

# A homogenization analysis of the field theoretic approach to the quasi-continuum method

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## Abstract

Using the orbital-free density functional theory as a model theory, we present an analysis of the field theoretic approach to quasi-continuum method. In particular, by perturbation method and multiple scale analysis, we provide a formal justification for the validity of numerical coarse-graining of various fields in the quasi-continuum reduction of field theories by taking the homogenization limit. Further, we derive the homogenized equations that govern the behavior of electronic fields in regions of smooth deformations. Using Fourier analysis, we determine the far-field solutions for these fields in the presence of local defects, and subsequently estimate cell-size effects in computed defect energies.

## 1 Introduction

The quasi-continuum method has, in the past decade, become an important computational technique in the study of defects in materials where a wide range of interacting length scales govern their behavior. The main idea behind the quasi-continuum method is a seamless bridging between various length scales of interest by imposing kinematic constraints and systematically coarse-graining away from the regions of interest. The quasi-continuum method was first proposed for empirical interatomic potentials (Tadmor et al., 1996), where the energy of the system was expressed as a non-local sum over the positions of atoms. The kinematic constraints on the positions of atoms—degrees of freedom in the formulation—are imposed via an unstructured finite-element triangulation of representative atoms with full atomistic resolution in regions of interest, for instance at the core of a defect, and rapidly coarse-graining away to capture the long-range elastic effects. Apart from the kinematic constraints introduced on the degrees of freedom, further approximations are introduced to reduce the computational complexity of the formulation. The differing nature of these approximations, which include invoking the Cauchy-Born hypothesis in some regions of the model or introducing cluster summation rules in the spirit of numerical quadratures, have resulted in many different formulations of the quasi-continuum method. We refer to Shenoy et al. (1999); Knap & Ortiz (2001); Miller & Tadmor (2002); Shimokawa et al. (2004); Eidel & Stukowski (2009) and reference therein for a comprehensive overview of the different formulations of the method. Recent investigations and numerical analysis of the method (Shimokawa et al., 2004; E et al., 2006; Dobson & Luskin, 2008; Luskin & Ortner, 2009; Dobson et al., 2009)

suggest that these approximations can result in undesirable consequences, namely, lack of a variational structure, lack of stability and consistency of the approximation schemes, and uncontrolled errors in some cases.

In a recent work (Gavini et al., 2007a) the quasi-continuum method was developed for electronic structure calculations using orbital-free density functional theory (OFDFT). OFDFT, which is an approximation to the widely used Kohn-Sham formulation of density functional theory (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), describes the ground-state energy of the system as an explicit functional of electron-density and is valid in materials systems whose electronic structure is close to a free electron gas (cf. Parr & Yang (1989); Wang & Teter (1992); Smargiassi & Madden (1994); Wang et al. (1998, 1999) for a comprehensive overview). The quasi-continuum reduction of OFDFT was achieved using a real-space local variational formulation, and a coarse-graining of the electronic-fields and positions of atoms—degrees of freedom in the formulation—through kinematic constraints imposed using nested finite-element triangulations. An important difference in the mathematical structure of quasi-continuum formulation for OFDFT in comparison to empirical interatomic potentials is that OFDFT is a local field theory as opposed to the non-local description of extended interactions in empirical potentials. A local field formulation, as in the case of OFDFT, admits quadrature approximations to further reduce the computational complexity without introducing the undesirable consequences characteristic of conventional quasi-continuum formulations.

In the prequel to this article (Iyer & Gavini, 2011), we suggest a field formulation for commonly used interatomic potentials, where the extended interactions in these potentials are reformulated into a local form by constructing partial differential equations (PDE’s) whose Green’s functions correspond to the kernels of the non-local interactions. We further demonstrate that the quasi-continuum reduction of these field formulations is variational, a consistent numerical approximation, and provides significantly better accuracy than previous formulations. Moreover, the field formulation of interatomic potentials provides a unified framework where the quasi-continuum reduction is solely a numerical approximation scheme irrespective of the field theory used to describe the system—density functional theory or field theories that represent interatomic interactions.

In the quasi-continuum reduction of field theories (Iyer & Gavini, 2011; Gavini et al., 2007a), the various fields that appear in the formulation are decomposed into predictor fields and corrector fields. The predictor fields are computed by performing a periodic calculation using the Cauchy-Born hypothesis, and the corrector fields are subsequently computed from the variational formulation. For smooth deformations which do not depend on the atomic-scale, Blanc et al. (2002) show that the various fields are given, to the leading order, by a periodic calculation using the Cauchy-Born hypothesis. Hence, in regions away from the defect-core it is expected that the predictor fields are good approximations to the fields. Thus, the corrector fields are represented on a finite-element triangulation which is subatomic near the core and coarse-grains away to become superatomic, and this constitutes the quasi-continuum reduction of field formulations.

