Surface lattice Green’s functions for high-entropy alloys

Wolfram G Nöhring1,∗, Jan Grießer1, Patrick Dondl2,3 and Lars Pastewka1,3

1 Department of Microsystems Engineering, University of Freiburg, Georges-Köhler-Allee 103, 79110 Freiburg, Germany
2 Department of Applied Mathematics, University of Freiburg, Hermann-Herder-Str. 10, 79104, Freiburg, Germany
3 Cluster of Excellence livMatS, Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany

E-mail: w.noehring@web.de

Received 23 July 2021, revised 7 November 2021
Accepted for publication 22 November 2021
Published 17 December 2021

Abstract
We study the surface elastic response of pure Ni, the random alloy FeNiCr and an average FeNiCr alloy in terms of the surface lattice Green’s function. We propose a scheme for computing per-site Green’s function and study their per-site variations. The average FeNiCr alloys accurately reproduces the mean Green’s function of the full random alloy. Variation around this mean is largest near the edge of the surface Brillouin-zone and decays as $q^{-2}$ with wavevector $q$ towards the Γ-point. We also present expressions for the continuum surface Green’s function of anisotropic solids of finite and infinite thickness and show that the atomistic Green’s function approaches continuum near the Γ-point. Our results are a first step towards efficient contact calculations and Peierls–Nabarro type models for dislocations in high-entropy alloys.

Keywords: atomistic simulation, elastic Green’s function, surface stiffness, half-space

(Some figures may appear in colour only in the online journal)

∗Author to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
1. Introduction

Atomistic simulations are routinely used to study atomic-scale details of elastic or plastic deformation of materials [1]. Frequently the number of atoms which are needed to resolve the most important details is small in comparison to the number of atoms that must be included in the simulation in order to reduce spurious boundary effects. One example is the simulation of a dislocation [2]. Here, one may be interested in atoms close to the dislocation core. However, a large number of atoms around the core must be included in the simulation to minimize image forces coming from the boundary. Another example is the simulation of a half-space subjected to surface traction [3], where one may want to focus on atoms near the surface. Simulation of an ideal half-space (infinite depth) is impossible, but it can be approximated by a domain with finite depth and fixed boundary conditions at the bottom. To avoid finite size effects, perturbations at the surface must be decoupled from the fixed boundary. The wavelength of the largest in-plane perturbation is equal to the width of the domain, and according to St. Venant’s principle, the depth at which the perturbations will attenuate is proportional to this wavelength. Hence, a large depth, i.e. a large number of subsurface atoms, may be necessary to simulate a wide half-space free from finite-size effects.

Fortunately, there are methods for reducing the number of atoms while minimizing boundary effects. The general approach is to work in linear response where the relationship between displacements and forces at the boundary can be expressed using a Green’s function that captures the sub-surface deformation. This is most straightforward in small-strain elasticity that is linear by construction. Such continuum approaches rely either on a discretization of the continuum domain (e.g. by finite elements—see for example references [4–9]) or through analytical or semianalytical Green’s functions (e.g. references [10–13]). Here, we focus on a class of methods where the atomistic domain is coupled to a flexible atomistic boundary governed by an elastic lattice Green’s function, see e.g. references [14–20]. The use of lattice Green’s function allows a coupling scheme that is seamless since it can be formulated within a single Hamiltonian [20] and hence does not give rise to ghost forces [21].

In the Green’s function method described in references [18, 20], the response of the removed substrate atoms is approximated by modifying the forces on atoms in the boundary region, see figure 1. The forces on atoms in this region are given by an effective stiffness tensor, the inverse of the elastic Green’s function of the boundary layer. References [18, 20] and the present work only regard the static limit, but the general approach outlined below is also amenable to a dynamic treatment [20, 22–24].

Let \( f_s(x_1, x_2, x_3) \) be the (static) force on the atoms in the boundary region as a function of coordinates \( x_1 \) and \( x_2 \) in the plane, and coordinate \( x_3 \) perpendicular to the plane with positive \( x_3 \) pointing into the substrate. Taking the Fourier transform with respect to the in-plane coordinates yields the representation \( \tilde{f}_s(q_1, q_2, x_3) \), with wavenumbers \( q_1 \) and \( q_2 \). If no external forces act on the substrate atoms, and \( \tilde{f}_s(q_1, q_2, x_3) \) were known, then in the static limit the displacements \( \tilde{u}_s(q_1, q_2, x_3) \) in the boundary could be calculated using the elastic Green’s function \( G_s(q_1, q_2, x_3) \),

\[
\tilde{u}_s(q_1, q_2, x_3) = G_s(q_1, q_2, x_3) \cdot \tilde{f}_s(q_1, q_2, x_3).
\]  

(1)

Inversion yields

\[
\tilde{f}_s(q_1, q_2, x_3) = \Phi_s(q_1, q_2, x_3) \cdot \tilde{u}_s(q_1, q_2, x_3),
\]

(2)

where \( \Phi_s = G_s^{-1} \) is a matrix of complex stiffness coefficients, which depends on the substrate configuration. The problem has thus been shifted from simulating substrate atoms to...
determining $\Phi_s$. In the case of unary systems, $G_s$ and $\Phi_s$ have been measured in molecular dynamics simulations using a fluctuation-dissipation theorem [18, 25], or directly calculated using a transfer matrix or renormalization group approach [20].

The outlined method is limited to homogeneous crystals, since it relies on the assumption that the Green’s functions are invariant under translation. This assumption breaks down in alloys. We are interested in the particular case of multi-principal element random alloys, where random occupation of lattice sites will render the Green’s functions random variables. Extension of the Green’s function method to this case may be possible using stochastic homogenization. We envision an approximation based on two-scale homogenization, where $\Phi_s$ is assumed to be composed of long-wavelength components at scale $\vec{x} = x_i (i = 1, 2, 3)$, and short-wavelength components at scale $\varepsilon$,

$$\Phi_s = \Phi_s \left( \frac{\vec{x}}{\varepsilon} \right). \quad (3)$$

A formal asymptotic expansion can be written as [26, 27]

$$\Phi_s \left( \frac{\vec{x}}{\varepsilon} \right) \approx \Phi_{s,1} \left( \frac{\vec{x}}{\varepsilon} \right) + \varepsilon \Phi_{s,2} \left( \frac{\vec{x}}{\varepsilon} \right) + \cdots \quad (4)$$

$\Phi_{s,1}$ and $\Phi_{s,2}$ are correctors in the sense of homogenization theory. The first represents an average effective stiffness. It bears mentioning that in the case of a 1D system with randomly distributed elastic constants, $\Phi_{s,1}$ is the harmonic average of those constants. In our example, $\Phi_{s,2}$ would presumably correct for fluctuations of $\Phi_s$ due specific site occupations within radius $r \propto \varepsilon$ around the atom.

The present manuscript is intended as the first step towards a stochastic homogenization model of Green’s functions of multi-principal element random alloys. For simplicity, we focused on the special case where only atoms in the boundary layer are retained, see figure 1. $\Phi_s$ is then the surface stiffness.

The first contribution of our manuscript is to show how to compute the exact distribution of $\Phi_s$ in molecular statics simulations with embedded atom method (EAM) [28] potentials. We calculated $\Phi_s$ by inversion of the Hessian matrix $H$ of the potential energy, the analytical solution of which we have derived for this class of interatomic potentials. We compared the stiffness
Figure 2. (a) Configuration used for calculating the surface stiffness $\Phi_s$ in side view (left) and top view (right). Atoms in the substrate layers (blue, thickness two times the potential cutoff radius) were fixed in positions corresponding to static equilibrium under fully periodic boundary conditions. Atoms in the subsurface (red) and surface (yellow) layers were free. Periodic boundary conditions were applied in the $x_1$- and $x_2$-directions. The (001) planes (perpendicular to the $x_3$-direction) are square lattices with $N_e$ atoms along the edges; the subsurface region consists of $N_p \ (001)$ planes. (b) Illustration of the calculation of $\Phi_s$: the upper left block of the Hessian matrix $H$ (left) involves only surface and subsurface atoms; this block is inverted and Fourier-transformed to obtain Green’s functions $G$ (middle); the upper left $3N_e \times 3N_e$ sub-block corresponding to interactions between surface atoms contains the surface Green’s functions $G_s$; each of the $N_e^2 \ 3 \times 3$ blocks contains the values of Green’s functions for one pair of atoms $\nu\mu$, i.e. one wavevector $(q_1, q_2)$ in the plane; one row of blocks corresponds to the Green’s functions with one site $\nu$ fixed; the surface stiffness matrices $\Phi_s$ are the harmonic averages obtained by first averaging block rows of $G_s$ and then calculating the matrix inverse of each block.
of the true random alloy to the stiffness of a mean-field model of the alloy, where we used the average-atom (A-atom) [29] approximation. Additionally, we present the anisotropic-elastic solution for $\Phi$, of a continuous half-space with finite thickness and compare the continuum stiffness to atomistic data. The A-atom and the continuum solution yield effective stiffnesses which could be used in place of $\Phi_{s,1}$.

Our results show that the atomistic solutions converges to the continuum in the limit of long wavelengths. At short wavelengths, the local environment of atoms controls $\Phi$, hence the continuum solution is a poor estimate. The average alloy model is a fair approximation for the mean stiffness of the true random alloy at all wavelengths, but fluctuations grow substantially as the wavelength decreases below $\lambda_c \approx 15.5a$, where $a$ is the lattice parameter.

2. Methods

2.1. Atomistic stiffness

We calculated the stiffnesses of the (001) surface of face-centered cubic (fcc) crystals using square slab configurations, see figure 2. The simulation cell was a rectangular prism with a square base. Consider a Cartesian coordinate system with directions $x_1$ and $x_2$ in the plane of the base. In order to simulate a half-space, we applied periodic boundary conditions along the $x_1$- and $x_2$-directions, and open boundary conditions along the $x_3$-direction. The lattice directions [110], [1\overline{1}0], and [00\overline{1}] of the crystal were parallel to the $x_1$-, $x_2$-, and $x_3$-directions of the cell.

The set of (001) planes can be partitioned into surface, subsurface, and substrate planes. There is only one surface plane, but $N_s$ subsurface and $N_u$ substrate planes. We call the corresponding sets of atoms $\Omega_s$, $\Omega_p$, and $\Omega_u$. Atoms in (001) planes form a 2D square lattice with lattice parameter $a = a_0/\sqrt{2}$, where $a_0$ is the fcc lattice parameter. Let there be $N_s$ atoms along the edge in the $x_1$- or $x_2$-direction, then there are $N_s^2$ atoms in each plane, and the total number of atoms is $N = (1 + N_p + N_u)N_s^2$. In order to eliminate surface effects at the bottom boundary, we fixed the substrate atoms in positions corresponding to static equilibrium under fully periodic boundary conditions and made the fixed substrate layer thicker than the maximum interaction distance of the potential. We used EAM [28] potentials, hence the required thickness was two times the cutoff radius $r_{cut}$ of the potential. The process of constructing the configurations depends on the material and is explained in detail below.

To determine the surface stiffnesses $\Phi_s$, we first calculated the Green’s functions $G$ by inverting the Hessian matrix $H$ of the potential energy $V^{int}$, see figure 2(b). The components of $H$ are

$$H_{3(\mu-1)+(3(\nu-1)+j)} = \left. \frac{\partial^2 V^{int}(\{\vec{x}\})}{\partial x_\nu^{(i)} \partial x_\mu^{(j)}} \right|_{\{\vec{x}\}_0},$$

where indices $\mu, \nu \in [1, N]$ refer to atoms, and indices $i, j \in [1, 2, 3]$ refer to the three components of a vector in $x_1$-, $x_2$- and $x_3$-direction. In this equation $\{\vec{x}\}$ is the set of position vectors of the atoms $\{\vec{x}\} \equiv \{x^{(1)}, \ldots, x^{(N)}\}$, and $x_\nu^{(i)}$ is the coordinate of atom $\nu$ in $i$-direction. $\{\vec{x}\}_0$ is the set of equilibrium positions where the force on the atoms vanishes. We used the analytical solution of $H$ for EAM potentials, see the derivation in appendix A. This solution is implemented in the Python package matscipy [30].

