbf{x},t) = \begin{cases} A_I \mathbf{p}_I e^{i(\mathbf{k}_I \cdot \mathbf{x} - \omega t)} + A_{RP} \mathbf{p}_{RP} e^{i(\mathbf{k}_{RP} \cdot \mathbf{x} - \omega t)} + A_{RS} \mathbf{p}_{RS} e^{i(\mathbf{k}_{RS} \cdot \mathbf{x} - \omega t)}, & \mathbf{x} \in \Omega_2 \\ A_{TP} \mathbf{p}_{TP} e^{i(\mathbf{k}_{TP} \cdot \mathbf{x} - \omega t)} + A_{TS} \mathbf{p}_{TS} e^{i(\mathbf{k}_{TS} \cdot \mathbf{x} - \omega t)}, & \mathbf{x} \in \Omega_1 \end{cases}$$
(5.65)

where

$$\mathbf{p}_I = \mathbf{k}_I / |\mathbf{k}_I| \times \mathbf{e}_2 = (-\cos\theta_I, 0, \sin\theta_I),$$

 \mathbf{p}_{RP} , \mathbf{p}_{RS} , \mathbf{p}_{TP} and \mathbf{p}_{TS} (cf. (5.52)) denote the corresponding directions of oscillation. From the continuity condition (5.38) at interface Γ we have

$$\begin{cases} k_I \sin \theta_I = k_{RP} \sin \theta_{RP} = k_{RS} \sin \theta_{RS} = k_{TP} \sin \theta_{TP} = k_{TS} \sin \theta_{TS} =: k_1, \\ -A_I \cos \theta_I + A_{RP} \sin \theta_I + A_{RS} \cos \theta_{RS} = A_{TP} \sin \theta_{TP} - A_{TS} \cos \theta_{TS}, \\ A_I \sin \theta_I - A_{RP} \cos \theta_I + A_{RS} \sin \theta_{RS} = A_{TP} \cos \theta_{TP} + A_{TS} \sin \theta_{TS}. \end{cases}$$
(5.66)

Since the frequency is an invariant during reflection and refraction, we have

$$k_I v_{2t} = k_{RP} v_{2l} = k_{RS} v_{2t} = k_{TP} v_{1l} = k_{TS} v_{1t} = \omega,$$
(5.67)

which implies

$$k_{RP} = \frac{v_{2t}}{v_{2l}}k_I, \qquad k_{RS} = k_I, \qquad k_{TP} = \frac{v_{2t}}{v_{1l}}k_I, \qquad k_{TS} = \frac{v_{2t}}{v_{1t}}k_I.$$
 (5.68)

Now θ_{RP} , θ_{RS} , θ_{TP} and θ_{TS} are solved as

$$\theta_{RP} = \sin^{-1} \left(\frac{v_{2l}}{v_{2t}} \sin \theta_I \right), \qquad \theta_{RS} = \theta_I,$$

$$\theta_{TP} = \sin^{-1} \left(\frac{v_{1l}}{v_{2t}} \sin \theta_I \right), \qquad \theta_{TS} = \sin^{-1} \left(\frac{v_{1t}}{v_{2t}} \sin \theta_I \right).$$
(5.69)

With the assumption of isotropic domains, the balance of traction (5.42) at the interface Γ (cf. (5.57)) requires

$$iA_{TP}k_{TP}\begin{pmatrix}2\mu_{1}\sin\theta_{TP}\cos\theta_{TP}\\0\\\lambda_{1}+2\mu_{1}\cos^{2}\theta_{TP}\end{pmatrix}+iA_{TS}k_{TS}\begin{pmatrix}\mu_{1}(\sin^{2}\theta_{TS}-\cos^{2}\theta_{TS})\\0\\2\mu_{1}\sin\theta_{TS}\cos\theta_{TS}\end{pmatrix}$$
$$-iA_{RS}k_{RS}\begin{pmatrix}\mu_{2}(\sin^{2}\theta_{RS}-\cos^{2}\theta_{RS})\\0\\-2\mu_{2}\sin\theta_{RS}\cos\theta_{RS}\end{pmatrix}-iA_{RP}k_{RP}\begin{pmatrix}-2\mu_{2}\sin\theta_{RP}\cos\theta_{RP}\\0\\\lambda_{2}+2\mu_{2}\cos^{2}\theta_{RP}\end{pmatrix}$$
(5.70)
$$-iA_{I}k_{I}\begin{pmatrix}\mu_{2}(\sin^{2}\theta_{I}-\cos^{2}\theta_{I})\\0\\2\mu_{2}\sin\theta_{I}\cos\theta_{I}\end{pmatrix}-k_{1}^{2}Q_{S}\begin{pmatrix}A_{TP}\sin\theta_{TP}-A_{TS}\cos\theta_{TS}\\0\\0\end{pmatrix}=0.$$



Figure 5.16: Amplitude ratios of reflection and refraction with incident SV-wave at interface of Cu ($v_{1t} = 2195$ m/s, $\mu_1 = 48$ Gpa) and Al ($v_{2t} = 3100$ m/s, $\mu_2 = 26$ Gpa). ($\theta_I = 15^o$, $\mu_s = 2 \times 10^5$ J/m², $\lambda_s = 6 \times 10^5$ J/m²)