The representation of the corrector fields on a coarse-grained triangulation is valid under the hypothesis that corrector fields do not exhibit oscillations on the atomic-scale in regions away from a defect-core. In this work, we provide a formal justification for this hypothesis. We conduct our analysis in the framework of OFDFT and latter comment on other field the-

ories. We first use the perturbation method to find the governing equations for the corrector fields corresponding to a weak defect. While the defect plays the role of a source (forcing function), the coefficients of these governing equations are given by the unperturbed (predictor) electronic fields. Further, since the unperturbed electronic fields oscillate at the atomistic scale, which is much smaller than the macroscopic supercell and the considered perturbation associated with the defect, we employ the multi-scale analysis (Cioranescu & Donato, 1999) to determine the behavior of corrector electronic fields. In particular, we demonstrate that the corrector electronic fields to their leading order and first order are independent of the lattice parameter, and hence do not exhibit atomic-scale oscillations. We further derive the homogenized equations for the corrector fields that are given by a second-order linear system of PDE's. By Fourier analysis, we find their Green's functions explicitly, which show that the correctors fields in OFDFT, corresponding to electrostatic potential and electron density, decay exponentially. Additionally, we compute their solutions for a situation representative of a vacancy in an infinite crystal. Using these solutions, we analyze the cell-size effects arising from a computation on a finite domain and estimate the domain size required for achieving chemical accuracy in vacancy formation energy. Our results show that a cell-size of the order of 1,000 atoms is required to attain a converged value for the vacancy formation energy in aluminum, which is much larger than the cell-sizes that are commonly used in numerical simulations. This estimate is in agreement with recent cell-size studies in Gavini et al. (2007a); Radhakrishnan & Gavini (2010). We further note that the cell-size effects are likely to be more significant for defects like dislocations where the decay in electronic and elastic fields is much slower.

We remark that the limit considered in this analysis is the homogenization limit of the corrector fields, and not the thermodynamic limit. The thermodynamic limit, which has been widely studied in the context of crystalline solids (Blanc et al., 2002; Garcia-Cervera et al., 2007), describes the energy density of an infinite crystal undergoing a smooth macroscopic deformation. The homogenization and thermodynamic limits result in different scalings for the predictor fields, and an analysis similar to the one conducted in the present work using the thermodynamic limit is a challenging open problem. Recent work by Cancés & Ehrlicher (2010); Cancés et al. (2008) are the first efforts in studying the thermodynamic limit of defects in crystalline solids. Interestingly, the exponential decay of the corrector electronic fields away from a local defect, derived in the homogenization limit in the present work, is recovered in the special case of a homogeneous host crystal in the thermodynamic limit (Cancés & Ehrlicher, 2010).

The remainder of this paper is organized as follows. In section 2 we formulate OFDFT with Thomas-Fermi-Weizsacker kinetic energy functionals, and present the problem definition and the assumptions made in this analysis. In section 3 we discuss the perturbation analysis of the corrector fields, and present the multi-scale analysis of these fields and derive the homogenized equations in section 4. In sections 5 and 6 we derive the Green's functions of the homogenized equations and compute their solutions for a spherical defect representing a vacancy. In section 7 we comment on the extension of this analysis to other flavors of OFDFT which use non-local kernel energies and other field formulations representing empirical interatomic potentials. We finally conclude in section 8 providing an outlook.

## 2 Problem definition

Consider an infinite crystal with lattice points given by  $\mathcal{L}_a = a\mathcal{L}$  and  $\mathcal{L} = \{\sum_{i=1}^3 \nu_i \hat{\mathbf{e}}_i : \nu_1, \nu_2, \nu_3 \in \mathbb{Z}\}$ , where  $a$  denotes the lattice parameter and  $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_3 \in \mathbb{R}^3$  are the rescaled lattice vectors satisfying  $\hat{\mathbf{e}}_3 \cdot (\hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2) = 1$ . We refer to

$$U_a = \left\{ \sum_{i=1}^3 at_i \hat{\mathbf{e}}_i : -\frac{1}{2} < t_1, t_2, t_3 < \frac{1}{2} \right\}$$

as the unit cell. Let  $Y_0 = (-L, L)^3$  be a macroscopic supercell such that  $\eta := a/L \ll 1$  and it overlaps with a large integer number of unit cells. Further, let

$$U_0 = \frac{1}{\eta} U_a$$

be the macroscopic rescaled unit cell (comparable with the supercell  $Y_0$ ),  $Z$  be the charge at each nucleus measured in units of electron charge, and  $\mathbf{y} : Y_0 \rightarrow Y$  be a smooth macroscopic deformation that carries a reference point  $\mathbf{x}_0 \in Y_0$  to a new point  $\mathbf{y}(\mathbf{x}_0) \in Y$ . In this work we are interested only in macroscopic deformations. We assume that the positions of nuclei are given by the Cauchy-Born rule, and hence the nuclear charge distribution in the deformed configuration is given by

$$b_{\mathbf{y}}(\mathbf{x}) = \sum_{\mathbf{x}_0 \in \mathcal{L}_a \cap Y_0} Z \tilde{\delta}(\mathbf{x} - \mathbf{y}(\mathbf{x}_0)),$$

where  $\tilde{\delta}$  represents the regularized charge distribution of a nucleus.

To present our ideas we consider the energy of a system described by OFDFT. We remark that the ideas presented here are general and can be equally applied to any field theory, for instance, fields theories that describe empirical interatomic potentials discussed in [Iyer & Gavini \(2011\)](#). In density functional theory, the energy of a material system is given by

$$E(u, b_{\mathbf{y}}) = T_s(u) + E_{xc}(u) + E_H(u) + E_{ext}(u, b_{\mathbf{y}}) + E_{zz}(b_{\mathbf{y}}), \quad (1)$$

where  $u$  denotes the square-root electron density,  $T_s$  denotes the kinetic energy of non-interacting electrons,  $E_{xc}$  denotes the exchange and correlation energies that account for the quantum mechanical effects, and  $E_H$ ,  $E_{ext}$ ,  $E_{zz}$  denote classical electrostatic interaction energies between electrons and nuclei. In OFDFT,  $T_s$  is approximated by explicit functional forms of electron density as opposed to the Kohn-Sham approach where it is computed exactly within the mean field approximation. A simple choice for this approximation is the Thomas-Fermi-Weizsacker (TFW) family of kinetic energy functionals ([Parr & Yang, 1989](#)):