However, the method for calculating Green’s functions that we present in the following is not specific to EAM potentials. It does not matter how $H$ is computed, and one could use any other class of potentials, or even ab initio methods. The matscipy package also
implements analytical solutions for $H$ of (12-6 and 8-4 [31]) Lennard-Jones [32] potentials; polydisperse potentials [33, 34]; and cluster- and bond-order-potentials: Stillinger–Weber [35], Tersoff–Brenner [36, 37], and Kumagai et al [38]. If no analytical solution for $H$ is available, a numerical approximation could still be calculated using finite differences.

$H$ is a real symmetric $3N \times 3N$ matrix. It is sparse, because the range of interaction between atoms is limited. Consider an arbitrary displacement of the atoms, written as a $3N$-dimensional vector $\vec{u}$. Within the harmonic approximation, the components of the resulting force vector $\vec{f}$ are

$$f_{3(\nu-1)+i} = H_{3(\nu-1)\cup(3(\mu-1)+j)} u_{3(\mu-1)+j}, \quad (i = 1, 2, 3)$$

(6)

where repeated indices imply summation over the corresponding range. Recall that the atoms in $\Omega_u$ are fixed in their equilibrium positions, hence $\vec{u}$ vanishes for those atoms. To impose this constraint, we computed $H$ of the whole configuration, but then eliminated elements in $H$ corresponding to pairs of atoms where one or both of them are in $\Omega_u$. The remaining $3(1 + N_p)N_s \times 3(1 + N_p)N_s$ elements correspond to pairs of atoms in $\Omega_u \cup \Omega_p$. It is convenient to label the atoms such that these elements form the upper left block of $H$ (see figure 2(b)).

This block was then inverted to obtain Green’s functions $G_{3(\nu-1)\cup(3(\mu-1)+j)}$, which solve

$$u_{3(\nu-1)+i} = G_{3(\nu-1)\cup(3(\mu-1)+j)} f_{3(\mu-1)+j}, \quad (i = 1, 2, 3)$$

(7)

where $\nu, \mu \in \Omega_u \cup \Omega_p$. To bring out the block structure of $G_{3(\nu-1)\cup(3(\mu-1)+j)}$, we can rewrite this equation as

$$\vec{u}^{(\nu)} = \sum_{\mu \in \Omega_u \cup \Omega_p} G^{(\nu, \mu)} \cdot \vec{f}^{(\mu)}, \quad \nu \in \Omega_u$$

(8)

where $\vec{u}^{(\nu)}$ is the displacement vector of atom $\nu$, with components $u_{3(\nu-1)+i}(i = 1, 2, 3)$ in equation (7); $G^{(\nu, \mu)}$ is the $3 \times 3$ block $G_{3(\nu-1)\cup(3(\mu-1)+j)}$; and $\vec{f}^{(\mu)}$ corresponds to the components $f_{3(\mu-1)+i}(i = 1, 2, 3)$.

We inverted $H$ via Cholesky factorization, using petsc [39, 40] and mumps [41, 42]. The latter allows parallel calculation of the selected entries [43] in the upper left block of the matrix. Our C code can be obtained from reference [44]. Construction and inversion of $H$ are the most expensive steps in terms of computation time and memory. We investigated the scaling of the cost with problem size. The results are presented in appendix B. In brief, time and memory required for construction of $H$ grow approximately linearly with the number of atoms. The memory required for selective inversion also scales linearly with problem size, but the computation time grows approximately quadratically. Note that for pure crystals, the surface Green’s function can be computed efficiently using renormalization group approaches for system sizes beyond billions of atoms [20].

Using the same argument to eliminate the substrate atoms from $H$, we now eliminate the subsurface atoms from $G$: the forces on the subsurface atoms must vanish since we are working static limit—which means that all subsurface atoms remain in their equilibrium positions. The remaining quantity is a $3N_s \times 3N_s$ matrix $G_s$ describing the degrees of freedom corresponding to the surface atoms. Equation (8) (with $\nu, \mu \in \Omega_u$) can be interpreted as a signal measured at $3N_s \times 3N_s$ points $\{(x_1^{(\nu)}, x_2^{(\nu)}) | \nu \in \Omega_u\}$ in the plane, and we write

$$\vec{u}_s(x_1^{(\nu)}, x_2^{(\nu)}) = \sum_{\mu \in \Omega_u} G_s(x_1^{(\nu)}, x_2^{(\nu)}; x_1^{(\mu)}, x_2^{(\mu)}) \cdot \vec{f}_s(x_1^{(\mu)}, x_2^{(\mu)}),$$

(9)
In a pure crystal with translational symmetry in the plane, Green’s functions would only depend on the relative distance between points, i.e. $G_s(x_1^{(o)}, x_2^{(o)}, x_1^{(o)}, x_2^{(o)}) \rightarrow G_s(x_1^{(o)} - x_1^{(o)}, x_2^{(o)} - x_2^{(o)})$, and equation (9) would be a convolution. According to the convolution theorem, taking the discrete Fourier transform of equation (9) would then produce equation (2).

However, in random alloys translational symmetry is broken. Thus, we studied the variation of stiffness across sites. We denote the Green’s functions of site $\nu$ as

$$G_s^{(o)}(x_1^{(o)} - x_1^{(o)}, x_2^{(o)} - x_2^{(o)}) \equiv G_s(x_1^{(o)}, x_2^{(o)}, x_1^{(o)}, x_2^{(o)})$$

in what follows. Note that in equation (10) the argument of $G_s^{(o)}$ is measured with respect to the position of the site $x^{(o)}$ such that we can carry out a Fourier-transform for each site. This representation is useful for comparison with the unary system and the continuum solution, where the per-site variation disappears from equation (10). Neglecting non-affine microdistortions [45–47], the atoms are arranged approximately in a simple cubic lattice within the periodic domain. Hence in equilibrium

$$(x_1^{(o)} - x_1^{(o)}, x_2^{(o)} - x_2^{(o)}) \approx (ma, na),$$

with $m, n \in \{0, \ldots, N_e - 1\}$. The discrete Fourier transform of $G_s^{(o)}(ma, na)$ is

$$G_s^{(o)} \left( \frac{2\pi}{a N_e} k, \frac{2\pi}{a N_e} l \right) = \sum_{m=0}^{N_e-1} \sum_{n=0}^{N_e-1} G_s^{(o)}(ma, na)$$

$$\times \exp \left\{ -2\pi i \left( \frac{mk}{N_e} + \frac{ml}{N_e} \right) \right\}, \quad \text{with } k, l \in \{0, \ldots, N_e - 1\}. \quad (12)$$

Thus, we map the solution to $N_e \times N_e$ wavevectors in the first Brillouin zone with components

$$q_1, q_2 \in \left\{ \left\{ \frac{N_e}{2}, \ldots, \frac{N_e}{2} - 1 \right\}, \frac{2\pi}{a N_e} \right\} \quad \text{if } N_e \text{ even}$$

$$\left\{ \left\{ \frac{N_e - 1}{2}, \ldots, \frac{N_e - 1}{2} \right\}, \frac{2\pi}{a N_e} \right\} \quad \text{if } N_e \text{ odd}. \quad (13)$$

However, due to symmetry only the quadrant $0 \leq q_1, q_2 \leq \pi/a$ is unique.

In an unary system, $G_s^{(o)}(q_1, q_2)$ is the same for all sites $\nu$. In a random alloy, on the other hand, there are site-by-site variations, and the components $G_s^{(o)}(q_1, q_2)$ of $G_s^{(o)}(q_1, q_2)$ become complex random variables.

Rather than discussing the surface Green function $G_s(q)$ itself, it is convenient to discuss its inverse, the surface stiffness $\Phi_s(q)$. This is because in the long-wavelength (continuum) limit $\Phi_s(q) \propto q$ [10, 18, 20] while $G_s(q)$ diverges. The question we will discuss in the following is how to characterize the mean response of the solid and the magnitude of per-site fluctuations.

We first computed a mean stiffness $\Phi_s(q_1, q_2)$. Consider the related problem of stochastic homogenization of an elastic continuum with fluctuating elastic constants. Here, the effective stiffness of the homogenized medium can be computed using the solution of a corrector equation [26, 27]. The solutions of the equation with random coefficients then converge to the solution of the homogenized equation in mean. In the one-dimensional case, the stiffness is a scalar, and it can be shown that the correct homogenized stiffness is the harmonic mean of the fluctuating site stiffness values, see for example [48]. A rigorous proof for higher dimensions is
not available, nevertheless we follow this approach and compute the harmonic mean stiffness. Let

\[ \Phi_\nu(q_1, q_2) \equiv (G_\nu(q_1, q_2))^{-1} \]  

be the stiffness of site \( \nu \). Following the continuum approach, we computed the average surface stiffness as

\[ \Phi_s(q_1, q_2) = \left\langle (\Phi_\nu(q_1, q_2))^{-1} \right\rangle^{-1} = G_s^{-1}(q_1, q_2), \]  

where \( \langle \ldots \rangle \) indicates the arithmetic mean over all sites, i.e. the components of \( G_s(q_1, q_2) \) are

\[ G_{s,ij}(q_1, q_2) = \frac{1}{N^2} \sum_{\nu=1}^{N^2} G_{\nu,ij}(q_1, q_2). \]  

Equations (12) and (14)–(16), have been implemented in the Python package \texttt{surface_stiffness} [49].

We calculated \( \Phi_s(q_1, q_2) \) of pure Ni, and \( \Phi_s(q_1, q_2) \) of a random solid solution of Fe, Ni and Cr with equal concentration of all elements. In both cases, we used the EAM potential by Bonny \textit{et al} [50], which has a smooth cutoff with continuous first and second derivatives. We prepared the random Fe–Ni–Cr alloy by randomly assigning the constituent elements to the lattice sites. Additionally, we performed calculations with a mean-field model. Here, we replaced the different real elements by a single ‘average’ element, the A-atom [29, 51]. It behaves like a pure metal with similar average properties as the true random solution. A module for generating A-atom potentials has been implemented in the Python package \texttt{matscipy} [30]. In pure Ni and the A-atom crystal, \( \Phi_\nu(q_1, q_2) \) is the same for all surface sites \( \nu \), hence \( \Phi_s(q_1, q_2) = \Phi_\nu(q_1, q_2) \).

The harmonic mean of the random alloy data according to equation (15) can be compared to the A-atom solution and the continuum solution. The latter requires only the thickness of the slab and three cubic elastic constants as input.

In the case of the Ni and A-atom configurations, our starting point was a perfect crystal lattice with the appropriate 0 K lattice parameter. We then minimized the potential energy of the surface and subsurface atoms using \texttt{fire} [52, 53]. The substrate atoms were fixed during minimization and the iteration was stopped as soon as the Euclidean norm of the global force vector fell below \( 1 \times 10^{-6} \) eV Å\(^{-1} \). In order to create the random FeNiCr alloy, we started from a thicker, fully periodic configuration. We added an additional slab of atoms of thickness greater than 2\( r_{\text{cut}} \) below the substrate and then minimized the potential energy under fully periodic boundary conditions. This minimization allowed the substrate atoms to move to their non-affine equilibrium positions in the bulk. Afterwards, we opened the boundary along the \( x_3 \)-direction and removed the extra atoms. Finally, we minimized the potential energy of the open system with fixed substrate atoms.

The required lattice parameters and elastic constants of the three materials are listed in table 2 in appendix C. See this appendix also for details on how the values were computed.

We consider Ni and FeNiCr as model materials, hence some deviation of materials parameters, such as elastic constants and surface energies, from their real-world values can be tolerated. However, we wanted to rule out that our key observations are specific to the EAM potential that we used. Thus, we performed a limited parameter study, where we repeated the calculation for average-alloy and random FeCuNi, as simulated with the EAM potential of reference [54]. The results are reported in appendix D. They agree qualitatively with the results for FeNiCr reported below.
Figure 3. Model used for deriving a continuum solution of the surface Green function and the associated stiffness tensor; the surface at \( x_3 = 0 \) is subjected to tractions \( \vec{Q}_s(x_1, x_2) \); we consider finite thickness \( h \) with fixed boundary conditions at \( x_3 = h \), and the limit \( h \rightarrow \infty \); the solid is infinite along \( x_1 \) and \( x_2 \); the material has anisotropic elastic constants \( C_{ijkl} \), which are constant throughout the body.