Amplitude ratios

Combining equation (5.66) and (5.70), the amplitude ratios RP, RS, TP and TS (cf. (5.59)) can be solved by

$$\begin{bmatrix} \sin \theta_{RP} & \cos \theta_{RS} & -\sin \theta_{TP} & \cos \theta_{TS} \\ -\cos \theta_{RP} & \sin \theta_{RS} & -\cos \theta_{TP} & -\sin \theta_{TS} \\ \frac{\nu_{2I}}{\nu_{2I}} \sin 2\theta_{RP} & \cos 2\theta_{RS} & \left(\frac{\mu_1 \nu_{2I}}{\mu_2 \nu_{1I}} \sin 2\theta_{TP} & \left(-\frac{\mu_1 \nu_{2I}}{\mu_2 \nu_{1I}} \cos 2\theta_{TS} \\ + ik_1 \frac{Q_s \nu_{2I}}{\mu_2 \nu_{1I}} \sin^2 \theta_{TP}\right) & -ik_1 \frac{Q_s \nu_{2I}}{2\mu_2 \nu_{1I}} \sin 2\theta_{TS} \end{bmatrix} \begin{bmatrix} RP \\ RS \\ TP \\ TS \end{bmatrix} \\ \begin{bmatrix} -\frac{\nu_{2I}}{\nu_{2I}} \cos 2\theta_{RS} & \sin 2\theta_{RS} & \frac{\mu_{1} \nu_{2I} \nu_{II}}{\mu_{2} \nu_{II}^2} \cos 2\theta_{TS} & \frac{\mu_{1} \nu_{2I}}{\mu_{2} \nu_{II}} \sin 2\theta_{TS} \end{bmatrix} \end{bmatrix}$$
(5.71)

We numerically calculate the amplitude ratios of reflection and refraction for incident SV-waves at Cu-Al interface shown in Figure 5.16. Similar to the previous cases, the amplitude ratios are also observed to be frequency dependent. It is worth mentioning that when the incident wave is perpendicular to the interface $\theta_I = 0$, by equation (5.71) we have RP = 0 and TP = 0. Therefore, we conclude that reflected and refracted waves of perpendicular incident SV-wave are SV-waves only.

Energy rates of reflection and refraction

According to the balance of energy flux at the interface Γ (cf. (5.45)), we have

$$\rho_2 \omega^2 |A_I|^2 v_{2t} (\mathbf{k}_I / |\mathbf{k}_I| \cdot \mathbf{e}_3)$$

$$-\rho_2 \omega^2 |A_{RP}|^2 v_{2l} (\mathbf{k}_{RP} / |\mathbf{k}_{RP}| \cdot \mathbf{e}_3) - \rho_2 \omega^2 |A_{RS}|^2 v_{2t} (\mathbf{k}_{RS} / |\mathbf{k}_{RS}| \cdot \mathbf{e}_3)$$
(5.72)
$$= \rho_1 \omega^2 |A_{TP}|^2 v_{1l} (\mathbf{k}_{TP} / |\mathbf{k}_{TP}| \cdot \mathbf{e}_3) + \rho_1 \omega^2 |A_{TS}|^2 v_{1t} (\mathbf{k}_{TS} / |\mathbf{k}_{TS}| \cdot \mathbf{e}_3)$$

Now we define the *energy rate of reflection and refraction* of P-waves and SV-waves as $\hat{RP}(\theta_I, k_I), \hat{RS}(\theta_I, k_I), \hat{TP}(\theta_I, k_I), \hat{TS}(\theta_I, k_I) \in (0, 1).$

$$\hat{RP}(\theta_{I},k_{I}) = \frac{\rho_{2}\omega^{2}|A_{RP}|^{2}v_{2l}(\mathbf{k}_{RP}/|\mathbf{k}_{RP}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2t}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{v_{2l}\cos\theta_{RP}}{v_{2t}\cos\theta_{I}}|RP|^{2},$$

$$\hat{RS}(\theta_{I},k_{I}) = \frac{\rho_{2}\omega^{2}|A_{RS}|^{2}v_{2t}(\mathbf{k}_{RS}/|\mathbf{k}_{RS}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2t}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = |RS|^{2},$$

$$\hat{TP}(\theta_{I},k_{I}) = \frac{\rho_{1}\omega^{2}|A_{TP}|^{2}v_{1l}(\mathbf{k}_{TP}/|\mathbf{k}_{TP}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2t}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{\rho_{1}v_{1l}\cos\theta_{TP}}{\rho_{2}v_{2t}\cos\theta_{I}}|TP|^{2},$$

$$\hat{TS}(\theta_{I},k_{I}) = \frac{\rho_{1}\omega^{2}|A_{TS}|^{2}v_{1t}(\mathbf{k}_{TS}/|\mathbf{k}_{TS}|\cdot\mathbf{e}_{3})}{\rho_{2}\omega^{2}|A_{I}|^{2}v_{2l}(\mathbf{k}_{I}/|\mathbf{k}_{I}|\cdot\mathbf{e}_{3})} = \frac{\rho_{1}v_{1t}\cos\theta_{TS}}{\rho_{2}v_{2t}\cos\theta_{I}}|TS|^{2}.$$
(5.73)

We find that the energy ratios for incident SV-wave also depend on the frequency of incident wave. Similarly, one can verify that

$$\hat{RP} + \hat{RS} + \hat{TP} + \hat{TS} = 1$$
 (5.74)

Existence of reflected and refracted waves and critical angles

For the case of incident SV-wave, we first consider the existence condition of reflected waves: since $v_{2l} > v_{2t}$, there always exist an critical angle above which the reflected P-wave vanishes. Let

$$\theta_{cr} = \sin^{-1}(v_{2t}/v_{2l}) \tag{5.75}$$

the be critical angle of reflected P-waves. Therefore, situations of existence of reflected waves are

- $\theta_I < \theta_{cr}$. Both reflected P-wave and SV-wave exist.
- $\theta_I \ge \theta_{cr}$. Only reflected SV-wave exists and the assumed reflected P-wave becomes an interfacial wave.