$$T_s(u) = C_F \int_Y u^{10/3} d\mathbf{x} + \frac{\lambda}{2} \int_Y |\nabla u|^2 d\mathbf{x}, \quad (2)$$

where  $0 \leq \lambda \leq 1$  is a parameter and  $C_F = \frac{3}{10}(3\pi^2)^{2/3}$ . More accurate kinetic energy functionals have been proposed in the past decade which account for the linear response of a

uniform electron gas. For clarity we postpone our analysis of these functionals to section 7. By choosing the Thomas-Fermi-Weizsacker functionals (2) for kinetic energy, and following the real-space formulation of OFDFT proposed in Gavini et al. (2007b), we express the total energy of the system as

$$E(u, \phi; b_{\mathbf{y}}) = \int_Y \left[ f(u) + \frac{\lambda}{2} |\nabla u|^2 - \frac{1}{8\pi} |\nabla \phi|^2 + (u^2 + b_{\mathbf{y}}) \phi \right] d\mathbf{x}, \quad (3)$$

where  $f(u) = C_F u^{10/3}$  and  $\phi$  denotes the trial electrostatic potential. In the above, we ignore exchange and correlation energies and comment on them in section 7. The ground state of  $(\phi, u, \mathbf{y})$  is determined by the following min-max problem

$$\mathcal{E}_{tot}(0) := \min_{\mathbf{y} \in \mathcal{Y}} \left\{ \mathcal{E}(\mathbf{y}) := \min_{u \in \mathcal{U}(b_{\mathbf{y}})} \max_{\phi \in H_{per}^1(Y)} E(u, \phi; b_{\mathbf{y}}) \right\}, \quad (4)$$

where

$$\begin{aligned} \mathcal{Y} &:= \{ \mathbf{y} \in \chi : \nabla \mathbf{y} \text{ periodic in } Y_0 \}, \\ \mathcal{U}(b_{\mathbf{y}}) &:= \{ u \in H_{per}^1(Y) : \int_Y (u^2 + b_{\mathbf{y}}) d\mathbf{x} = 0, u \geq 0 \}. \end{aligned} \quad (5)$$

In the above definitions,  $\chi$  is a suitable function space that admits minimizers of  $\mathcal{E}(\mathbf{y})$ . In this analysis, since our focus is to derive and analyze the far-field behavior of the displacement and electronic fields, we restrict our attention to a local minimizer of  $\mathcal{E}(\mathbf{y})$  in  $\mathcal{Y}$ .

Let  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$  be a solution of the min-max problem for a smooth deformation  $\mathbf{y} \in \mathcal{Y}$

$$\mathcal{E}(\mathbf{y}) = E(u_{\mathbf{y}}, \phi_{\mathbf{y}}; b_{\mathbf{y}}) = \min_{u \in \mathcal{U}(b_{\mathbf{y}})} \max_{\phi \in H_{per}^1(Y)} E(u, \phi; b_{\mathbf{y}}). \quad (6)$$

The existence of a solution for the saddle point problem (6) can be established following the ideas in Gavini et al. (2007b), where the analysis was carried out in a non-periodic setting with Dirichlet boundary conditions on a bounded domain. We remark that the arguments in Gavini et al. (2007b) can be appropriately modified to the periodic setting, and these details are not discussed in this article to maintain our focus on multi-scale analysis. We also refer to Lieb (1981) for results on the existence and uniqueness of solutions for various flavors of OFDFT.

It is clear from the definition (3), if  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$  is a solution to the min-max problems in equation (6), so is  $(\phi_{\mathbf{y}} + c, u_{\mathbf{y}})$  for any  $c \in \mathbb{R}$ . By the standard first-variation calculations it follows that there exists a solution to the min-max problem in equation (6), denoted by  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$ , satisfying

$$\begin{cases} \Delta \phi_{\mathbf{y}} + 4\pi(u_{\mathbf{y}}^2 + b_{\mathbf{y}}) = 0 & \text{on } Y, \\ -\lambda \Delta u_{\mathbf{y}} + f'(u_{\mathbf{y}}) + 2u_{\mathbf{y}} \phi_{\mathbf{y}} = 0 & \text{on } Y, \\ \text{subject to: } u_{\mathbf{y}} \in \mathcal{U}(b_{\mathbf{y}}); \quad \phi_{\mathbf{y}} \in H_{per}^1(Y). \end{cases} \quad (7)$$

Note that, in the above equation, the Lagrangian multiplier associated with the constraint in equation (5)<sub>2</sub> has been absorbed into the electrostatic potential  $\phi_{\mathbf{y}}$ . Thus, the solution  $\phi_{\mathbf{y}}$

to problem (7) no longer allows an arbitrary additive constant (cf. [Catto et al. \(1998\)](#) for further discussion on this point).

We now discuss the nature of the solution  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$  to problem (7). First we assume a homogeneous deformation with  $\nabla \mathbf{y} = \mathbf{F}_0 \in \mathbb{R}^{3 \times 3}$  on  $Y_0$ . Consider problem (7) on the deformed unit cell  $\mathbf{F}_0 U_a$

$$\begin{cases} \Delta \phi + 4\pi(u^2 + b_{\mathbf{y}}) = 0 & \text{on } \mathbf{F}_0 U_a, \\ -\lambda \Delta u + f'(u) + 2u\phi = 0 & \text{on } \mathbf{F}_0 U_a, \\ \text{subject to: } \int_{\mathbf{F}_0 U_a} (u^2 + b_{\mathbf{y}}) d\mathbf{x} = 0, \quad u, \phi \in H_{per}^1(\mathbf{F}_0 U_a). \end{cases} \quad (8)$$