Moreover, we have verified that key observations are not specific to the \{1 0 0\} facet on which we focus here. In appendix E, we report additional calculations for the \{1 1 0\} facet of FeNiCr, which, however, agree qualitatively with the calculations for the \{1 0 0\} facet.

The method outlined in this section could also be extended to surfaces with a hexagonal symmetry, e.g. the fcc \{1 1 1\} surface. The Fourier transformation of the Green’s functions, equation (12) would then have to be performed on a hexagonal grid, using, for example, the fast hexagonal Fourier transform of Birdsong and Rummelt [55].

2.2. Continuum stiffness

We consider a semi-infinite solid, see figure 3. The body has a surface perpendicular to the \( x_3 \)-direction and extends to infinity in the \( x_1 \)- and \( x_2 \)- directions. Positive \( x_3 \) are located within the solid. In the \( x_3 \)-direction, the body may have a finite thickness \( h \), or infinite thickness \( h \rightarrow \infty \). We discuss both cases. Tractions \( \vec{Q}(x_1, x_2) \) are applied at the surface and there are no body forces. In the case where the body has finite thickness \( h \), we assume a fixed boundary, i.e. \( \vec{u}(x_1, x_2, h) = 0 \). The material is homogeneous and linear-elastic, with anisotropic elastic constants \( C_{ijkl} \) \((i, j, k, l \in [1, 2, 3])\) subject to the usual symmetry requirements [56]. For the fcc solid considered here, there are three indentent elastic constant that are typically denoted by \( C_{11}, C_{12} \) and \( C_{44} \).

We are interested in the surface displacements \( \vec{u}_s(x_1, x_2) \) in elastostatic equilibrium, where the divergence of the stress tensor \( \sigma \) vanishes,

\[
\partial_i \sigma_{ij} = 0. \tag{17}
\]

\( \partial_i \) indicates the partial derivative in direction \( i \) and Einstein summation convention applies. Equation (17) corresponds to requiring zero forces for the subsurface atoms in our atomistic calculations.

\( \vec{u}_s(x_1, x_2) \) can be calculated by a convolution of the tractions \( \vec{Q}(x_1, x_2) \) with surface Green’s function \( \vec{G}_s(x_1, x_2) \),

\[
\vec{u}_s(x_1, x_2) = \int dx'_1 dx'_2 \vec{G}_s(x_1 - x'_1, x_2 - x'_2) \cdot \vec{Q}(x'_1, x'_2). \tag{18}
\]
Fourier transformation yields equation (1) (with $x_3 = 0$ dropped). In appendix F, we derive $G_i(q_1, q_2)$ for finite $h$ and $h \to \infty$. The solution can be represented as a matrix product

$$G_i(q_1, q_2) = U(q_1, q_2, 0) \cdot F^{-1}(q_1, q_2).$$  \hspace{1cm} (19)

The matrices $U(q_1, q_2, 0)$ and $F(q_1, q_2)$ depend on the eigenvalues of the Fourier transform of the linear operator

$$M_i = C_{jkl} \partial_j \partial_k,$$  \hspace{1cm} (20)

and the admissible basis functions of the displacement field. No closed-form solution exists, but it is straightforward to calculate said eigenvalues and basis functions numerically. The inverse of $G_i(q_1, q_2)$ is the surface stiffness $\Phi_i(q_1, q_2)$. We have implemented the numerical solution of $\Phi_i(q_1, q_2)$ in the Python package ContactMechanics [57].

3. Results

We first calculated the surface stiffness of Ni to obtain reference data for a pure metal. The atomic configuration had $N_p = 31$ atoms along the edge, and $N_e = 44$ subsurface planes. All $N^2 = 961$ solutions of $\Phi_i^{(n)}$ for different surface sites $n$ are equal due to translational symmetry in the plane. Notice that $\tilde{F}^{(n)}$ in equation (9) of the atomistic solution is a force, whereas $\tilde{Q}$ in equation (18) of the continuum solution is a traction (units of N m$^{-2}$). In order to compare atomistic and continuum Green’s functions, we need to divide the former by the mean area per atom $a^2 = a_0^2/2$. The resulting Green’s function has SI units of N m$^{-3}$, but it is more convenient to use GPa Å$^{-1}$, since $\Phi_{x,11}$, for example, should converge to $C_{44}/h$ in the limit of infinite wavelength.

Figure 4 shows $\Re(\Phi_{x,33}(q_1, q_2))$ in the quadrant of the surface Brillouin zone where $0 \leq q_1$, $q_2 \leq \pi/a$. Here and in the following, $\Re$ and $\Im$ refer to the real and imaginary parts of a complex number, respectively. The other quadrants are symmetric with respect to the $q_1$- and $q_2$-axes. The stiffness is minimal in the long-wavelength limit $q_1 = q_2 = 0$ and increases with decreasing wavelength. The origin $q_1 = q_2 = 0$ is called $\Gamma$. The center of the edge of the Brillouin zone along $q_1$ is called $X$, and the corner is called $M$. Below, we show plots of values along the path $\bar{\Gamma} - \bar{X} - \bar{M} - \bar{\Gamma}$. To study convergence in the long-wavelength limit, we also consider a shorter path $\bar{\Gamma} - \bar{X}' - \bar{M}' - \bar{\Gamma}'$, where $\bar{X}'$ is on the line $q_2 = 0$, at 20% of the distance from $\bar{\Gamma}$ to $\bar{X}$. Point $\bar{M}'$ corresponds to a wavelength of $20a$ along the $x_1$- and $x_2$-directions.

The upper two rows of figure 5 show the six independent components of $\Phi_i$ along the path $\bar{\Gamma} \bar{X} \bar{M} \bar{\Gamma}$. Four moduli are purely real, namely the normal moduli $\Phi_{x,11}$, $\Phi_{x,22}$, and $\Phi_{x,33}$, as well as the in-plane shear modulus $\Phi_{x,12}$. The out-of-plane shear moduli $\Phi_{x,23}$ and $\Phi_{x,13}$ are purely imaginary. The discrepancy between the continuum data and the atomistic data increases as one moves away from the long-wavelength limit near $\bar{\Gamma}$ towards $X$ or $M$. The difference is maximum at corner of the surface Brillouin zone $M$, which represents the short-wavelength limit in both in-plane directions. In the case of the shear moduli, the continuum model fails to predict the extrema between $X$ and $M$ (zone edge), and between $M$ and $\Gamma$ (zone diagonal). The bottom row of figure 5 shows the components $\Phi_{x,11}$, $\Phi_{x,22}$, and $\Phi_{x,12}$ along the path $\bar{\Gamma} \bar{X}' \bar{M}' \bar{\Gamma}'$. These plots indicate that the continuum and atomistic solutions converge near $\bar{\Gamma}$. The solutions for $\Phi_{x,12}$ agree qualitatively. The atomistic value of $\Phi_{x,11}$ and $\Phi_{x,22}$ at $\bar{\Gamma}$ is 1.6 GPa Å$^{-1}$, which is equal to $C_{44}/h$ with $C_{44} = 125$ GPa and $h = (1 + N_p)a_0/2 = 45a_0/2 = 79.2$ Å.

Having examined the surface stiffness of pure Ni, we now attend to the alloy case. We created 500 random alloy samples and one average alloy sample with $N_p = 44$ and $N_e = 31$. In
Figure 4. Real part of stiffness component $\Phi_{33}$ of Ni in a quadrant of the surface Brillouin zone; in other figures we have plotted the values along the paths $\bar{\Gamma}-\bar{X}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}^\prime-\bar{X}^\prime-\bar{M}^\prime-\bar{\Gamma}$.

case of the random alloy, we checked the influence of $N_p$ by repeating the calculation with $N_p = 1 \ldots 44$ (one sample each), see appendix G. $N_p = 44$ is sufficient to achieve convergence in the short-wavelength region. Below, we report the arithmetic mean of $\Phi_{33}(q_1, q_2)$ of all random alloy samples. However, sample-by-sample variations of $\Phi_{33}(q_1, q_2)$ are small, since this is the homogenized stiffness with fluctuations averaged out. Additionally, we quantified site-by-site fluctuations by calculating the 10th and 90th percentiles of the sitespecific stiffness tensors $\Phi_{33}(q_1, q_2)$ at all sites in all samples, i.e. $500 \cdot N_e^2 = 480500$ sites in total.

Figure 6 shows the stiffness components along the paths $\bar{\Gamma}-\bar{X}-\bar{M}-\bar{\Gamma}$ and $\bar{\Gamma}^\prime-\bar{X}^\prime-\bar{M}^\prime-\bar{\Gamma}$. The upper two rows show the real parts of $\Phi_{11}, \Phi_{22}, \Phi_{33}, \Phi_{12}$, as well as the imaginary parts of $\Phi_{13}$ and $\Phi_{23}$ along $\bar{\Gamma}-\bar{X}-\bar{M}-\bar{\Gamma}$. The bottom row shows $\Re\Phi_{11}, \Re\Phi_{22}$, and $\Re\Phi_{12}$ along the long-wavelength path $\bar{\Gamma}^\prime-\bar{X}^\prime-\bar{M}^\prime-\bar{\Gamma}$. The average alloy behaves like a pure metal, hence $G_s(q_1, q_2)$ is the same for all surface sites, and there is one unique $3 \times 3$ stiffness matrix $\Phi_s(q_1, q_2)$ for every point $(q_1, q_2)$ in the Brillouin zone. In the random alloy, by contrast, $G_s(q_1, q_2)$ fluctuates, therefore a different stiffness $\Phi_s(q_1, q_2)$ would be obtained for a different element distribution. In figure 6, markers indicate the harmonic mean $\Phi_s(q_1, q_2)$, and shaded areas the 10th and 90th percentiles of the site stiffnesses $\Phi^{(v)}(q_1, q_2)$. Sample-by-sample variations of $\Phi_s(q_1, q_2)$ are negligible. The difference between the corresponding 10th and 90th percentiles is less than the size of the markers of $\Phi_s(q_1, q_2)$ in the plot.
Figure 5. Surface stiffness of Ni; markers: atomistic model; lines: anisotropic-elastic model; the upper two rows show the variation of the six independent components along the path $\bar{\Gamma}-\bar{X}-\bar{M}-\bar{\Gamma}$ through the first quadrant of the surface Brillouin zone (see figure 4); the normal moduli $\Phi_{s,11}$, $\Phi_{s,22}$, and $\Phi_{s,33}$, as well as the shear modulus $\Phi_{s,12}$ are purely real; the two in-plane shear moduli $\Phi_{s,23}$ and $\Phi_{s,13}$ are purely imaginary; atomistic and continuum models disagree near points $\bar{X}$ and $\bar{M}$, which are short wavelength limits; the lower row shows the values of $\Phi_{s,11}$, $\Phi_{s,22}$, and $\Phi_{s,12}$ along the shorter path $\bar{\Gamma}-\bar{X'}-\bar{M'}-\bar{\Gamma}$ through the long wavelength region; the relative difference between atomistic and continuum models decreases with increasing wavelength.

$\Phi_s(q_1,q_2)$ should be compared to the corresponding average alloy data and the continuum solution. All three models yield similar results in the long-wavelength limit. For example, the mean value of $\Re\Phi_{s,11}$ and $\Re\Phi_{s,22}$ at $\bar{\Gamma}$ is 1.70 GPa Å$^{-1}$. The average-alloy value is 1.74 GPa Å$^{-1}$ and the continuum solution is 1.70 GPa Å$^{-1}$. The continuum solution fails at short wavelengths, as was observed already in the Ni example. However, the average-alloy data remain comparatively close to the mean values of the random alloy. For example, the relative difference between $\Re\Phi_{s,11}$ of the average and random alloy varies between 3% and 4% along the path. The continuum solution, on the other hand, underestimates the mean along most of the path, except near $\Gamma$. Near $X$, the continuum value is 46% lower than the mean value of the random alloy. The absolute value of the relative difference between $\Re\Phi_{s,22}$ of the average and random alloy varies between 3% and 11%. In the case of $\Re\Phi_{s,33}$, the absolute relative difference does not exceed 4%. Recall that the continuum solution for $\Re\Phi_{s,12}$ of pure Ni was qualitatively different from the atomistic solution. The same is true for the alloy. The continuum solution has a local minimum at $M$, whereas both atomistic solutions have their minimum between $M$ and $\Gamma$.