Besides, the existence conditions of refracted waves are similar to the discussions in Section 5.3.2:

• $v_{2t} < v_{1t}$. In this case, we consider two critical angles:

$$\theta_{cp} = \sin^{-1}(v_{2t}/v_{1l}), \qquad \theta_{cs} = \sin^{-1}(v_{2t}/v_{1t}).$$
 (5.76)

To discuss the range of incident angle, we have

- $\theta_i < \theta_{cp}$. Since $\sin \theta_{TS} < \sin \theta_{TP} < 1$, both refracted SV-wave and P-wave exist.
- $\theta_{cp} \leq \theta_i < \theta_{cs}$. Since $\sin \theta_{TS} < 1 \leq \sin \theta_{TP}$, only refracted SV-wave exists and the originally assumed refracted P-wave becomes an interfacial wave.
- − θ_i ≥ θ_{cs}. Since 1 ≤ sin θ_{TS} < sin θ_{TP}, no refracted wave exist. Both the originally assumed refracted P-wave and SV-wave become interfacial waves. The total reflection occurs in this case.
- $v_{1t} < v_{2t} < v_{1l}$. Since $\sin \theta_{TS} < \sin \theta_l$ refracted SV wave always exists. We only need to consider one critical angle:

$$\theta_{cp} = \sin^{-1}(v_{2t}/v_{1l}).$$

When $\theta_I \ge \theta_{cp}$, only refracted SV-wave exists and the originally assumed refracted P-wave becomes an interfacial wave.

• $v_{2t} > v_{1l} \sin \theta_{TS} < \sin \theta_{TP} < \sin \theta_l$, both refracted P-wave and SV-wave exist

Chapter 6

Application: size dependence of the phase transition temperature for ferroelectric nano-particles

6.1 Introduction

Physical properties of ferroelectric materials are observed to be size dependent and have been extensively studied. Such size effects include variation of transformation strain [101], dielectric constants [102] and most importantly phase transition temperature (Curie temperature). The size dependence of phase transition temperature has been observed for various ferroelectric nano-particles, including PbTiO₃ [5, 6], BaTiO₃ [7, 103, 101] and SrBi₂Ta₂O₉ [104]. Similar phenomena are also found in ferromagnetic nano-particles [105, 106, 107] and nano-films [106, 108, 109]). Some studies show that such characteristic of these different kinds of materials can be correlated [110]. Moreover, such size effect is in general not limited to microscopic crystal structures: the phase transition temperature of ferroelectric ceramics is found to be size dependent on its grain size [111, 112]). Due to the vast applications in materials of different length scales, it is of great importance to fundamentally study the size dependence of phase transition temperature.

To date the quantitative models of phase transition temperature include empirical [6], thermodynamic [113, 110, 114] and Landau-Ginzberg models [115]. Though there have been lots of efforts in the physical explanation, in practice the reason of size effect seems to be complicated since it may depend on many factors including the depolarization field in particles [116] and the "clustering effect" between particles [117]. However as a crucial factor in nano science, the surface effect particularly the impact of surface stress is not noticed in most of the previous works, except for a few studies where "surface layers" with different properties from the inner body of particles are assumed [115, 118]. In nano structure of materials, due to large surface-volume ratio the surface effect has significant impact on physical and chemical properties of materials. It has been noticed in both experiments [119] and MD simulations [24] of Au nano-structures that the surface stress may cause phase transition. Therefore in this article, the surface energy is regarded as an important factor of determining the phase transition temperature for ferroelectric particles.

Recently, as ferroelectric devices become smaller and smaller, the *critical size* of ferroelectric particles draws more attention. At nanometer scale, the phase transition temperature will drop significantly with decrease of particle size until it reaches zero at the *critical size*, where the phase transition does not occur at all. For instance, the critical size of PbTiO₃ particles is within 10nm-20nm [120]. In this paper, with consideration of surface energy based on Gurtin & Murdoch's theory [27] of surface elasticity, we propose a phenomenological model for the size effect of phase transition temperature of ferroelectric nano-particles. The general model set up applies to ferromagnetic materials as well. Starting from Laudau-Ginzberg theory we define the free energy of single domain ferroelectric nano-particles. By minimizing the free energy we obtain a relation between particle size and phase transition temperature with two physical parameters and predict the critical size. The model agrees well with experimental data of ferroelectric particles.

6.2 Model

Let $\Omega \subset \mathbb{R}^3$ be the reference configuration of a single-crystal ferroelectric body. Assume that during the transformation, the body undergoes a deformation $\mathbf{y} : \Omega \to \mathbb{R}^3$ and gain a spontaneous polarization $\mathbf{p} : \Omega \to \mathbb{R}^3$. To model the process of phase transition, we employ the Landau phenomenological theory with (\mathbf{y}, \mathbf{p}) being the thermodynamic state variables (order parameters). At some certain temperature T, we postulate that the total free energy of the body is given by

$$F[\mathbf{y},\mathbf{p};T] = \int_{\Omega} \frac{\alpha}{2} |\nabla \mathbf{p}|^2 + \frac{\varepsilon_0}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 + \int_{\Omega} \Psi(\nabla \mathbf{y},\mathbf{p};T) + \int_{\partial \Omega} W_s(\nabla \mathbf{y};T), \quad (6.1)$$

where $\alpha > 0$ is the exchange constant, ε_0 is the vacuum permittivity, and the electrostatic potential $\phi : \mathbb{R}^3 \to \mathbb{R}$ satisfies the Maxwell equation:

$$\operatorname{div}[-\varepsilon_0 \nabla \phi + \mathbf{p} \chi_\Omega] = 0 \qquad \text{in } \mathbb{R}^3.$$