For  $f(u) = \frac{3}{10}(3\pi^2)^{2/3}u^{10/3}$ , [Catto et al. \(1998\)](#) have shown that the periodic extension of the solution to problem (8) with respect to the period  $\mathbf{F}_0 U_a$ , denoted by  $(\phi^*, u^*)$ , is the solution to problem (7):

$$\phi_{\mathbf{y}}(\mathbf{x}) = \phi^*(\mathbf{x}), \quad u_{\mathbf{y}}(\mathbf{x}) = u^*(\mathbf{x}) \quad \forall \mathbf{x} \in \mathbf{F}_0 Y_0. \quad (9)$$

For future convenience, we denote by

$$\phi_p(\mathbf{F}_0, \mathbf{x}) = \phi^*(\eta \mathbf{x}), \quad u_p(\mathbf{F}_0, \mathbf{x}) = u^*(\eta \mathbf{x}), \quad (10)$$

where the subscript  $p$  signifies that  $\mathbf{x} \mapsto (\phi_p(\mathbf{F}_0, \mathbf{x}), u_p(\mathbf{F}_0, \mathbf{x}))$  are periodic with period equal to the rescaled unit cell  $\mathbf{F}_0 U_0$ . It is worthwhile noticing that  $(\phi_p, u_p)$  are considered as being defined by the exact solutions to the unit cell problem (8) through equation (10), instead of the solutions in the thermodynamic limit discussed in [Blanc et al. \(2002\)](#). By equations (9) and (10), we have

$$\phi_{\mathbf{y}} = \phi_p(\mathbf{F}_0, \tilde{\mathbf{x}}), \quad u_{\mathbf{y}} = u_p(\mathbf{F}_0, \tilde{\mathbf{x}}), \quad (11)$$

where  $\tilde{\mathbf{x}} = \mathbf{x}/\eta$  denotes the fast variable in the subsequent homogenization calculation. We remark that, in Section 4, equations (11) and the fact that  $\eta \ll 1$  will be used to derive the homogenized equations that govern the far-field behavior of the perturbations to electronic fields created by local defects. Further, we remark that the solution to problem (8) is also a solution of the min-max problem

$$W(\mathbf{F}_0) := \min_u \max_{\phi} \int_{\mathbf{F}_0 U_a} \left[ f(u) + \frac{\lambda}{2} |\nabla u|^2 - \frac{1}{8\pi} |\nabla \phi|^2 + (u^2 + b_{\mathbf{y}}) \phi \right] d\mathbf{x} \quad (12)$$

subject to the same constraints as in equation (8). Here and subsequently,  $f_{\Omega}(\cdot) = \frac{1}{\text{volume}(\Omega)} \int_{\Omega}(\cdot)$  denotes the averaged value of the integrand over the domain  $\Omega$ . In terms of the solutions  $(\phi_p, u_p)$  to the unit cell problem, we define the following quantities for future use

$$\begin{aligned} \alpha(\mathbf{F}_0) &= \int_{\mathbf{F}_0 U_0} u_p(\mathbf{F}_0, \tilde{\mathbf{x}}) d\tilde{\mathbf{x}}, & \beta(\mathbf{F}_0) &= \int_{\mathbf{F}_0 U_0} \phi_p(\mathbf{F}_0, \tilde{\mathbf{x}}) d\tilde{\mathbf{x}}, \\ \gamma(\mathbf{F}_0) &= \int_{\mathbf{F}_0 U_0} \left[ -\frac{1}{2} f''(u_p(\mathbf{F}_0, \tilde{\mathbf{x}})) \right] d\tilde{\mathbf{x}} + \beta(\mathbf{F}_0). \end{aligned} \quad (13)$$

As in classical continuum mechanics, all the functions  $W, \alpha, \beta, \gamma : \mathbb{R}^{3 \times 3} \rightarrow \mathbb{R}$  satisfy the material frame indifference and material symmetries

$$\begin{aligned} W(\mathbf{R}\mathbf{F}_0) &= W(\mathbf{F}_0) & \forall \mathbf{R} \in SO(3) \text{ \& } \mathbf{F}_0 \in \mathbb{R}^{3 \times 3} \text{ with } \det \mathbf{F}_0 > 0, \\ W(\mathbf{F}_0\mathbf{H}) &= W(\mathbf{F}_0) & \forall \mathbf{H} \in \mathcal{G}(\mathbf{F}_0), \end{aligned} \quad (14)$$

where  $SO(3)$  consists of all rigid rotation matrices,  $\mathcal{G}(\mathbf{F}_0)$  is the point group associated with the Bravais lattice  $\mathbf{F}_0\mathcal{L}$ , and  $W$  can be replaced by  $\alpha$ ,  $\beta$ , or  $\gamma$  in equation (14). Equation (14) can be verified directly from the definitions (12) and (13).