Fluctuations in the random alloy data are close to zero at $\bar{\Gamma}$, but increase with decreasing wavelength. For example, the relative difference between the 90th percentile of the site-specific
Figure 6. Surface stiffness of an equicomposition FeNiCr alloy; the upper two rows show the real parts of $\Phi_{s,11}$, $\Phi_{s,22}$, $\Phi_{s,33}$, $\Phi_{s,12}$, as well as the imaginary parts of $\Phi_{s,13}$ and $\Phi_{s,23}$ along the path $\bar{\Gamma}–\bar{X}–\bar{M}–\bar{\Gamma}$ through the first quadrant of the surface Brillouin zone (see figure 4); the stiffness of the average alloy is close to the effective mean stiffness of the true random alloy according to equation (15); turquoise areas indicate the range between the 10th and 90th percentile of the distribution of site stiffnesses; stiffness fluctuations are small at long wavelengths; with the exception of $\Phi_{s,33}$, fluctuations grow significantly at short wavelengths; the lower row shows the values of $\Phi_{s,11}$, $\Phi_{s,22}$, and $\Phi_{s,12}$ along the path $\bar{\Gamma}–\bar{X'}–\bar{M'}–\bar{\Gamma}$ through the long wavelength region; fluctuations in the random alloy, and the relative discrepancy between the atomistic data and the anisotropic-elastic model (red line) are smaller than at short wavelengths.

values of $\Re \Phi_{s,11}$ and the mean according to equation (15) increases from less than 1% of the mean value at $\bar{\Gamma}$ to 70% at $\bar{X}$. Interestingly, it decreases to 38% at $\bar{M}$, even though $\bar{M}$ represents the limit of short wavelengths in both in-plane directions. The maximum fluctuations of $\Re \Phi_{s,33}$ are smaller than those of $\Re \Phi_{s,11}$ and $\Re \Phi_{s,22}$.

Figure 7 gives a more detailed view of convergence in the long wavelength limit, using the example of $\Re \Phi_{s,11}$. Figure 7(a) shows the ratio between the real values of the atomistic and continuum data along the diagonal $\bar{\Gamma}–\bar{M}$. At $\bar{\Gamma}$, the relative error between random alloy and continuum is below 1%. The average alloy stiffness is 2% higher than the continuum value. Figure 7(b) distinguishes between contributions from different elements. Let $\Omega_{\text{Fe}}$ be the set of sites occupied by Fe atoms. To generate the corresponding curve in figure 7(b), the average in equation (16) was restricted to sites $\nu \in \Omega_{\text{Fe}}$. Similarly, the 10th and 90th percentiles of $\Phi^{(\nu)}(q_1,q_2)$ were computed only for this subset. The calculation for the other elements is analogous. All three mean values converge in the limit of long wavelengths to the mean stiffness across all sites, and all fluctuations become minimal. Finally, in figure 7(c) we examined the growth of the dispersion of $\Re \Phi^{(\nu)}_{s,11}$ along $\bar{\Gamma}–\bar{M}$. The figure shows the difference between the
Figure 7. (a) Real part of $\Phi_{s,11}$ of average and true random FeNiCr, divided by the continuum solution; values along the diagonal $\Gamma - M$ of the first quadrant of the Brillouin zone; the shaded area shows the range between the 10th and 90th percentile of the site stiffness distribution in the random alloy; fluctuations in the random alloy go to zero as $\vec{q} \to \Gamma$; the mean value and the average alloy stiffness approach the continuum stiffness; (b) (same y-axis as (a)) shows the mean value and the standard deviation of $\Phi_{s}^{(\nu)}$ in the random alloy for sites $\nu$ with different elements; the fluctuations go to zero as $\vec{q} \to \Gamma$ and the mean values converge; (c) difference between the 90th and 10th percentile of $\Phi_{s}^{(\nu)}$, divided by the harmonic mean; the dashed line with a slope of 0.59 Å (slope/a = 0.24) is the result of a linear least-squares fit between $\Gamma$ and $q_1a = q_2a = 1.22$ (wavelength $\lambda_1 = \lambda_2 \approx 5a$).

90th and 10th percentile of $\Re\Phi_{s,11}^{(\nu)}$, divided by the harmonic mean. Between $\Gamma$ and $q_1a = q_2a = 1.22$ (corresponding to a wavelength of $\lambda_1 = \lambda_2 \approx 5a$), the ratio grows approximately linearly. A linear least-squares fit yields a slope of 0.59 Å.

4. Discussion

We observed that the average alloy accurately approximates the mean surface stiffness of the true random alloy over the surface Brillouin zone. The normal stiffness components $\Phi_{s,11}$, $\Phi_{s,22}$, and $\Phi_{s,33}$ are particularly important, because they generate the largest contributions to the force. The relative difference between the corresponding A-atom and random alloy values is typically small. We observed the largest relative errors in $\Phi_{s,22}$ near $X$, which represents the limit of short $x_1$-wavelength and infinite $x_2$-wavelength (and vice-versa by symmetry). However, the absolute value of $\Phi_{s,22}$ is also comparatively small between $\Gamma$ and $X$, yielding larger relative errors. $\Phi_{s,22}$ quickly increases with decreasing wavelength in $x_2$-direction and the relative error decreases. $\Phi_{s,11}$ behaves similarly near the upper corner of the Brillouin zone. Given that the overall errors are small over the full surface Brillouin zone, we conclude that the average alloy provides an accurate estimate of the mean forces on atoms in the random. This result is not surprising, since it was already shown in reference [29] that the A-atom has similar elastic constants as the corresponding true random alloy and the dependence of $\Phi_s$ near the Brillouin-zone edge is determined primarily by lattice structure. However, it is noteworthy that the average alloy matches the harmonic mean of the random alloy data, which is the appropriate case from the viewpoint of stochastic homogenization.

Another question is when continuum elasticity becomes a good approximation. This question can only be answered with respect to a relative measure that quantifies what we mean by 'good'. Figure 7(a) shows such a relative measure for one of the components of the stiffness
tensor. The point at $\bar{\Gamma}$ and next to it are affected by the finite depth of the sample, as they represent homogeneous deformation and deformation with a wavelength equal to the size of our box. The next point has an error of around 20% and corresponds to an 11- and 22-wavelength of $15.5a$. It is fair to conclude that for distances beyond $\lambda_c \approx 15.5a$, the continuum approximation is reasonable. The decomposition into the individual atomic sites (figure 7(b)) underlines this behavior, as the individual stiffnesses for Fe, Ni and Cr sites converge to a unified value near the point where the continuum solution appears appropriate.

A connected question is how the per-site fluctuations decay as a function of wavevector. It is clear that at large wavelength, where the continuum approximation holds, the per-site variation of $\Phi_s^{(0)}$ must be small. The per-site fluctuations are particularly small for the out-of-plane stiffness $\Phi_{s,33}$ (see figure 6(c)) where the continuum result has a lower error at intermediate wavelength as compared with the in-plane components $\Phi_{s,11}$ and $\Phi_{s,22}$ (figures 6(a) and (b)). The characteristic distance of $\lambda_c$ is therefore also a representative length beyond which per-site fluctuations become negligible. We now attempt a more quantitative analysis of this behavior. We divide the amplitude of the per-site fluctuations, as measured by the difference between the 90th and 10th percentile, by the stiffness matrix itself. As shown in figure 7(c), this ratio depends linearly on the wavevector $q$. Since $\Phi \propto q$, this implies that the amplitude of per-site fluctuations decays with wavelength $\lambda$ as $\lambda^{-2}$. This decay of the fluctuations should be compared to the decay of the error in quantitative stochastic homogenization [58–60], as shorter wavelengths are akin to taking smaller representative volumes of lateral length $\lambda$. Stochastic homogeneization predicts a scaling of $\lambda^{-2}$ for two-dimensional lattices.

Note that $\Phi_{s,33}$ is important for contact calculations [18, 20] while $\Phi_{s,11}$ and $\Phi_{s,22}$ are required for extended Peierls–Nabarro [61, 62] models of dislocations [63, 64] or sliding friction [65]. For dislocations in high-entropy alloys it is therefore of particular importance to capture the by-site fluctuations appropriately. Our results show that the A-atom potential could be used for calculating the mean $\Phi_{s,11}$ in equation (4). This observation is particularly interesting because Green’s functions of unary systems, such as the A-atom material, can be computed more efficiently than with the present brute-force approach, using a transfer matrix or renormalization group approach [20]. The per-site fluctuations, and the corrector $\Phi_{s,22}$, on the other hand, could then be obtained from the local structure within regions of size $\sim \lambda_c$ around the site of interest using perturbative approaches [66–70] or multipole expansions [71]. Since a local evaluation up to a cutoff distance scales linearly with the number of sites, this would give rise to a feasible computational scheme.

As a model material, we have considered only the case of a random ternary alloy in this study. Our method is not limited to the ternary case, and we do not expect qualitative changes in other random alloys. We speculate that fluctuations decrease in alloys with short range order (SRO), where site occupations are correlated. SRO also poses a problem for modeling the first corrector using the A-atom method, which assumes entirely uncorrelated site occupations. There is also a simple practical limitation when it comes to calculating the surface stiffness of other alloys: a suitable potential needs to be available. This potential should have a continuous and smooth cutoff such that the Hessian is well-defined (i.e. does not exhibit jumps). It is known that cutoff schemes can lead to spurious effects, for example when calculating the phonon spectrum [72, 73], which also implicitly relies on the Hessian.
5. Summary and outlook

We have calculated the effective surface stiffness of unary crystals and a three-component random (high-entropy) alloys. Our results show that the surface stiffness has significant per-site variation near the edge of the surface Brillouin-zone, but that these variations disappear for larger wavelengths upon approach to the continuum limit. We identify a length of roughly 15.5 atomic distances as the threshold where the continuum limit applies and per-site variations are small. At smaller distances, the average-atom approach of Varvenne and co-workers [29] accurately captures the mean response of the solid. Our results are a first step towards building multi-scale Peierls–Nabarro type models for dislocations in high-entropy alloys, that require an accurate model for the elastic response of the crystalline material that encloses the dislocation. The next step is to derive a perturbative expansion around the mean-field results presented here that allows the efficient calculation of per-site surface stiffnesses.