We remark that the first term on the right hand side of (6.1), the *exchange energy*, reflects the long-range ordering of polarization in a ferroelectric crystal and the constant α is related to the length scales of domain structures in a ferroelectric body; the second term is the electric field energy induced by the polarization; the third term is the *bulk* internal energy. Finally, the last term arises from the *surface* internal energy

By scaling arguments, for a macroscopic body it can be shown that the exchange energy and the electric field energy may be neglected in analyzing the phase transition temperature since (1) the polarizations form domains which would diminish the exchange energy, and (2) polarization in different domains tends to form "pole-free" interfaces and cancel each other which would make the field energy negligible (De Simone 1993 [121]). Also, we can neglect the surface internal energy (i.e., the last term in (6.1)) which may be intuitively understood by comparing the number of surface atoms with the number of atoms in the bulk. By these considerations, we can safely conclude that the phase transition temperature of a macroscopic ferroelectric body is determined by the *bulk* internal energy: $\int_{\Omega} \Psi(\nabla \mathbf{y}, \mathbf{p}, T)$.

By the principle of frame indifference, the bulk internal energy density function $\Psi: \mathbb{R}^{3\times 3} \times \mathbb{R}^3 \times \mathbb{R} \to \mathbb{R}$ shall satisfy

$$\Psi(\mathbf{F},\mathbf{p};T) = \Psi(\mathbf{RF},\mathbf{Rp};T) \quad \forall \mathbf{R} \in So(3).$$

Assume that the phase transition temperature (Curie temperature) is given by T_c^0 for a macroscopic single-crystal body and that the spontaneous deformation gradient and polarization of the ferroelectric phase is given by $(\mathbf{U}^*, \mathbf{p}^*) \in \mathbb{R}^{3 \times 3}_{sym} \times \mathbb{R}^3$. For a given material, the transition temperature, spontaneous strain and polarization can be accurately measured (Mitsui et al., 1969). To reflect these experimental results, we shall require that the bulk internal energy density function $\Psi(\mathbf{F}, \mathbf{p}; T)$ has a "multiwell structure" in a neighborhood of the transition temperature T_c^0 and satisfies the following (Shu and Bhattacharya, 2001 [122]):

- For any T, $(\mathbf{I}, 0)$ and $(\mathbf{U}^*, \mathbf{p}^*)$ are local minimizers of $\Psi(\mathbf{F}, \mathbf{p}; T)$.
- If $T > T_c^0$, $\Psi(\mathbf{I}, 0; T) \le \Psi(\mathbf{F}, \mathbf{p}; T)$ for any (\mathbf{F}, \mathbf{p}) , and in particular,

$$\Psi(\mathbf{I},0;T) < \Psi(\mathbf{U}^*,\mathbf{p}^*;T).$$
(6.2)

- If $T = T_c^0$, $\Psi(\mathbf{I}, 0; T) = \Psi(\mathbf{U}^*, \mathbf{p}^*, T) \le \Psi(\mathbf{F}, \mathbf{p}; T)$ for any (\mathbf{F}, \mathbf{p}) .
- If $T < T_c^0$, $\Psi(\mathbf{U}^*, \mathbf{p}^*, T) \le \Psi(\mathbf{F}, \mathbf{p}; T)$ for any (\mathbf{F}, \mathbf{p}) , and in particular,

$$\Psi(\mathbf{U}^*, \mathbf{p}^*; T) < \Psi(\mathbf{I}, 0; T).$$
(6.3)

For a quantitative and explicit exposition, we further assume that the bulk internal energy is smooth so that it can be well approximated by truncated Taylor expansions in neighborhoods of $(\mathbf{U}^*, \mathbf{p}^*)$ and $(\mathbf{I}, 0)$ for a certain temperature *T*:

$$\begin{cases} \Psi(\mathbf{F},\mathbf{p};T) \approx \Psi(\mathbf{I},0;T) + B_T^1(\mathbf{U} - \mathbf{I},\mathbf{p}) & \forall (\mathbf{F},\mathbf{p}) \in \mathscr{N}(\mathbf{I},0), \\ \Psi(\mathbf{F},\mathbf{p};T) \approx \Psi(\mathbf{U}^*,\mathbf{p}^*;T) + B_T^2(\mathbf{U} - \mathbf{U}^*,\mathbf{p} - \mathbf{p}^*) & \forall (\mathbf{F},\mathbf{p}) \in \mathscr{N}(\mathbf{U}^*,\mathbf{p}^*), \end{cases}$$
(6.4)

where the linear terms are absent since $(\mathbf{U}^*, \mathbf{p}^*)$ and $(\mathbf{I}, 0)$ are local minimizers, B_T^1 and B_T^2 are nonnegative quadratic forms and the coefficients of these quadratic forms in a linear setting can be interpreted as some familiar material properties such as stiffness tensor, dielectric constants and piezoelectric coupling coefficients. Further, if $|T - T_c^0| << 1$, the leading terms in (6.4) can be further approximated as

$$\begin{cases} \Psi(\mathbf{I}, 0, T) \approx \Psi(\mathbf{I}, 0, T_c^0) + k_1(T - T_c^0), \\ \Psi(\mathbf{U}^*, \mathbf{p}^*, T) \approx \Psi(\mathbf{U}^*, \mathbf{p}^*, T_c^0) + k_2(T - T_c^0), \end{cases}$$
(6.5)

where k_1, k_2 are expansion constants. To conform with the requirements (6.3)-(6.5), we immediately have

$$k := k_1 - k_2 < 0. \tag{6.6}$$

We now consider the surface internal energy associated with the body before and after phase transition. By the Gurtin-Murdoch's model of surface elasticity, we have assumed that the surface internal energy density is given by $W_s(\mathbf{F};T)$ in (6.1) where, for simplicity, the polarization dependence of surface energy has been neglected. Following the paradigm of classic nonlinear elasticity, upon linearization one can then show that