We now consider the case when the deformation  $\mathbf{y}$  has a smooth macroscopic deformation gradient  $\hat{\mathbf{F}} : Y \rightarrow \mathbb{R}^{3 \times 3}$  on the current configuration

$$\hat{\mathbf{F}}(\mathbf{x}) = \mathbf{F}(\mathbf{y}^{-1}(\mathbf{x})) \quad \forall \mathbf{x} \in Y, \quad \mathbf{F}(\mathbf{x}_0) = \nabla \mathbf{y}(\mathbf{x}_0) \quad \forall \mathbf{x}_0 \in Y_0. \quad (15)$$

A priori, for this case, we have no knowledge on the solution to (7). Since  $\eta \ll 1$ , motivated by Blanc et al. (2002) we hypothesize that the solution to (7) is given by

$$\phi_{\mathbf{y}}(\mathbf{x}) = \phi_p(\hat{\mathbf{F}}(\mathbf{x}), \tilde{\mathbf{x}}), \quad u_{\mathbf{y}}(\mathbf{x}) = u_p(\hat{\mathbf{F}}(\mathbf{x}), \tilde{\mathbf{x}}), \quad (16)$$

and the elastic energy is given by

$$\mathcal{E}(\mathbf{y}) = E(u_{\mathbf{y}}, \phi_{\mathbf{y}}; b_{\mathbf{y}}) = \int_Y W(\hat{\mathbf{F}}(\mathbf{x})) d\mathbf{x}, \quad (17)$$

where  $(\phi_p, u_p)$  are defined by the exact solutions to the unit cell problem (8) through equation (10), and  $W : \mathbb{R}^{3 \times 3} \rightarrow \mathbb{R}$  is the elastic energy density on the deformed configuration  $Y$  given by equation (12).

The solution to the outer minimization problem (4) may not be unique, and throughout this work we will restrict our attention to local minimizers that satisfy the Euler-Lagrange equation corresponding to the energy in equation (17), which is the familiar equilibrium equation of elasticity

$$\text{Div } \mathbf{S}(\nabla \mathbf{y}^*) = 0 \quad \text{on } Y_0, \quad (18)$$

where

$$[\mathbf{S}(\nabla \mathbf{y}^*)]_{pi} = \frac{\partial JW}{\partial \mathbf{F}_{pi}}(\nabla \mathbf{y}^*), \quad J(\mathbf{F}) = \det(\mathbf{F}).$$

Note that in equation (18),  $\mathbf{S}$  is the first Piola-Kirchhoff stress and  $[\text{Div } \mathbf{S}]_p = \frac{\partial \mathbf{S}_{pi}}{\partial \mathbf{x}_{0i}}$ .

### 3 Perturbation analysis

We now consider the effect of defects on electronic fields  $(\phi, u)$ . A defect breaks the lattice symmetry, which in effect is a perturbation of the forcing term,  $b_{\mathbf{y}}$ , in equation (7). Thus, we replace the forcing term in equation (7) by a small perturbation of  $b_{\mathbf{y}}$ :  $b_{\mathbf{y}}^\varepsilon = b_{\mathbf{y}} + \varepsilon b_c$  with  $\varepsilon \ll 1$  and consider  $b_c$  to be a macroscopic perturbation which allows us to subsequently



pass to the homogenization limit in section 4. If  $b_c$  has a compact support, this perturbation can be interpreted as a weak local defect, formed by slowly reducing the charges on the nuclei in a macroscopic region, in an otherwise perfect crystal undergoing a smooth deformation. We are interested in calculating the influence of this perturbation (defect) on the ground state of OFDFT and, in particular, on the total energy. As in equation (4), the ground state of the system is governed by

$$\mathcal{E}_{tot}(b_c) := \min_{\mathbf{y} \in \mathcal{Y}} \left\{ \mathcal{E}^\varepsilon(\mathbf{y}; b_c) := \min_{u \in \mathcal{U}(b_{\mathbf{y}}^\varepsilon)} \max_{\phi \in H_{per}^1(Y)} E(u, \phi; b_{\mathbf{y}} + \varepsilon b_c) \right\}. \quad (19)$$

Note that if  $b_c = 0$ , i.e., the system is unperturbed, then  $\mathcal{E}_{tot}(b_c = 0)$  is equal to  $\mathcal{E}_{tot}(0)$  in equation (4).

We solve the above problem approximately by perturbation method. We first consider the inner min-max problem in equation (19) for given  $\mathbf{y} \in \mathcal{Y}$ . Let

$$\phi^\varepsilon = \phi_{\mathbf{y}} + \varepsilon \phi_c \in H_{per}^1(Y), \quad u^\varepsilon = u_{\mathbf{y}} + \varepsilon u_c \in \mathcal{U}(b_{\mathbf{y}}^\varepsilon), \quad (20)$$

be the solutions, where  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$ , the solutions to the unperturbed problem (7), are referred to as the predictor fields in the quasi-continuum formulation, and  $(\phi_c, u_c)$  are referred to as the corrector fields (Gavini et al., 2007a). Inserting equation (20) into equation (5)<sub>2</sub>, we obtain the charge neutrality constraint

$$\int_Y [2u_{\mathbf{y}}u_c + \varepsilon u_c^2 + b_c] d\mathbf{x} = 0. \quad (21)$$

Inserting equation (20) into equation (3), we expand the energy as

$$\begin{aligned} E(u^\varepsilon, \phi^\varepsilon; b_{\mathbf{y}} + \varepsilon b_c) &= E(u_{\mathbf{y}}, \phi_{\mathbf{y}}; b_{\mathbf{y}}) + \varepsilon \int_Y \left\{ [f'(u_{\mathbf{y}}) - \lambda \Delta u_{\mathbf{y}} + 2u_{\mathbf{y}}\phi_{\mathbf{y}}] u_c \right. \\ &\quad \left. + [\frac{1}{4\pi} \Delta \phi_{\mathbf{y}} + u_{\mathbf{y}}^2 + b_{\mathbf{y}}] \phi_c + b_c \phi_{\mathbf{y}} \right\} d\mathbf{x} + \varepsilon^2 E_2(u_c, \phi_c, \mathbf{y}; b_c) + o(\varepsilon^2) \\ &= E(u_{\mathbf{y}}, \phi_{\mathbf{y}}; b_{\mathbf{y}}) + \varepsilon \int_Y b_c \phi_{\mathbf{y}} d\mathbf{x} + \varepsilon^2 E_2(u_c, \phi_c, \mathbf{y}; b_c) + o(\varepsilon^2), \end{aligned} \quad (22)$$

where the second equality follows from the Euler-Lagrange equations in (7) for  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$ , and

$$E_2(u_c, \phi_c, \mathbf{y}; b_c) = \int_Y \left[ \frac{1}{2} f''(u_{\mathbf{y}}) u_c^2 + \frac{\lambda}{2} |\nabla u_c|^2 - \frac{1}{8\pi} |\nabla \phi_c|^2 + (2u_{\mathbf{y}}u_c + b_c) \phi_c + \phi_{\mathbf{y}} u_c^2 \right] d\mathbf{x}. \quad (23)$$