Acknowledgments

We are grateful for many useful discussions with Mark Robbins, Tristan Sharp, Joseph Monti and Antoine Sanner. Simulations were carried out with lammps [74] and ase [75]. Atomic configurations were rendered with ovito [76]. The authors acknowledge support from the Deutsche Forschungsgemeinschaft (Grants PA 2023/4, DO 1412/4) and the European Research Council (Grant 757343). Simulations were carried out at the Jülich Supercomputing Centre (Grant hka18) and on NEMO at the University of Freiburg (DFG Grant INST 39/963-1 FUGG).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix A. Hessian matrix within the embedded atom method

Below, we present the analytical solution for the Hessian matrix of the total potential energy in the EAM approximation. Greek superscripts refer to atom identifiers. For \( N \) consecutively numbered atoms \( \mu, \nu, \gamma, \delta \in [1,N] \). Lowercase roman subscripts refer to the components of a vector or tensor with respect to the three axes of a Cartesian coordinate system, i.e. \( i, j \in [1,2,3] \). \( x^{(\nu)}_i \) is the coordinate of atom \( \nu \) in direction \( i \). The \( i \)-component of the distance vector between atoms \( \nu \) and \( \mu \) is

\[
x^{(\nu \mu)}_i = x^{(\nu)}_i - x^{(\mu)}_i.
\]  

The absolute value of the distance vector is

\[
x^{(\nu \mu)} = \left( \left( x^{(\nu \mu)}_1 \right)^2 + \left( x^{(\nu \mu)}_2 \right)^2 + \left( x^{(\nu \mu)}_3 \right)^2 \right)^{1/2}.
\]

(A1)
Furthermore, we use the abbreviations
\[ \tilde{x}_i^{(\nu\mu)} \equiv \tilde{x}_i^{(\nu\mu)} \quad \text{and} \quad \tilde{x}_{ij}^{(\nu\mu)} \equiv \tilde{x}_i^{(\nu\mu)} \tilde{x}_j^{(\nu\mu)}. \] (A3)

The two symbols represent a normalized distance vector and the outer product of a normalized distance vector with itself, respectively. The expression for the Hessian involves the following derivatives of a pair distance vector and its absolute value:
\[ \frac{\partial x_i^{(\gamma\delta)}}{\partial x_j^{(\nu\mu)}} = \delta_{ij} \left( \delta_{\mu\delta} - \delta_{\gamma\nu} \right), \] (A5)
\[ \frac{\partial x_i^{(\gamma\delta)}}{\partial x_j^{(\nu\mu)}} = \tilde{x}_i^{(\gamma\delta)} \left( \delta_{\mu\delta} - \delta_{\gamma\nu} \right), \] (A6)

where \( \delta_{ij} \) is Kronecker’s delta, i.e. \( \delta_{ij} = 1 \) if \( i = j \) and \( \delta_{ij} = 0 \) otherwise.

In the EAM, the total potential energy \( V_{\text{int}} \) due to interaction between atoms is the sum of pair and embedding energy contributions [28],
\[ V_{\text{int}} = V_{\text{pair}} + V_{\text{embed}}. \] (A7)

The pair energy contribution is
\[ V_{\text{pair}} = \frac{1}{2} \sum_{\gamma} N \sum_{\delta \neq \gamma} \phi^{(\gamma\delta)} \left( x^{(\gamma\delta)} \right), \] (A8)

where \( \phi^{(\nu\mu)} \left( x^{(\gamma\delta)} \right) \) is the pair potential of atoms \( \mu \) and \( \nu \), evaluated at \( x^{(\gamma\delta)} \). For the sake of brevity, we use the abbreviation \( \phi^{(\gamma\delta)} \equiv \phi^{(\gamma\delta)} \left( x^{(\gamma\delta)} \right) \) in the following.

The embedding energy contribution is
\[ V_{\text{embed}} = \sum_{\gamma} U^{(\gamma)} \left( \rho^{(\gamma)} \right), \] (A9)

where \( U^{(\gamma)} \) is the embedding energy functional of atom \( \gamma \). \( \rho^{(\gamma)} \) is a functional of the total electron density at the site of \( \gamma \), which is computed as
\[ \rho^{(\gamma)} = \sum_{\delta \neq \gamma} g^{(\delta)} \left( x^{(\gamma\delta)} \right), \] (A10)

where \( g^{(\delta)} \left( x^{(\gamma\delta)} \right) \) is the electron density function of atom \( \delta \). For the sake of brevity, we write \( g^{(\gamma\delta)} \equiv g^{(\delta)} \left( x^{(\gamma\delta)} \right) \).

The Hessian matrix \( H \) is the \( 3N \times 3N \) matrix of second derivatives of \( V_{\text{int}} \) with respect to the coordinates of the atoms. The components of \( H \) are
\[ H_{(3(\nu-1)+i)(3(\mu-1)+j)} = \frac{\partial^2 V_{\text{int}}}{\partial x_i^{(\nu\mu)} \partial x_j^{(\nu\mu)}}. \] (A11)

We first write the gradient of \( V_{\text{int}} \). In the following, we use one and two dashes, respectively, to indicate the first and second derivatives of a function, e.g. \( g^{(\delta)}' \left( x^{(\gamma\delta)} \right) \equiv \frac{dg^{(\delta)}(x^{(\gamma\delta)})}{dx^{(\gamma\delta)}} \).
and \( g^{(\delta \delta)}(x^{(\delta \delta)}) \equiv \frac{d^2 g^{(\delta)}}{d x^{(\delta)}} / d x^{(\delta)} \). As before, we abbreviate the dependence on \( x^{(\delta \delta)} \) by writing \( g^{(\delta \delta \delta)} \equiv g^{(\delta)}(x^{(\delta \delta)}) \) and \( \phi^{(\delta \delta \delta)} \equiv \phi^{(\delta)}(x^{(\delta \delta)}) \), and likewise for the second derivative. With this notation, the expression for the gradient of \( \gamma^\text{int} \) becomes

\[
\frac{\partial \gamma^\text{int}}{\partial x_i^{(\nu)}} = \frac{\partial \gamma^\text{pair}}{\partial x_i^{(\nu)}} + \frac{\partial \gamma^\text{embed}}{\partial x_i^{(\nu)}} = -\sum_{\gamma \neq \nu} \left( \phi^\gamma x_i^{(\nu)} + U^\gamma x_i^{(\nu)} + U^{\gamma \gamma} x_i^{(\nu)} \right) \hat{x}_i^{(\nu)}.
\] (A12)

Like the gradient, the Hessian matrix can be split into contributions from \( \gamma^\text{pair} \) and \( \gamma^\text{embed} \).

\[
\frac{\partial^2 \gamma^\text{int}}{\partial x_i^{(\nu)} \partial x_j^{(\mu)}} = \frac{\partial^2 \gamma^\text{pair}}{\partial x_i^{(\nu)} \partial x_j^{(\mu)}} + \frac{\partial^2 \gamma^\text{embed}}{\partial x_i^{(\nu)} \partial x_j^{(\mu)}}.
\] (A13)

The pair contribution is

\[
\frac{\partial^2 \gamma^\text{pair}}{\partial x_i^{(\nu)} \partial x_j^{(\mu)}} = -\phi^{\mu \nu} x_i^{(\nu)} x_j^{(\mu)} + \frac{\phi^{\mu \nu}}{x^{(\mu)}} \left( \delta_{ij} - \hat{x}_i^{(\nu)} \hat{x}_j^{(\mu)} \right) + \delta_{ij} \sum_{\gamma \neq \nu \neq \mu} \phi^{\gamma \mu \nu} x_i^{(\nu)} x_j^{(\gamma)}
\] (A14)

The third and the fourth term are the sums of the first and second term, respectively, over the neighbors of \( \nu \). This expression is equal to the Hessian matrix for a pair potential, see reference [20].

The embedding contribution is the sum of eight terms,

\[
\frac{\partial^2 \gamma^\text{embed}}{\partial x_i^{(\nu)} \partial x_j^{(\mu)}} = \sum_{n=1}^{8} T_i^{(\nu \mu)}(x_j^{(\mu)}),
\] (A15)

where

\[
1 T_i^{(\nu \mu)} = \delta_{\mu \nu} U^{(\mu \mu)} \sum_{\gamma \neq \nu} N g^{(\gamma \nu)} x_i^{(\nu)} \sum_{\gamma \neq \nu} N g^{(\gamma \nu)} x_j^{(\gamma)},
\] (A16)

\[
2 T_i^{(\nu \mu)} = -U^{(\nu \mu \nu)} g^{(\nu \mu)} x_i^{(\nu)} \sum_{\gamma \neq \nu \neq \mu} N g^{(\gamma \nu)} x_j^{(\gamma)},
\] (A17)

\[
3 T_i^{(\nu \mu)} = U^{(\nu \mu \nu)} g^{(\nu \mu \nu)} x_i^{(\nu)} \sum_{\gamma \neq \nu \neq \mu} N g^{(\gamma \nu \nu)} x_j^{(\gamma)},
\] (A18)

\[
4 T_i^{(\nu \mu)} = -\left( U^{(\nu \mu \nu)} g^{(\nu \mu \nu)} + U^{(\nu \mu \nu)} g^{(\nu \mu \nu)} \right) \hat{x}_i^{(\nu \mu)},
\] (A19)

\[
5 T_i^{(\nu \mu)} = \delta_{\mu \nu} \sum_{\gamma \neq \nu \neq \mu} \left( U^{(\gamma \nu \nu)} g^{(\gamma \nu \nu)} + U^{(\gamma \nu \nu)} g^{(\gamma \nu \nu)} \right) \hat{x}_i^{(\nu \mu)},
\] (A20)
Table 1. mumps control parameters specified on the command line with -mat_mumps_icntl_<icntl>; see the mumps manual [41, 42] (version 5.4.1) for the meaning of the parameters.

| icntl | Value | icntl | Value |
|-------|-------|-------|-------|
| 6     | 0     | 7     | 7     |
| 9     | 1     | 10    | 0     |
| 11    | 0     | 14    | 60    |
| 20    | 0     | 21    | 0     |
| 22    | 0     | 24    | 1     |
| 28    | 2     | 29    | 1     |
| 30    | 0     | 35    | 0     |

\[ 6 T_{ij}^{(\nu \mu)} = -\frac{U^{(\nu \mu)} \delta_{ij}}{g^{(\nu \mu)} g^{(\nu \mu)'} x^{(\nu \mu)'} x^{(\nu \mu)}} + \left( \delta_{ij} - s^{(\nu \mu)}_{ij} \right), \tag{A21} \]

\[ 7 T_{ij}^{(\nu \mu)} = \delta_{ij} \sum_{\gamma \neq \nu}^{N} \frac{U^{(\gamma \nu)} g^{(\gamma \nu)'} g^{(\gamma \nu)'} x^{(\gamma \nu)'} x^{(\gamma \nu)}}{g^{(\nu \gamma)} g^{(\nu \gamma)'} x^{(\nu \gamma)'} x^{(\nu \gamma)}} \left( \delta_{ij} - s^{(\nu \gamma)}_{ij} \right), \tag{A22} \]

and

\[ 8 T_{ij}^{(\nu \mu)} = \sum_{\gamma \neq \mu, \gamma \neq \mu}^{N} \frac{U^{(\gamma \nu)} g^{(\gamma \nu)'} g^{(\gamma \nu)'} x^{(\gamma \nu)'} x^{(\gamma \nu)}}{g^{(\gamma \mu)} g^{(\gamma \mu)'} x^{(\gamma \mu)'} x^{(\gamma \mu)}}. \tag{A23} \]

Note that the terms remain the same when the index pairs \((i, \nu)\) and \((j, \mu)\) are interchanged, which is necessary for the Hessian to be symmetric. Terms \(5 T_{ij}^{(\nu \mu)}\) and \(7 T_{ij}^{(\nu \mu)}\) are the sums of terms \(4 T_{ij}^{(\nu \mu)}\) and \(6 T_{ij}^{(\nu \mu)}\), respectively, over the neighbors of atom \(\nu\). Terms \(1 T_{ij}^{(\nu \mu)}\) and \(2 T_{ij}^{(\nu \mu)}\) are zero if atoms \(\mu\) and \(\nu\) are not neighbors, i.e. if \(r_{\mu \nu} > r_{\text{cut}}\), where \(r_{\text{cut}}\) is the cutoff radius of the potential. Term \(8 T_{ij}^{(\nu \mu)}\) is the most complex term. In order to compute this term, one needs to determine the common neighbors of atoms \(\mu\) and \(\nu\), even if \(\mu\) and \(\nu\) are not neighbors themselves.

### Appendix B. Computational cost

We determined the computation time and memory consumption of the two most expensive tasks, construction and partial inversion of the Hessian matrix, as a function of problem size. To this end, we repeated the calculations of appendix G on a single node of the BwForCluster nemo computer cluster at the University of Freiburg. The node is equipped with two Intel Xeon E5-2630v4 (Broadwell) processors, corresponding to a total number of 20 cores, and has 256 GB of DDR4 working memory. The programs for construction and inversion of the Hessian matrix are executed through singularity [77] from a singularity container image. The corresponding containers can be downloaded from [49].