$$W_s(\mathbf{F};T) \approx W_s^0(T) + \mathbf{S}_T^0 \cdot (\mathbf{U} - \mathbf{I}), \tag{6.7}$$

where $\mathbf{S}_T^0 \in \mathbb{R}_{\text{sym}}^{3 \times 3}$ is the residual surface stress which in general depends on the orientation of the local surface. We remark that since surfaces/interfaces are of two dimensions, the surface elastic energy shall depend only on the stretching within the surface, and hence the residual surface stress "lives only on the surface" in the sense that

$$\mathbf{S}_T^0 \in \mathbb{M} := \{ \mathbf{M} \in \mathbb{R}^{3 \times 3}_{\text{sym}} : \mathbf{Mn} = 0 \},\$$

where **n** is the unit normal on the surface $\partial \Omega$. For simplicity, we further assume that the residual surface stress is "hydrostatic" on the surface:

$$\mathbf{S}_T^0 = \tau(T)(\mathbf{I} - \mathbf{n} \otimes \mathbf{n}). \tag{6.8}$$

In addition, the scalar function $\tau(T)$ may be expanded and truncated as

$$\tau(T) \approx \tau(T_c^0) + \beta(T - T_c^0), \tag{6.9}$$

where $\beta \in \mathbb{R}$ is again an expansion constant.

Based on the above approximations, we are ready to address how the phase transition temperature T_c depends on the shape and size of the particle Ω . We will assume that the particle is small enough such that it would have uniform polarization with a



Figure 6.1: Ferroelectric ellipsoidal pariticle

single domain after transiting to the ferroelectric phase. Further, we assume that the particle Ω is of the shape of an axisymmetric ellipsoid with semi-axis length *a*,*b*, and that the angle between the spontaneous polarization \mathbf{p}^* is given by θ (See Fig. 6.1). From the classic theory of electrostatics, it is well-known that the associated field energy of a uniformly polarized ellipsoid is given by

$$\frac{\varepsilon_0}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 = \frac{1}{2\varepsilon_0} |\Omega| \mathbf{p}^* \cdot \mathbf{D} \mathbf{p}^*, \qquad (6.10)$$

where $\mathbf{D} \in \mathbb{R}^{3 \times 3}_{\text{sym}}$ is the *depolarization matrix* which depends only on the aspect ratio of the ellipsoid.

In account of the field energy and the surface energy, the transition temperature T_c shall be such that the non-ferroelectric phase has the same free energy as the ferroelectric phase:

$$F[\mathbf{x},0;T_c] = F[\mathbf{U}^*\mathbf{x},\mathbf{p}^*;T_c].$$

In other words, by (6.1), (6.7) and (6.10) we have

$$|\Omega|\Psi(\mathbf{I},0;T_c) + |\partial\Omega|W_s(\mathbf{I};T_c) = |\Omega|\Psi(\mathbf{F}^*,\mathbf{p}^*;T_c) + \frac{1}{2\varepsilon_0}|\Omega|\mathbf{p}^*\cdot\mathbf{D}\mathbf{p}^* + |\partial\Omega|W_s(\mathbf{F}^*;T_c).$$

Inserting (6.8)-(6.9) into the above equation, by (6.5) and (6.6) we obtain

$$k(T_c - T_c^0) = \frac{1}{2\varepsilon_0} \mathbf{p}^* \cdot \mathbf{D} \mathbf{p}^* + \frac{|\partial \Omega|}{|\Omega|} \gamma_s, \qquad (6.11)$$

where

$$\gamma_s = [\tau^0 + \beta (T_c - T_c^0)] \mathbf{v}, \qquad \mathbf{v} = \int_{\partial \Omega} (\mathbf{F}^* - \mathbf{I}) \cdot (\mathbf{I} - \mathbf{n} \otimes \mathbf{n})$$

Solving (6.11) for T_c we conclude that

$$T_c - T_c^0 = \frac{1}{k - \beta \nu |\partial \Omega| / |\Omega|} \left(\frac{1}{2\varepsilon_0} \mathbf{p}^* \cdot \mathbf{D} \mathbf{p}^* + \frac{\nu \tau^0 |\partial \Omega|}{|\Omega|} \right).$$
(6.12)

Particularly for spherical particles, equation (6.12) writes

$$T_c - T_c^0 = \frac{1}{k - 3\beta \nu/r} \left(\frac{1}{2\varepsilon_0} \mathbf{p}^* \cdot \mathbf{D} \mathbf{p}^* + \frac{3\nu \tau^0}{r} \right), \tag{6.13}$$

where r is the radius and

$$\mathbf{v} = \frac{2}{3} \mathrm{Tr}(\mathbf{F}^* - \mathbf{I}).$$

6.3 Conclusion and discussion

The plots of size dependence of phase transition temperature and estimations of critical size for $PbTiO_3$ and $BaTiO_3$ nano-particles are shown in Figure 6.2 and 6.3, respectively. Since the surface tension τ_0 of these particles are very small (around $1J/m^2$), the second term in bracket of (6.13) is ignorable comparing to the first term. The estimated relations are obtained by fitting the parameters *k* and α . The model also predicts the critical sizes of particles by

$$r_c = \frac{3\beta v}{\frac{\mathbf{p}^* \cdot \mathbf{D} \mathbf{p}^*}{2\varepsilon_0 T_c^0} + k}.$$
(6.14)

The surface stress plays an important role in our model, since for small particles the surface energy becomes important in the total free energy. From (6.13), the internal energy change rate k determines the gap of Curie temperature between bulk and micrometer scale particles. The term $3\beta v/r$ on the denominator is contributed by the surface tension, which results in the temperature drop when r gets smaller in this model. v is a constant in phase transition denoting percentage of surface area change for particles.