Neglecting  $o(\varepsilon^2)$ -terms in equation (22), by the inner min-max problem in equation (19) we arrive at the following min-max problem for  $(u_c, \phi_c)$ :

$$\mathcal{E}_2(\mathbf{y}; b_c) := \min_{u_c} \max_{\phi_c} E_2(u_c, \phi_c, \mathbf{y}; b_c) \quad (24)$$

subject to the constraints (cf. equation (21))

$$\phi_c \in H_{per}^1(Y), \quad u_c \in H_{per}^1(Y), \quad \int_Y (2u_{\mathbf{y}}u_c + b_c) d\mathbf{x} = 0. \quad (25)$$



We remark that the zeroth and first order terms in equation (22) are absent in the min-max problem (24) since they are independent of  $(\phi_c, u_c)$ . By the standard first-variation calculations, we show that the Euler-Lagrange equations for  $(\phi_c, u_c)$  associated with the min-max problem (24) are

$$\begin{cases} \Delta\phi_c + 4\pi(2u_{\mathbf{y}}u_c + b_c) = 0 & \text{on } Y, \\ -\lambda\Delta u_c + (f''(u_{\mathbf{y}}) + 2\phi_{\mathbf{y}})u_c + 2u_{\mathbf{y}}\phi_c = 0 & \text{on } Y, \end{cases} \quad (26)$$

where, as in equation (7), we have absorbed into the potential  $\phi_c$  the Lagrangian multiplier associated with the last constraint in equation (25), which is a constant independent of  $\mathbf{x}$ . We further notice that equations (26) can be obtained by linearizing equation (7) near the solutions  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$ . We remark that although the perturbation analysis was conducted under the assumption of weak local defects, the perturbation expansion given by equation (20) is a reasonable assumption in regions away from defects that are not necessarily weak. This follows as the perturbations in electronic fields decay away from the defect core due to the elliptic nature of the PDE's, and the governing equations for corrector fields will subsequently be valid in these regions.

## 4 Homogenization

We now turn towards establishing certain properties of the corrector fields which play a fundamental role in the construction of quasi-continuum reduction of field formulations proposed in Gavini et al. (2007a); Iyer & Gavini (2011), and provide a formal mathematical justification for the method. Before proceeding to details, we notice the following useful identity. Let  $f(\mathbf{x}, \tilde{\mathbf{x}})$  be a smooth function which is periodic in the second variable  $\tilde{\mathbf{x}}$  with period  $\hat{\mathbf{F}}(\mathbf{x})U_0$ . If  $\eta \ll 1$ , we have the identity (cf. e. g. Cioranescu & Donato (1999), Chapter 2),

$$\int_Y f(\mathbf{x}, \frac{\mathbf{x}}{\eta}) d\mathbf{x} = \int_Y \int_{\hat{\mathbf{F}}(\mathbf{x})U_0} f(\mathbf{x}, \tilde{\mathbf{x}}) d\tilde{\mathbf{x}} d\mathbf{x} + o(1). \quad (27)$$

Since the unperturbed solutions  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$  given by equation (16) oscillate at the atomic scale- $a$ , presumably the corrector field solutions  $(\phi_c, u_c)$  to the governing equations in (26) oscillate at the  $a$ -scale as well. In this section, we determine the order of this  $a$ -scale oscillation in the corrector fields  $(\phi_c, u_c)$  and whether this atomic-scale oscillation is important to the leading order in energy. Further, we determine the homogenized equations that govern the macroscopic behavior of these corrector fields. To this end, following the method of the multiple scale expansions, we assume

$$\begin{cases} \phi_c(\mathbf{x}) = \phi_c^0(\mathbf{x}, \tilde{\mathbf{x}}) + \eta\phi_c^1(\mathbf{x}, \tilde{\mathbf{x}}) + \dots, \\ u_c(\mathbf{x}) = u_c^0(\mathbf{x}, \tilde{\mathbf{x}}) + \eta u_c^1(\mathbf{x}, \tilde{\mathbf{x}}) + \dots, \end{cases} \quad (28)$$

where  $\tilde{\mathbf{x}} = \mathbf{x}/\eta$  is the fast variable,  $\phi_c^i(\mathbf{x}, \tilde{\mathbf{x}})$ ,  $u_c^i(\mathbf{x}, \tilde{\mathbf{x}})$  ( $i = 0, 1, \dots$ ) are assumed to be periodic in the fast variable  $\tilde{\mathbf{x}}$  with period  $\hat{\mathbf{F}}(\mathbf{x})U_0$ . Replacing  $(\phi_{\mathbf{y}}, u_{\mathbf{y}})$  by the right hand side of equation (16), we rewrite  $E_2$  in equation (23) as

$$E_2(u_c, \phi_c, \mathbf{y}; b_c) = \int_Y \left[ \left( \frac{1}{2} f''(u_p) + \phi_p \right) u_c^2 + \frac{\lambda}{2} |\nabla u_c|^2 - \frac{1}{8\pi} |\nabla \phi_c|^2 + (2u_p u_c + b_c) \phi_c \right] d\mathbf{x}. \quad (29)$$