Below, we report the time for construction of the Hessian matrix, as measured using \texttt{time.time} from the Python (version 3.8.5) standard library. The reported values are the averages of three invocations of \texttt{calculate_hessian_matrix} (\texttt{matscipy} version 0.7.0 + 2.gffcaaed). In three separate invocations, we measured the peak memory allocation using \texttt{tracemalloc} from the Python standard library.
Figure 8. Scaling of time (a) and memory (b) required for Hessian matrix $H$ construction (black points) and selective inversion (red crosses); the two horizontal axes show, respectively, the number of free planes $N_p + 1$, and the number of rows and columns in the upper left block of $H$; the latter is the relevant problem size for selective inversion; the construction effort depends on the total number of atoms $N$; pairs of black points have the same value, because despite having a different number of free planes, the configurations had the same $N$; time and memory for construction scale approximately linearly with $N$; the memory required for inversion scales linearly with the upper left block size; however, the time for inversion scales approximately quadratically with this size.

We have not parallelized construction of the Hessian matrix, and do not exploit symmetry with respect to the main diagonal, hence the computation time could still be reduced. Here, we are concerned with scaling. We expect linear scaling with the number of atoms, because evaluation of the potential energy with EAM potentials and neighbor lists scales linearly.

We used PETSc version 3.16.0 with mumps version 5.4.1 for inversion, with the mumps control parameters listed in table 1. The reported time and memory are the total time and memory returned in the performance summary requested with `-log_view`. The time includes I/O time. Note that selected inversion using mumps in PETSc is not fully parallelized.

The results of the scaling test are shown in figure 8. The required (a) time and (b) memory are plotted as a function of the number of free planes $1 + N_p$. Recall that this number defines
Table 2. 0 K fcc lattice parameter and cubic elastic constants of pure Ni, FeNiCr equicomposition random alloy, and the corresponding average alloy, modeled using the EAM potential by Bonny et al [50].

|                | Pure Ni  | Random alloy | Average alloy |
|----------------|----------|--------------|---------------|
| \(a_0\) (Å)    | 3.51929  | 3.52137      | 3.52182       |
| \(C_{11}\) (GPa) | 246.93   | 243.39       | 246.61        |
| \(C_{12}\) (GPa) | 147.07   | 157.45       | 158.12        |
| \(C_{44}\) (GPa) | 125.03   | 134.99       | 138.53        |

the size of the upper left block of the Hessian matrix, which gets inverted. This block size is the relevant problem size for inversion. In case of Hessian matrix construction, the total number of atoms is the relevant size. It does not increase monotonously with \(1 + N_p\) due to the way the configurations including the fixed atoms are constructed. Pairs of configurations have the same total number of atoms and therefore approximately the same time and memory requirement for Hessian matrix construction. The time and memory required for Hessian matrix construction scale approximately linearly with the total number of atoms. The memory required for selective inversion also grows nearly linearly, but the required time grows approximately quadratically.

Appendix C. Lattice parameters and elastic constants

The 0 K fcc lattice parameter and cubic elastic constants of Ni, A-atom FeNiCr, and random FeNiCr are listed in table 2.

The properties of Ni and A-atom FeNiCr were calculated in the same way. In order to determine the 0 K fcc lattice parameter, we minimized the pressure of a fully periodic \(5 \times 5 \times 5\) unit cell fcc crystal as a function of lattice parameter. The residual pressure was less than \(1 \times 10^{-2}\) Pa in both cases. The elastic constants were computed by imposing \((1 \times 10^{-6})\) strains \(\varepsilon_{ij}\) on a \(5 \times 5 \times 5\) unit cell fcc crystal and measuring the stress response \(\sigma_{ij}\).

In the case of random FeNiCr, we prepared three \(30 \times 30 \times 30\) unit cell configurations with random site occupations. As before, we determined the 0 K lattice parameter by minimizing the pressure. However, the cell lengths along \(x_1, x_2,\) and \(x_3\) were adjusted independently, and so each calculation yields three values for the lattice parameter. The value listed in table 2 is the average over spatial directions and samples. In order to determine the elastic constants, we imposed simple shear strain \(\varepsilon_{12}\) and uni-axial normal strain \(\varepsilon_{22}\) on the samples and measured the stress response. In the case of uniaxial tension/compression, Hooke’s law yields

\[
\sigma_{22} = C_{22}\varepsilon_{22}, \quad (C1)
\]

\[
\sigma_{11} = C_{12}\varepsilon_{22}, \quad (C2)
\]

\[
\sigma_{33} = C_{23}\varepsilon_{22}, \quad (C3)
\]

where \(C_{12} = C_{23}\) for cubic materials. In the case of simple shear

\[
\sigma_{12} = C_{44}\varepsilon_{12}. \quad (C4)
\]

We applied positive and negative shear, as well as tension and compression, with absolute values in the range \(1 \times 10^{-9}\) to \(1 \times 10^{-4}\).
Figure 9. Normal components of the {100} surface stiffness of FeCuNi, along the path $\Gamma-X-M-\Gamma$ through the first quadrant of the surface Brillouin zone (see figure 4); the stiffness of the average alloy is close to the effective mean stiffness of the true random alloy according to equation (15); turquoise areas indicate the range between the 10th and 90th percentile of the distribution of site stiffnesses.

Appendix D. FeCuNi

We calculated the {100} surface stiffness of equicomposition FeCuNi, using the interatomic potential by Bonny et al [54]. We used the same system size as in the main text, but considered only a single realization of the true random alloy. The calculated normal components of $\Phi_s$ are shown in figure 9. The results are similar to those of FeNiCr, see figure 6. Average and random alloy data are close along the whole path. Out of the three normal components, $\Phi_{s,22}$ exhibits the largest relative difference. At a wavelength of $q_1 a = 0.61$, close to $\Gamma$ on the $\Gamma-X$ path, the average alloy overestimates the harmonic mean stiffness of the true random alloy by 17% (1.3 GPa Å$^{-1}$). The anisotropic continuum solution was calculated using the mean lattice parameter ($a_0 = 3.548$ Å) and elastic constants ($C_{11} = 164$ GPa, $C_{12} = 133$ GPa, $C_{11} = 94$ GPa) of the random alloy. As before, the continuum solution converges to the atomistic solution at $\Gamma$, but significantly underestimates $\Phi_{s,11}$ and $\Phi_{s,22}$ at short wavelengths. The discrepancy between continuum and atomistics is again smallest in the $\Phi_{s,33}$ component. Compared to FeNiCr, the FeCuNi random alloy exhibits larger fluctuations. At some wavevectors, the 10th percentile even becomes negative. Moreover, the percentiles vary less smoothly. In figure 9(a) the 10th and 90th percentile have some local extrema between $X$ and $M$.

Appendix E. {1 1 0} surface

We calculated the {1 1 0} surface stiffness of FeNiCr. The $x_1$-, $x_2$-, and $x_3$-directions of the cell were parallel to the crystal directions [1 0 0], [0 1 1], and [0 1 1]. Accordingly, the lattice spacing was $a_0$ along the $x_1$-direction, and $a = a_0/\sqrt{2}$ along the $x_2$-direction. There were 31 and 44 atoms along the $x_1$- and $x_2$-edges, resulting in an approximately square surface with side length 109 Å. The height $h$ was also approximately 109 Å.

Due to the unequal grid spacing in the $x_1$- and $x_2$-directions, the Brillouin zone is not quadratic, but rectangular. The wavevectors in the reciprocal $x_1$-direction are given by equation (13), with $N_e = 31$, and $a$ replaced by $a_0$.

Figure 10 shows the normal components of $\Phi_s$ along the path $\Gamma-X-M$. We omitted the diagonal $\Gamma-M$, because drawing it would require interpolation between values of slightly off-diagonal points. In contrast to the calculation described in the main text, we considered only a single realization of the random alloy. Nevertheless, the results are similar to the {100} case. Most importantly, stiffness values of the average alloy are close to the corresponding
Figure 10. Normal components of the \{110\} surface stiffness of average-alloy and true random FeNiCr, along the path \(\bar{\Gamma} - \bar{X} - \bar{M}\) through the surface Brillouin zone; in contrast to the \{100\} surface, the \{110\} Brillouin zone is not orthogonal, because the lattice constant along the \(x_1\)-direction is larger than the one along the \(x_2\)-direction; the anisotropic continuum solution (red) was calculated using the mean lattice constant and the elastic constants of the true random alloy; similar to the \{100\} surface, the average alloy (black dots) gives a better approximation of the harmonic mean stiffness of the random alloy (blue crosses) than the continuum solution; shaded areas: region between the 10th and the 90th percentile of the 1364 site stiffnesses of the random alloy.

harmonic mean stiffness of the random alloy. In the case of \(\Phi_{s,22}\) and \(\Phi_{s,33}\), the error relative to the random alloy data does not exceed 5%. Larger errors are seen in the case of \(\Phi_{s,11}\), which, however, is also small compared to the other normal components. The largest error is 42 % (10 GPa Å\(^{-1}\)), on the path \(\bar{\Gamma} - \bar{X}\) next to \(\bar{X}\). Again, the continuum solution deviates significantly from the atomistic data already at much longer wavelengths. Finally, notice that the \{110\} is more compliant compared to the \{100\} surface, and that fluctuations in the random alloy are smaller.

Appendix F. Surface Green’s function for an anisotropic elastic continuum of finite thickness

No closed form solution for the surface Green’s function of the anisotropic elastic continuum exists. We here compute this Green’s function semi-analytically. Starting from the definition of the (small-strain) strain tensor

\[
\varepsilon_{ij} = \frac{1}{2} \left( \partial_i u_j + \partial_j u_i \right),
\]

where \(\vec{u}(x_1, x_2, x_3)\) is the displacement field, we obtain the stress tensor as

\[
\sigma_{ij} = C_{ijkl} \varepsilon_{kl} = \frac{1}{2} C_{ijkl} (\partial_k u_l + \partial_l u_k) = C_{ijkl} \partial_k u_l.
\]

\(C_{ijkl}\) is the fourth-order tensor of elastic constants with at most 27 independent components. Note that \(\partial_i\) indicates the partial derivative in direction \(i\) and Einstein summation convention applies to all latin indices in this paper. The usual symmetry relationships

\[
C_{ijkl} = C_{jikl}, \quad C_{ijkl} = C_{ijlk} \quad \text{and} \quad C_{ijkl} = C_{klji}
\]

have been used to obtain the last equality in equation (F2). Elastostatic equilibrium dictates \(\partial_i \sigma_{ij} = 0\). Inserting equation (F2) into this expression yield the generalization of the
Navier–Lamé equations,

\[ \partial_j (C_{ijkl} \partial_k u_l) = C_{ijkl} \partial_j \partial_k u_l = 0, \quad (F4) \]

where we have assumed that \( C_{ijkl} \) does not depend on position, i.e. we are dealing with a homogeneous half-space.

We now search for a solution of the displacements \( \vec{u}_s(x_1, x_2) \) within the plane of a surface subject to the traction boundary conditions \( P(x_1, x_2), Q_1(x_1, x_2) \) and \( Q_2(x_1, x_2) \). With \( \vec{Q} = (Q_1, Q_2, P) \), the displacements are given by \( \vec{u}_s(x_1, x_2) = \int \text{d}x_1' \text{d}x_2' \vec{G}_s(x_1 - x_1', x_2 - x_2') \). It is usually convenient to state the Fourier transform of this expression, \( \vec{u}_s(\vec{q}) = \vec{G}_s(\vec{q}) \cdot \vec{Q}(\vec{q}) \) where \( \vec{q} = (q_1, q_2) \) is the wavevector within the plane of the surface. \( \vec{G}_s \) is the surface Green’s function.