Figure 6.2: Comparison of model estimation (solid line) and experimental data (\circ [5] and \times [6]) of *PbTiO*₃ ($\mathbf{p}^* = 0.812 * (1,0,0)C/m^2$, v = 0.012 for spherical *PbTiO*₃ particles). Fitting parameters are $k = -6.815 \times 10^9 J/(m^3 * K)$ and $\beta = -1.184 \times 10^4 J/(m * K)$



Figure 6.3: Comparison of model estimation (solid line) and experimental data (\circ [7]) of $BaTiO_3$ ($\mathbf{p}^* = 0.263 * (1,0,0)C/m^2$, v = -0.00113 for spherical $BaTiO_3$ particles). Fitting parameters are $k = -5.851 \times 10^9 J/(m^3 * K)$ and $\beta = 6.149 \times 10^5 J/(m * K)$

Chapter 7 Conclusions

In this dissertation 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 (3.37) 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 M_1 and M_2 defined by (3.19) and (3.21) necessarily satisfy (3.31) and are such that the *algebraic Riccati equation* (3.32) admits a positive definite solution for every rational crystal plane. This places non-obvious restrictions on the underlying atomistic model that appear to have been unnoticed before. (iii) A simple surface reconstruction criterion is obtained, i.e., if $M_0 - M_1 + \Lambda$ is not positive definite, by (3.35) 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.

With the help of this framework we have developed a numerical method to quickly calculate the surface tensions in various directions for given material. The data agrees very well with prior MD simulations but much more efficient. The calculated surface tensions have been used for the Wulff construction to determine the equilibrium shape of crystals.

The impact of surface elasticity in wave propagation has been carefully analyzed. First, as an example of wave propagation in inhomogeneous media, we have performed FEM simulations for free surface wave in periodic half-space. The dispersion relation has been found to be nonlinear and the band gaps have been noticed.

Secondly, with consideration of surface elasticity, we have studied interfacial waves that propagate at the interface between two half spaces and decay away from the interface. A sufficient condition for the existence and uniqueness of subsonic interfacial waves is obtained for general anisotropic half spaces. As example, we present the explicit secular equation for determining the dispersion relation of subsonic interfacial waves for two isotropic half spaces with an isotropic interface. The secular equation can also be used to determine interfacial waves at the interface between solid and fluid. The important effects of surface elasticity on the dispersion relation of interfacial waves are then parametrically studied by explicitly solving the secular equation. In particular, we notice that the interfacial waves are now dispersive, strongly frequency-dependent, and surface-property dependent. We anticipate these fundamental results may have important applications in modeling dynamic behaviors of sandwich structures, designing acoustic wave guides and filters, and probing surface and bulk properties of material among others.

Thirdly, we have also analyzed the reflection and refraction of bulk waves at the interface of two solids when surface elasticity is taken into account. We have analytically derived the amplitude radios, energy rates, existence criteria and critical angles of reflected and refracted waves for incident SH-waves, P-waves and SV-waves respectively. Analytic derivations and numerical calculations in all the three cases show some new and distinct characteristics: (i) both the reflected and refracted waves have phase shifts from incident waves; (ii) The amplitude ratio becomes dependent on incident wave number; (iii) in some cases there may exist a critical incident angle bigger than which the reflected or refracted waves become typical interfacial waves studied in Section 5.2, and in those scenarios the wave propagation energy cannot penetrate through the interface.

Finally we have proposed a model for the size effect of phase transition temperature for ferroelectric nano-particles. In the model the surface stress has been found to be an important factor for the size effect. By fitting two physical parameters, the model agrees well with experimental data for some common ferroelectric particles. Further, the critical size of ferroelectric particles has been predicted by this model.

Appendix A

Core codes (Matlab) for speedy calculation of surface tension

```
function [dens] = evalden(r)
global BETA rhoe re
% Evaluate electron density contribution of one atom.
dens=exp(-BETA*(r/re-1))/rhoe;
end
function [ phi ] = evalpair( r )
% Evaluate pair potential between two atoms.
global PHIE GAMMA re
phi=PHIE*exp(-GAMMA*(r/re-1));
end
function [Frho] = evalembed(rden)
global EC PHIE BETA ALPHA GAMMA
8
   evaluate embedded energy
x=(rden) ^ (ALPHA/BETA);
y=(rden) ^ (GAMMA/BETA);
Frho=-EC*(1-log(x))*x-6*PHIE*y;
end
function [ sum ] = lsumd(d, ln)
% sum up electron density of a layer of atoms
global A data2;
```

```
sum=0;
for i=1:length(data2)
    if data2(i,1)==ln
    sum=sum+evalden(sqrt(d<sup>2</sup>+data2(i,2)*A<sup>2</sup>));
    end
function [ sum ] = lsump(d,ln)
% sum of pair potentials between layers
global A data2;
sum=0;
for i=1:length(data2)
    if data2(i,1) == \ln
      sum=sum+evalpair(sqrt(d^2+data2(i,2)*A^2));
    end
function X=solve_are(A,B,C,x0)
% solve Algebraic Riccati equation
if nargin==3, x0=rand(size(A));end
options=optimset('TolFun', 1e-6);
x=fsolve(@new_are,x0(:),[],A,B,C);
```

```
end
```