Inserting the multiple scale expansion (28) into equation (29), we have

$$\begin{aligned}
E_2(u_c, \phi_c, \mathbf{y}; b_c) &= \int_Y \left[ \left( \frac{1}{2} f''(u_p) + \phi_p \right) (u_c^0)^2 + \frac{\lambda}{2} \left| \frac{1}{\eta} \nabla_{\tilde{\mathbf{x}}} u_c^0 + \nabla_{\mathbf{x}} u_c^0 + \nabla_{\tilde{\mathbf{x}}} u_c^1 \right|^2 \right. \\
&\quad \left. - \frac{1}{8\pi} \left| \frac{1}{\eta} \nabla_{\tilde{\mathbf{x}}} \phi_c^0 + \nabla_{\mathbf{x}} \phi_c^0 + \nabla_{\tilde{\mathbf{x}}} \phi_c^1 \right|^2 + (2u_p u_c^0 + b_c) \phi_c^0 \right] d\mathbf{x} + O(\eta) \\
&= \frac{1}{2\eta^2} \int_Y \left[ \lambda |\nabla_{\tilde{\mathbf{x}}} u_c^0|^2 - \frac{1}{4\pi} |\nabla_{\tilde{\mathbf{x}}} \phi_c^0|^2 \right] d\mathbf{x} \\
&\quad + \frac{1}{\eta} \int_Y \left[ \lambda \nabla_{\tilde{\mathbf{x}}} u_c^0 \cdot (\nabla_{\mathbf{x}} u_c^0 + \nabla_{\tilde{\mathbf{x}}} u_c^1) - \frac{1}{4\pi} \nabla_{\tilde{\mathbf{x}}} \phi_c^0 \cdot (\nabla_{\mathbf{x}} \phi_c^0 + \nabla_{\tilde{\mathbf{x}}} \phi_c^1) \right] d\mathbf{x} \\
&\quad + \int_Y \left[ \left( \frac{1}{2} f''(u_p) + \phi_p \right) (u_c^0)^2 + \frac{\lambda}{2} |\nabla_{\mathbf{x}} u_c^0 + \nabla_{\tilde{\mathbf{x}}} u_c^1|^2 \right. \\
&\quad \left. - \frac{1}{8\pi} |\nabla_{\mathbf{x}} \phi_c^0 + \nabla_{\tilde{\mathbf{x}}} \phi_c^1|^2 + (2u_p u_c^0 + b_c) \phi_c^0 \right] d\mathbf{x} + O(\eta). \tag{30}
\end{aligned}$$

We neglect the higher order terms of  $O(\eta)$  in equation (30). Since  $\eta \ll 1$ , we consider the min-max problem (24) first for the leading  $\frac{1}{\eta^2}$ -terms in equation (30), which is given by

$$\min_{u_c^0} \max_{\phi_c^0} \int_Y \left[ \lambda |\nabla_{\tilde{\mathbf{x}}} u_c^0|^2 - \frac{1}{4\pi} |\nabla_{\tilde{\mathbf{x}}} \phi_c^0|^2 \right] d\mathbf{x}.$$

It is clear that a solution to the above problem necessarily satisfies

$$\nabla_{\tilde{\mathbf{x}}} u_c^0(\mathbf{x}, \tilde{\mathbf{x}}) = 0 \quad \text{and} \quad \nabla_{\tilde{\mathbf{x}}} \phi_c^0(\mathbf{x}, \tilde{\mathbf{x}}) = 0, \tag{31}$$

which means that  $\phi_c^0(\mathbf{x}, \tilde{\mathbf{x}})$  and  $u_c^0(\mathbf{x}, \tilde{\mathbf{x}})$  are independent of the fast variable  $\tilde{\mathbf{x}}$  and hence can be rewritten as

$$u_c^0(\mathbf{x}, \tilde{\mathbf{x}}) = u_c^0(\mathbf{x}) \quad \text{and} \quad \phi_c^0(\mathbf{x}, \tilde{\mathbf{x}}) = \phi_c^0(\mathbf{x}). \tag{32}$$

This shows that the leading order terms in the corrector fields do not exhibit atomic-scale oscillations, and thus the corrector fields can be resolved accurately on length scales larger than the lattice parameter. This key result formally justifies the coarse-graining of corrector fields introduced in the quasi-continuum reduction of field theories.

Further, in account of equation (31), the  $\frac{1}{\eta}$ -terms on the right hand side of equation (30) vanish. Finally, we consider the  $\frac{1}{\eta^0}$ -order terms on the right hand side of equation (30) which represent the leading order terms in the multiple scale expansion of  $E_2$ . Using equation (27) we can rewrite equation (30) as