Note that equation (F4) is a set of three linear partial differential equations for the three components of the displacement field \( \vec{u}(x_1, x_2, x_3) \) throughout the body. We are only interested in \( \vec{u}_s(x_1, x_2) = \vec{u}(x_1, x_2, 0) \). We can write equation (F4) as [78]

\[ M_d u_l = 0, \quad (F5) \]

with the linear operator

\[ M_d = C_{ijkl} \partial_j \partial_k, \quad (F6) \]

Because of equation (F3), the operator \( M \) is symmetric, \( M_d = M_d^\top \). In order to obtain the surface Green’s function, we need to impose the traction boundary conditions \( P, Q_1 \) and \( Q_2 \). At the surface \((x_3 = 0)\), the stress tensor fulfills

\[
\begin{align*}
\sigma_{33}(x_1, x_2, x_3 = 0) &= P(x_1, x_2), \\
\sigma_{13}(x_1, x_2, x_3 = 0) &= Q_1(x_1, x_2) \quad \text{and} \\
\sigma_{23}(x_1, x_2, x_3 = 0) &= Q_2(x_1, x_2).
\end{align*}
\quad (F7)
\]

To solve equation (F5) numerically under the boundary conditions given by equation (F7), we need to transform equation (F6) into an algebraic equation. Because we are interested in the solution for a plane interface, we have translational invariance in the \( x_1–x_2 \) plane. The Fourier transform of equation (F6) in this plane is given by

\[
M_d = -C_{111} q_1^2 - C_{222} q_2^2 - (C_{121} + C_{212}) q_1 q_2 \\
+ [i(C_{131} + C_{311}) q_1 + i(C_{231} + C_{321}) q_2] \partial_3 + C_{333} \partial_3^2,
\quad (F8)
\]

where \( q_1 \) and \( q_2 \) are the wavevectors in this plane. Any nontrivial solution to the homogeneous equation equation (F5) must fulfill \( \det M = 0 \). This fixes the admissible values of the eigenvalue \( iq_3 \) of the operator \( \partial_3 \). Since \( \det M \) is a sixth-order even polynomial in \( iq_3 \), for each \( q_1, q_2 \), we obtain six values for \( iq_3^{(\alpha)} \) that occur in symmetric pairs.

For six eigenvalues \( q_1^{(\alpha)} \) the displacement field is given by a superposition of the basis functions \( \vec{q}_1^{(\alpha)} \cdot \vec{e}_{3(\alpha)} \), where \( \vec{q}_1^{(\alpha)} \) is the solution of \( M \cdot \vec{q}_1^{(\alpha)} \vec{e}_{3(\alpha)} = 0 \). It is straightforward solve for both \( q_1^{(\alpha)} \) and \( \vec{q}_1^{(\alpha)} \) numerically. The general displacement field is then given by

\[
\vec{u} = \sum_{\alpha} c_{\alpha} \vec{q}_1^{(\alpha)} \vec{e}_{3(\alpha)} x_3 = U(q_1, q_2, x_3) \cdot \vec{c}
\quad (F9)
\]
with generally $\bar{c} = (c_1, c_2, c_3, c_4, c_5, c_6)$ and $U_{\alpha \beta}(q_1, q_2, x_3) = \eta_{\beta}^{(\alpha)} e^{i q_3^{(\alpha)} x_3}$ where $\eta_{\beta}^{(\alpha)}$ and $q_3^{(\alpha)}$ depend implicitly on $q_1$ and $q_2$. The constants $c_\alpha$ are now obtained from the displacement or traction boundary conditions on both top and bottom of the half-space.

For an infinite half-space, all $c_\alpha$ for $3q_3^{(\alpha)} < 0$ must vanish because the solution diverges as $q_3 \to \infty$. This leaves us with three relevant basis functions, that we label (without loss of generality) by $\alpha = 1, 2, 3$ (and hence $c_4 = c_5 = c_6 = 0$). The traction boundary condition, equation (F7), becomes

$$Q_1(q_1, q_2) = i C_{13}\eta_{3}^{(1)} c_1$$

$$Q_2(q_1, q_2) = i C_{23}\eta_{3}^{(2)} c_2$$

$$P(q_1, q_2) = i C_{33}\eta_{3}^{(3)} c_3$$

or in matrix notation

$$\bar{Q}(q_1, q_2) = F(q_1, q_2) \cdot \bar{c}$$

with $F_{\alpha}(q_1, q_2) = i C_{3\alpha}\eta_{3}^{(\alpha)}$ and $q_3^{(\alpha)} \equiv q_1$ and $q_3^{(\alpha)} \equiv q_2$. Combining equations (F9) and (F13) gives $G_{\alpha}(q_1, q_2) = U(q_1, q_2, 0) \cdot F^{-1}(q_1, q_2)$ or $F_{\alpha} = G_{\alpha}^{-1} = F \cdot U^{-1}$.

For a finite half-space, we need to keep all six basis functions $\alpha \in [1 \ldots 6]$ and require in addition a boundary condition at the bottom of the substrate. We here only discuss fixed displacement of all displacement or traction at the bottom of the substrate. In addition to equations (F10) to (F12), the displacement boundary condition leads to the additional equations

$$\sum_{\alpha} c_\alpha \phi_{\alpha}(y) e^{i q_3^{(\alpha)} h} \equiv u_{\alpha, b}$$

for $j = 1, 2, 3$. Here $u_{\alpha}$ are the displacements at the bottom of the substrate. In dyadic notation this becomes

$$\tilde{\varphi}(q_1, q_2) = F_{\alpha}(q_1, q_2) \cdot \bar{c},$$

where $\varphi$ contains forces at the top and displacements at the bottom of the substrate. $F_{\alpha}$ is a $6 \times 6$ matrix. The Green’s function is then given by the first three columns of $U \cdot F_{\alpha}^{-1}$.

Note that for the (special) isotropic case where $C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + 2\mu \delta_{il} \delta_{jk}$ with Lamé constants $\lambda$ and $\mu$, the solution of $\det M = 0$ is degenerate, $iq_3 = \pm \sqrt{q_1^2 + q_2^2}$, and the above analysis does not apply. The displacement field is then given by superposition of the basis functions $e^{i q_3^{(1)} x_3}, x_3 e^{i q_3^{(1)} x_3}, x_3^2 e^{i q_3^{(1)} x_3}, x_3 e^{i q_3^{(2)} x_3}$, and $x_3^2 e^{i q_3^{(2)} x_3}$.

The close-form solution for the infinite half-space in this limit is described in reference [10]. It yields the surface Green’s function

$$\mu G_{\alpha}(q) = \begin{pmatrix}
\frac{1}{q} - \frac{\nu q_1^2}{q^3} & \frac{\nu q_1 q_2}{q^3} & i(1 - 2\nu) q_1
\frac{1}{q} - \frac{\nu q_1 q_2}{q^3} & -\frac{\nu q_1^2}{q^3} & i(1 - 2\nu) q_2
-i\frac{(1 - 2\nu) q_1}{2q^2} & -i\frac{(1 - 2\nu) q_2}{2q^2} & \frac{1 - \nu}{q}
\end{pmatrix}$$

(F16)
with Poisson number $\nu = \lambda/[2(\lambda + \mu)]$. Inverse Fourier transform of equation (F16) leads to the well-known potential functions of Johnson [3].

**Appendix G. Effect of sample thickness**

Our samples consisted of one surface layer and $N_p$ subsurface layers. In the simulations reported in the main text $N_p = 44$. To see the effect of $N_p$, we repeated the calculation for random FeNiCr with $N_p = 1, 2, \ldots, 44$. Figure 11 shows the components of the harmonic mean stiffness $\Phi_s$ along the paths $\Gamma-X-M-\Gamma$ and $\Gamma-X'-M'-\Gamma$ through the Brillouin zone, like in figure 6 in the main text.

In the short-wavelength region, near $\bar{X}$ and $\bar{M}$, the mean values converge as $N_p$ increases. $N_p = 3-4$ is already sufficient to obtain curves that are almost indistinguishable from the curves for $N_p = 44$ on the scale of figures 11(a)–(f). This is expected, because the stiffness in the short-wavelength region is controlled by short-range interactions, and these do not change much beyond a minimum $N_p$. The data in the long-wavelength region, on the other hand, do not converge. This is expected based on the continuum solution. For example, $\lim_{\vec{q} \to 0} \Re \Phi_s,11 = C_{44}/h$, which depends explicitly on the sample thickness $h \propto N_p$. Figures 11(a) and (g) show that $\Re \Phi_s,11$ indeed decreases with $N_p$. 

![Figure 11. Harmonic mean stiffness of random FeNiCr for different values of the number of subsurface layers $N_p$; the upper two rows show the real parts of $\Phi_{s,11}, \Phi_{s,22}, \Phi_{s,33}$ and $\Phi_{s,12}$, as well as the imaginary parts of $\Phi_{s,13}$ and $\Phi_{s,23}$ along the path $\Gamma-\bar{X}-\bar{M}-\Gamma$ through the first quadrant of the surface Brillouin zone; the lower row shows the values of $\Phi_{s,11}, \Phi_{s,22}$ and $\Phi_{s,12}$ along the path $\bar{\Gamma}-\bar{X'}-\bar{M'}-\bar{\Gamma}$ through the long wavelength region.](image-url)
Figure 12. Difference between the 90th and 10th percentile of site stiffnesses $\Phi_s^{(\nu)}$ along the Brillouin zone diagonal $\bar{\Gamma} - \bar{M}$ for different values of the number of subsurface planes $N_p$; (a) component $\Phi_s^{(\nu)}$, (b) component $\Phi_s^{(\nu)}$, at large $N_p$ the difference converges to zero in the long-wavelength limit, at $\bar{\Gamma}$; differences between the curves for $N_p \gg 5$ grow as one moves towards the corner point $\bar{M}$, which represents the short-wavelength limit.

Additionally, we examined convergence of the dispersion of site stiffnesses $\Phi_s^{(\nu)}(q_1, q_2)$. For each sample, we computed the difference between the 10th and the 90th percentile of $\Phi_s^{(\nu)}(q_1, q_2)$.

$$\Delta p[\Phi_s^{(\nu)}, ij] = p_{90}[\Phi_s^{(\nu)}, ij] - p_{10}[\Phi_s^{(\nu)}, ij].$$

In contrast to the simulations reported in the main text, the statistics were computed using only $N^2_s = 961$ site data, since we prepared only one sample per value of $N_p$. In figure 12, we show the components $\Delta p[\Phi_s^{(\nu)}, 11]$ and $\Delta p[\Phi_s^{(\nu)}, 33]$ along the Brillouin zone diagonal $\bar{\Gamma} - \bar{M}$.

With increasing $N_p$, the curves converge to zero at $\bar{\Gamma}$. This is expected, because $\bar{\Gamma}$ corresponds to the limit of displacements with infinite wavelength, where the effect of fluctuations is averaged out. The smallest systems have nonzero dispersion at $\bar{\Gamma}$, with particularly large values in the case of $\Phi_s^{(\nu)}$. Differences between the curves grow as one moves towards the corner point $\bar{M}$, which represents the short-wavelength limit. However, the scatter is small relative to the absolute value of $\Delta p[\Phi_s^{(\nu)}, ij]$. Some variation is also expected due to the finite sample size.
We conclude that for $N_p \gg 5$, measurements with different $N_p$ yield similar dispersions at all wavelengths, and so our choice of $N_p = 44$ is acceptable.