X=reshape(x, size(A));

end end

end end

function [y]=new_are(x,A,B,C) % Define Algebraic Riccati equation X=reshape(x,size(A)); y1=A*X+B*X*X+C; y=y1(:); end

```
function [ Et] = Caltotenrgy( D )
```

```
%Calculate total energy for finite difference method
global N
rho0=lsumd(0,0); %Electron density of the layer the atom is in
den=zeros(100,1);
den=den+rho0;
% number of nearest interaction layers
for i=1:N
    dd=zeros(N+i-1,1);
    for j=1:N
        for k=0:j-1
        dd(j) = dd(j) + D(i+k);
        end
        den(i) = den(i) + lsumd(dd(j),j);
    end
    for j=1:i-1
        for k=1:j
        dd(j+N) = dd(j+N) + D(i-k);
        end
        den(i) = den(i) + lsumd(dd(j+N), j);
    end
    dd;
end
for i=N+1:80;
    dd=zeros(2*N,1);
    for j=1:N
        for k=0:j-1
        dd(j) = dd(j) + D(i+k);
        end
        den(i) = den(i) + lsumd(dd(j),j);
    end
    for j=1:N
        for k=1:j
        dd(j+N) = dd(j+N) + D(i-k);
        end
```

```
den(i)=den(i)+lsumd(dd(j+N),j);
   end
end
Et=0;
for i=1:80
   Et=Et+evalembed(den(i));
end
for i=1:80
   dd=0;
   for j=1:N
        dd=dd+D(i+j-1);
       Et=Et+lsump(dd,j);
    end
end
end
function [ e ] = calcuterg( d0)
% Calculate the surface energy contributed by broken bonds.
global A N
rho0=lsumd(0,0);
den=zeros(N,1);
den=den+rho0;
for i=1:N
   den=den+lsumd(i*d0,i);
end
for i=2:N
   for j=2:i
    den(i)=den(i)+lsumd((j-1)*d0,j-1);
   end
end
den0=rho0;
for i=1:N
   den0=den0+2*lsumd(i*d0,i);
end
```

```
den0;
e=-N*evalembed(den0);
den;
for i=1:N
    e=e+evalembed(den(i));
end
for i=1:N
    e=e-0.5*i*lsump(i*d0,i);
end
end
function [ Et ] = Etpftcrstl( d)
% Calculate total energy as function of neighboring layer distance
% so as to determine the equilibrium neighboring layer distance
global N;
rho0=lsumd(0,0);
rden=rho0;
for i=1:N
rden=rden+2*lsumd(i*d,i);
end
Et=evalembed(rden);
for i=1:N
Et=Et+lsump(i*d,i);
end
end
% Main file
global EC PHIE BETA ALPHA GAMMA A re rhoe data2 N
% Parameters of Au EAM potential
EC=3.93;
PHIE=0.65;
ALPHA=6.37;
BETA=6.67;
```

```
GAMMA=8.2;
A=4.08;
re=A/sqrt(2);
%Step size of finite difference method
delta=0.0002;
%Surface normal direction
n=[2,2,1]; %modify
%#of interactive neighboring atom layers
N=8;
          %modify
%Relative position of neighboring atoms
%FCC crystals, a unit is half of lattice constant
Cord=...
[1,1,0;
1,-1,0;
 -1,1,0;
 -1,-1,0;
 1, 0, 1;
 1,0,-1;
 -1,0,1;
 -1,0,-1;
 0,1,1;
 0,1,-1;
 0,-1,1;
 0,-1,-1;
 2,0,0;
 -2,0,0;
 0,2,0;
 0,-2,0;
 0,0,2;
 0,0,-2;
```

2,1,1; 2,1,-1; 2,-1,1; 2,-1,-1; -2,1,1; -2,1,-1; -2,-1,1; -2,-1,-1; 1,2,1; 1,2,-1; -1,2,1; -1,2,-1; 1,-2,1; 1,-2,-1; -1,-2,1; -1,-2,-1; 1,1,2; 1,-1,2; -1,1,2; -1,-1,2; 1,1,-2; 1,-1,-2; -1,1,-2; -1,-1,-2; 2,2,0; 2,-2,0; -2,2,0; -2,-2,0; 2,0,2; 2,0,-2; -2,0,2; -2,0,-2; 0,2,2; 0,2,-2;

-3,1,0; -3,-1,0;

0,-2,2; 0,-2,-2;

3,1,0; 3,-1,0; 3,0,1; 3,0,-1;

- -3,0,1;
- -3,0,-1;
- 1,3,0;
- -1,3,0;
- 0,3,1;
- 0,3,-1;
- 1,-3,0;
- -1,-3,0;
- 0,-3,1;
- 0,-3,-1;
- 1,0,3;
- -1,0,3;
- 0,1,3;
- 0,-1,3;
- 1,0,-3;
- -1,0,-3;
- 0,1,-3;
- 0,-1,-3];
- dd0=1/normest(n); $%(\star A/2)$

```
%Define positions of atoms in each layer
dott=zeros(78,4);
dott(:,1:3)=Cord;
for i=1:78
     Cord(i,4)=n(1)*Cord(i,1)+n(2)*Cord(i,2)+n(3)*Cord(i,3);
```

```
end
```

```
[Trash,I]=sort(Cord(:,4));
Cord=Cord(I,:);
j=1;
for i=1:78
   if Cord(i, 4) >= 0
       data(j,:)=Cord(i,:);
       j=j+1;
   end
end
l=length(data);
data2=zeros(1,2);
for i=1:1
    a=data(i,1:3);
    data2(i,1)=data(i,4);
    data2(i,2)=normest(a)^2-(dd0*data(i,4))^2;
    % all values should times A<sup>2</sup>/4
end
data2(:,2)=data2(:,2)/4;
%Total electron density of an atom in perfect crystal
rhoe=12*exp(-BETA*(re/re-1))+6*exp(-BETA*(sqrt(2)*re/re-1))
+24*exp(-BETA*(sqrt(3)*re/re-1))+12*exp(-BETA*(2*re/re-1))
+24*exp(-BETA*(sqrt(5)*re/re-1));
%Distance of Neighboring layer
d0=fminsearch(@(d) Etpftcrstl(d),3)
```

```
%Calculate matrix M_0
KK0=zeros(N,N);
D=zeros(100,1);
D0=D+d0;
Dxy=D0;
Dx=D0;
Dy=D0;
Dy=D0;
Dxy(2)=d0-delta;
```

```
Dx(1)=d0-delta;
Dy(1)=d0+delta;Dy(2)=d0-delta;
KK0(1,2)=(Caltotenrgy(Dxy)-Caltotenrgy(Dx)...
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
KK0(2,1)=KK0(1,2);
```

```
for i=3:N
```