**ORCID iDs**

Wolfram G Nöhring [https://orcid.org/0000-0003-4203-755X](https://orcid.org/0000-0003-4203-755X)
Jan Grießer [https://orcid.org/0000-0003-2149-6730](https://orcid.org/0000-0003-2149-6730)
Patrick Dondl [https://orcid.org/0000-0003-3035-7230](https://orcid.org/0000-0003-3035-7230)
Lars Pastewka [https://orcid.org/0000-0001-8351-7336](https://orcid.org/0000-0001-8351-7336)

**References**

[1] Tadmor E B and Miller R E 2011 *Modeling Materials: Continuum, Atomistic and Multiscale Techniques* (Cambridge: Cambridge University Press)
[2] Bulatov V V, Bulatov V and Cai W 2006 *Computer Simulations of Dislocations* (Oxford: Oxford University Press)
[3] Johnson K L 1985 *Contact Mechanics* (Cambridge: Cambridge University Press)
[4] Kohlhoff S, Gumbach P and Fischmeister H F 1991 Crack propagation in bcc crystals studied with a combined finite-element and atomistic model *Phil. Mag.* A **64** 851
[5] Tadmor E B, Ortiz M and Phillips R 1996 Quasicontinuum analysis of defects in solids *Phil. Mag.* A **73** 1529
[6] Shenoy V B, Miller R, Tadmor E B, Phillips R and Ortiz M 1998 Quasicontinuum models of interfacial structure and deformation *Phys. Rev. Lett.* **80** 742
[7] Xiao S P and Belytschko T 2004 A bridging domain method for coupling continua with molecular dynamics *Comput. Methods Appl. Mech. Eng.* **193** 1645
[8] Badia S, Bochev P, Lehoucq R, Parks M L, Fish J, Nuggehally M A and Gunzburger M 2007 A force-based blending model for atomistic-to-continuum coupling *Int. J. Multiscale Comput. Eng.* **5** 387
[9] Chen Y, Shabanov S and McDowell D L 2019 Concurrent atomistic-continuum modeling of crystalline materials *J. Appl. Phys.* **126** 101101
[10] Amba-Rao C L 1969 Fourier transform methods in elasticity problems and an application *J. Franklin Inst.* **287** 241
[11] Kalker J J and Van Randen Y 1972 A minimum principle for frictionless elastic contact with application to non-Hertzian half-space contact problems *J. Eng. Math.* **6** 193
[12] Stanley H M and Kato T 1997 An FFT-based method for rough surface contact *J. Tribol.* **119** 481
[13] Hodapp M, Ancliaux G and Curtin W A 2019 Lattice green function methods for atomistic/continuum coupling: theory and data-sparse implementation *Comput. Methods Appl. Mech. Eng.* **348** 1039
[14] Sinclair J E 1971 Improved atomistic model of a bcc dislocation core *J. Appl. Phys.* **42** 5321
[15] Sinclair J E, Gehlen P C, Hoagland R G and Hirth J P 1978 Flexible boundary conditions and nonlinear geometric effects in atomic dislocation modeling *J. Appl. Phys.* **49** 3890
[16] Gallego R and Ortiz M 1993 A harmonic/anharmonic energy partition method for lattice statics computations *Modelling Simul. Mater. Sci. Eng.* **1** 417
[17] Li X 2009 Efficient boundary conditions for molecular statics models of solids *Phys. Rev. B* **80** 104112
[18] Campañá C and Múser M H 2006 Practical Green’s function approach to the simulation of elastic semi-infinite solids *Phys. Rev. B* **74** 075420
[19] Trinkle D R 2008 Lattice green function for extended defect calculations: computation and error estimation with long-range forces *Phys. Rev. B* **78** 014110
[20] Pastewka L, Sharp T A and Robbins M O 2012 Seamless elastic boundaries for atomistic calculations *Phys. Rev. B* **86** 075459
[21] Miller R E and Tadmor E B 2009 A unified framework and performance benchmark of fourteen multiscale atomistic/continuum coupling methods *Modelling Simul. Mater. Sci. Eng.* **17** 053001
[22] Kajita S, Washizu H and Ohmori T 2012 Simulation of solid-friction dependence on number of surface atoms and theoretical approach for infinite number of atoms Phys. Rev. B 86 075453
[23] Kajita S 2016 Green’s function nonequilibrium molecular dynamics method for solid surfaces and interfaces Phys. Rev. E 94 033301
[24] Monti J M, Pastewka L and Robbins M O 2021 Green’s function method for dynamic contact calculations Phys. Rev. E 103 053305
[25] Kong L T, Bartels G, Campañá C, Denniston C and Müser M H 2009 Implementation of Green’s function molecular dynamics: an extension to LAMMPS Comput. Phys. Commun. 180 1004
[26] Kozlov S M 1979 Averaging of random operators Mat. Sb. (N.S.) 109 188–202
[27] Papanicolaou G C and Varadhan S R S 1981 Boundary value problems with rapidly oscillating random coefficients Random Fields, Vol I, II (Esztergom, 1979) (Colloquia Mathematica Societatis János Bolyai) vol 27 (Amsterdam: North-Holland) pp 835–73
[28] Daw M S and Baskes M I 1984 Embedded-atom method: derivation and application to impurities, surfaces, and other defects in metals Phys. Rev. B 29 4643
[29] Varvenne C, Luque A, Nöhring W G and Curtin W A 2016 Average-atom interatomic potential for random alloys Phys. Rev. B 93 104201
[30] Kermode J and Pastewka L matscipy: materials science with Python at the atomic-scale https://github.com/libAtoms/matscipy
[31] Kobayashi S, Maeda K and Takeuchi S 1980 Computer simulation of atomic structure of Cu57Zr43 amorphous alloy J. Phys. Soc. Japan 48 1147
[32] Lennard-Jones J E 1924 On the determination of molecular fields: II. From the equation of state of a gas Proc. R. Soc. A 106 463
[33] Ninarello A, Berthier L and Coslovich D Models and algorithms for the next generation of glass transition studies Phys. Rev. E 7 021039
[34] Lerner E 2019 Mechanical properties of simple computer glasses J. Non-Cryst. Solids 522 119570
[35] Stillinger F H and Weber T A Computer simulation of local order in condensed phases of silicon Phys. Rev. B 31 5262
[36] Tersoff J Modeling solid-state chemistry: interatomic potentials for multicomponent systems Phys. Rev. B 39 5566
[37] Brenner D W Empirical potential for hydrocarbons for use in simulating chemical vapor deposition of diamond films Phys. Rev. B 42 9458
[38] Kumagai T, Izumi S, Haras S and Sakai S 2007 Development of bond-order potentials that can reproduce the elastic constants and melting point of silicon for classical molecular dynamics simulation Comput. Mater. Sci. 39 457
[39] Balay S et al 2019 PETSc: Users Manual, Tech. Rep. ANL-95/11—Revision 3.11 Argonne National Laboratory
[40] Balay S, Gropp W D, McInnes L C and Smith B F 1997 Efficient management of parallelism in object-oriented numerical software libraries Modern Software Tools in Scientific Computing ed E Arge, A M Bruaset and H P Langtangen (Basel: Birkhäuser) pp 163–202
[41] Amestoy P R, Duff I S, L’Excellent J-Y and Koster J 2001 A fully asynchronous multifrontal solver using distributed dynamic scheduling SIAM J. Matrix Anal. Appl. 23 15
[42] Amestoy P, Buttari A, L’Excellent J-Y and Mary T 2019 Performance and scalability of the block low-rank multifrontal factorization on multicore architectures ACM Trans. Math. Softw. 45 1–26
[43] Amestoy P R, Duff I S, L’Excellent J-Y and Rouet F-H 2015 Parallel computation of entries of $a^{-1}$ SIAM J. Sci. Comput. 37 C268
[44] Griessler J and Nöhring W 2021 Greens_Functions https://github.com/griessej/Greens_Functions
[45] Song H, Tian F, Hu Q-M, Vitos L, Wang Y, Shen J and Chen N 2017 Local lattice distortion in high-entropy alloys Phys. Rev. Mater. 1 023404
[46] Owen L R and Jones N G 2018 Lattice distortions in high-entropy alloys J. Mater. Res. 33 2954
[47] Owen L R and Jones N G 2020 Quantifying local lattice distortions in alloys Scr. Mater. 187 428
[48] Berlyand L and Rybalko V Getting acquainted with homogenization and multiscale Compact Textbooks in Mathematics (Berlin: Springer)
[49] Nöhring W 2021 surface_stiffness https://github.com/wgnoehring/surface_stiffness
[50] Bonny G, Terentyev D, Pasianot R C, Poncè S and Bakaev A 2011 Interatomic potential to study plasticity in stainless steels: the FeNiCr model alloy Modelling Simul. Mater. Sci. Eng. 19 085008
[51] Smith R W and Was G S 1989 Application of molecular dynamics to the study of hydrogen embrittlement in Ni–Cr–Fe alloys Phys. Rev. B 40 10332
[52] Bitzek E, Koskinen P, Gähler F, Moseler M and Gumbsch P 2006 Structural relaxation made simple Phys. Rev. Lett. 97 170201
[53] Guénolé J, Nöhring W G, Vaid A, Houllé F, Xie Z, Prakash A and Bitzek E 2020 Assessment and optimization of the fast inertial relaxation engine (fire) for energy minimization in atomistic simulations and its implementation in lammps Comput. Mater. Sci. 175 105984
[54] Bonny G, Pasianot R, Castin N and Malerba L Ternary Fe–Cu–Ni many-body potential to model reactor pressure vessel steels: first validation by simulated thermal annealing Phil. Mag. 89 3531
[55] Birdsong J B and Rummelt N I 2016 The hexagonal fast Fourier transform 2016 IEEE Int. Conf. on Image Proc. (ICIP)
[56] Barber J 1992 Elasticity 3 (Solid Mechanics and Its Applications, vol 172) (Dordrecht: Springer Netherlands) XIX, 534
[57] Sanner A, Junge T and Pastewka L 2020 ContactMechanics: contact mechanics using elastic half-space methods https://github.com/ComputationalMechanics/ContactMechanics
[58] Gloria A and Otto F 2011 An optimal variance estimate in stochastic homogenization of discrete elliptic equations Ann. Probab. 39 779
[59] Gloria A, Neukamm S and Otto F 2013 Quantification of ergodicity in stochastic homogenization: optimal bounds via spectral gap on Glauber dynamics Invent Math. 199 455
[60] Armstrong S, Kuusi T and Mourrat J-C 2019 Quantitative stochastic homogenization and large-scale regularity Grundlehren der Mathematischen Wissenschaften (Fundamental Principles of Mathematical Sciences) vol 352 (Berlin: Springer) p xxxviii + 518
[61] Peierls R 1940 The size of a dislocation Proc. Phys. Soc. 52 34
[62] Nabarro F R N 1947 Dislocations in a simple cubic lattice Proc. Phys. Soc. 59 256
[63] Sharp T A, Pastewka L and Robbins M O 2016 Elasticity limits structural superlubricity in large contacts Phys. Rev. B 93 121402(R)
[64] Sharp T A, Pastewka L, Lignères V L and Robbins M O 2017 Scale- and load-dependent friction in commensurate sphere-on-flat contacts Phys. Rev. B 96 155436
[65] Monti J M and Robbins M O 2020 Sliding friction of amorphous asperities on crystalline substrates: scaling with contact radius and substrate thickness ACS Nano 14 16997
[66] Tewary V K 1973 Green-function method for lattice statics Adv. Phys. 22 757
[67] Tewary V K, Fuller E R and Thomson R M 1989 Lattice statics Green’s function method for calculation of atomistic structure of grain boundary interfaces in solids: part I. Harmonic theory J. Mater. Res. 4 309
[68] Thomson R, Zhou S J, Carlson A E and Tewary V K 1992 Lattice imperfections studied by use of lattice Green’s functions Phys. Rev. B 46 10613
[69] Tewary V K and Thomson R 1992 Lattice statics of interfaces and interfacial cracks in bimaterial solids J. Mater. Res. 7 1018
[70] Ohsawa K, Kuramoto E and Suzuki T 1996 Lattice statics Green’s function for a semi-infinite crystal Phil. Mag. A 74 431
[71] Bella P, Giunti A and Otto F 2020 Effective multipoles in random media Commun. PDE 45 561
[72] Mizuno H, Silbert L E, Sperl M, Mossa S and Barrat J-L 2016 Cutoff nonlinearities in the low-temperature vibrations of glasses and crystals Phys. Rev. E 93 043314
[73] Shimada M, Mizuno H and Ikeda A 2018 Anomalous vibrational properties in the continuum limit of glasses Phys. Rev. E 97 022609
[74] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics J. Comput. Phys. 117 1–19
[75] Hjorth Larsen A et al 2017 The atomic simulation environment—a Python library for working with atoms J. Phys.: Condens. Matter. 29 273002
[76] Stukowski A 2009 Visualization and analysis of atomistic simulation data with OVITO—the open visualization tool Modelling Simul. Mater. Sci. Eng. 18 015012
[77] Kurtzer G M et al 2020 Sylabs/Singularity: Singularity 3.5.3
[78] Chen S J and Howitt D G 1996 On the Galerkin vector and the Eshelby solution in linear elasticity J. Elast. 44 1–8