Dxy=D0;

Dx=D0;

Dy=D0;

_

Dxy(1)=d0-delta;Dxy(i-1)=d0+delta;Dxy(i)=d0-delta;

```
Dx(1)=d0-delta;
```

Dy(i-1)=d0+delta;Dy(i)=d0-delta;

KK0(1,i) = (Caltotenrgy(Dxy) - Caltotenrgy(Dx)...

```
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
```

```
KKO(i,1)=KKO(1,i);
```

end

```
for i=2:N-1
Dxy=D0;
Dx=D0;
Dy=D0;
Dxy(i+1)=d0-delta;Dxy(i-1)=d0+delta;
Dx(i)=d0-delta;Dx(i-1)=d0+delta;
Dy(i)=d0+delta;Dy(i+1)=d0-delta;
KK0(i,i+1)=(Caltotenrgy(Dxy)-Caltotenrgy(Dx)...
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
KK0(i+1,i)=KK0(i,i+1);
end
```

```
for j=2:N-2
for i=2:N-j
Dxy=D0;
Dx=D0;
```

```
Dy=D0;
Dxy(i-1)=d0+delta;Dxy(i)=d0-delta;Dxy(i-1+j)=d0+delta;Dxy(i+j)=d0-delta;
Dx(i-1)=d0+delta;Dx(i)=d0-delta;Dy(i-1+j)=d0+delta;Dy(i+j)=d0-delta;
KK0(i,i+j)=(Caltotenrgy(Dxy)-Caltotenrgy(Dx)...
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
KK0(i+j,i)=KK0(i,i+j);
end
end
```

```
%calculate matrix M.1 and M.2
k=zeros(N,1);
Dxy=D0;
Dx=D0;
Dy=D0;
Dxy(51)=d0-delta;Dxy(49)=d0+delta;
Dx(50)=d0-delta;Dx(49)=d0+delta;
Dy(50)=d0+delta;Dy(51)=d0-delta;
k(1)=(Caltotenrgy(Dxy)-Caltotenrgy(Dx)...
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
for j=2:N
Dxy=D0;
Dx=D0;
Dy=D0;
```

```
Dxy(49)=d0+delta;Dxy(50)=d0-delta;Dxy(49+j)=d0+delta;Dxy(50+j)=d0-delta;
Dx(49)=d0+delta;Dx(50)=d0-delta;Dy(49+j)=d0+delta;Dy(50+j)=d0-delta;
k(j)=(Caltotenrgy(Dxy)-Caltotenrgy(Dx)...
-Caltotenrgy(Dy)+Caltotenrgy(D0))/delta^2;
end
```

```
k0=0;
for i=1:N
k0=k0-2*k(i);
end
```

```
KKl=zeros(N,N);
KK2=zeros(N,N);
for i=1:N
    for j=1:i
       KK2(i,j)=k(N-i+j);
    end
end
for i=1:N
   KK1(i,i)=k0;
end
for i=2:N
   for j=1:i-1
        KK1(i,j)=k(i-j);
        KK1(j,i)=KK1(i,j);
    end
end
for i=1:N
    KK0(i,i) = - sum(KK0(i,:));
    for j=1:i
       KKO(i,i)=KKO(i,i)+k(N+1-j);
    end
end
%Calculate vector f
Dx=D0;
Dy=D0;
Dx(1) = d0 - delta;
Dy(1)=d0+delta;
F0=zeros(N,1);
F0(1) = (Caltotenrgy(Dx) - Caltotenrgy(Dy)) / (2 * delta);
```

```
Dx=D0;
Dy=D0;
Dx(i-1)=d0+delta;Dx(i)=d0-delta;
Dy(i-1)=d0-delta;Dy(i)=d0+delta;
F0(i)=(Caltotenrgy(Dx)-Caltotenrgy(Dy))/(2*delta);
end
```

```
%Amplify the constant matrices for accurate results
AA=KK1*1e10;
B=KK2*1e10;
C=KK2'*1e10;
X=solve_are(AA,B,C); %Solve Algeraic Riccati Equation
ei=eig(X)
```

```
%Solve layer displacements
KK = KK0 + KK2 * X;
u0=(KK0+KK2 \star X) \setminus (-F0);
uu=[u0;X*u0;
X*X*u0;
X*X*X*u0];
mm=length(uu);
dis=zeros(mm-1,1);
for i=1:mm-1 % for upper half space
    dis(i)=uu(i+1)-uu(i);
end
dis
dis0=dis-dis(mm-1); %components: w2-w1;w3-w2;....%
uuu=zeros(N,1);
%Calculate layer distance changes
for j=1:N
for i=j:mm-1
    uuu(j)=uuu(j)-dis0(i);
```

end

end

%Calculate relaxation energy erax=0.5*dot(uuu,F0) %Calculate broken bonds energy ecut=calcuterg(d0) %Total surface energy (ev/atom) ES=ecut+erax %Surface tension es=ES*16.02/(A^3/4/(dd0*A/2))% d0

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