$$\begin{aligned}
E_2(u_c, \phi_c, \mathbf{y}; b_c) &\approx \int_Y \int_{\hat{\mathbf{F}}(\mathbf{x}) U_0} \left[ \frac{\lambda}{2} |\nabla_{\mathbf{x}} u_c^0|^2 - \frac{1}{8\pi} |\nabla_{\mathbf{x}} \phi_c^0|^2 \right] d\tilde{\mathbf{x}} d\mathbf{x} \\
&\quad + \int_Y \int_{\hat{\mathbf{F}}(\mathbf{x}) U_0} \left[ \left( \frac{1}{2} f''(u_p(\hat{\mathbf{F}}(\mathbf{x}), \tilde{\mathbf{x}})) + \phi_p(\hat{\mathbf{F}}(\mathbf{x}), \tilde{\mathbf{x}}) \right) |u_c^0|^2 \right. \\
&\quad \left. + 2u_p(\hat{\mathbf{F}}(\mathbf{x}), \tilde{\mathbf{x}}) u_c^0 \phi_c^0 + b_c \phi_c^0 \right] d\tilde{\mathbf{x}} d\mathbf{x} \\
&\quad + \int_Y \int_{\hat{\mathbf{F}}(\mathbf{x}) U_0} \left[ \frac{\lambda}{2} (2\nabla_{\mathbf{x}} u_c^0 + \nabla_{\tilde{\mathbf{x}}} u_c^1) \cdot \nabla_{\tilde{\mathbf{x}}} u_c^1 - \frac{1}{8\pi} (2\nabla_{\mathbf{x}} \phi_c^0 + \nabla_{\tilde{\mathbf{x}}} \phi_c^1) \cdot \nabla_{\tilde{\mathbf{x}}} \phi_c^1 \right] d\tilde{\mathbf{x}} d\mathbf{x}. \tag{33}
\end{aligned}$$

Since  $u_c^1(\mathbf{x}, \tilde{\mathbf{x}})$  and  $\phi_c^1(\mathbf{x}, \tilde{\mathbf{x}})$  are periodic on  $\hat{\mathbf{F}}(\mathbf{x})U_0$  for every  $\mathbf{x}$ , from equation (32) we have

$$\int_{\hat{\mathbf{F}}(\mathbf{x})U_0} \nabla_{\mathbf{x}} u_c^0 \cdot \nabla_{\tilde{\mathbf{x}}} u_c^1 d\tilde{\mathbf{x}} = 0 \quad \text{and} \quad \int_{\hat{\mathbf{F}}(\mathbf{x})U_0} \nabla_{\mathbf{x}} \phi_c^0 \cdot \nabla_{\tilde{\mathbf{x}}} \phi_c^1 d\tilde{\mathbf{x}} = 0 \quad \forall \mathbf{x} \in Y. \quad (34)$$

From the min-max problem (24), we maximize the expression in equation (33) over admissible  $\phi_c^1$  and minimize it over admissible  $u_c^1$ , and obtain

$$\nabla_{\tilde{\mathbf{x}}} u_c^1(\mathbf{x}, \tilde{\mathbf{x}}) = 0 \quad \text{and} \quad \nabla_{\tilde{\mathbf{x}}} \phi_c^1(\mathbf{x}, \tilde{\mathbf{x}}) = 0. \quad (35)$$

Thus, it follows that the corrector fields do not exhibit atomic-scale oscillations up to the second order terms in the multiple scale expansion (28). Further, from equation (35), the last term on the right hand side of equation (33) vanishes, and by equations (13) and (32) we identify the first two terms in equation (33) as

$$\int_Y \left[ \frac{\lambda}{2} |\nabla_{\mathbf{x}} u_c^0|^2 - \frac{1}{8\pi} |\nabla_{\mathbf{x}} \phi_c^0|^2 + \gamma(\hat{\mathbf{F}}(\mathbf{x})) |u_c^0|^2 + 2\alpha(\hat{\mathbf{F}}(\mathbf{x})) u_c^0 \phi_c^0 + b_c \phi_c^0 \right] d\mathbf{x} =: E_2^0(u_c^0, \phi_c^0, \mathbf{y}; b_c), \quad (36)$$

where the  $\gamma$  and  $\alpha$  are defined in equation (13). In conclusion, from the min-max problem in equation (24), assuming the multiple scale expansion given by equation (28), and keeping only the leading order terms, we have

$$\mathcal{E}_2(\mathbf{y}; b_c) \approx \min_{u_c^0} \max_{\phi_c^0} E_2^0(u_c^0, \phi_c^0, \mathbf{y}; b_c) \quad (37)$$

subject to

$$\phi_c^0 \in H_{per}^1(Y), \quad u_c^0 \in H_{per}^1(Y), \quad \int_Y (2\alpha(\hat{\mathbf{F}}(\mathbf{x})) u_c^0 + b_c) d\mathbf{x} = 0, \quad (38)$$

where the constraint on  $u_c^0$  follows from equations (25), (13), and neglecting higher order terms in equation (28). Equations (37)-(38) constitute the governing equations for the corrector fields in their leading order.

We now proceed to derive the governing equations that describe the elastic response of the defect. From equations (22) and (37) we see that  $\mathcal{E}^\varepsilon : \mathcal{Y} \rightarrow \mathbb{R}$  defined in equation (19) is given by

$$\begin{aligned} \mathcal{E}^\varepsilon(\mathbf{y}; b_c) &= E(u_{\mathbf{y}}, \phi_{\mathbf{y}}, b_{\mathbf{y}}) + \varepsilon \int_Y b_c \phi_{\mathbf{y}} d\mathbf{x} + \varepsilon^2 \mathcal{E}_2(\mathbf{y}; b_c) + o(\varepsilon^2) \\ &= \int_Y W(\hat{\mathbf{F}}(\mathbf{x})) d\mathbf{x} + \varepsilon \int_Y b_c \phi_{\mathbf{y}} d\mathbf{x} + \varepsilon^2 \mathcal{E}_2(\mathbf{y}; b_c) + o(\varepsilon^2), \end{aligned} \quad (39)$$

where in the second equality we have used equation (17) for  $E(u_{\mathbf{y}}, \phi_{\mathbf{y}}, b_{\mathbf{y}})$ . Let  $\mathbf{y}^* : Y_0 \rightarrow Y$  be the unperturbed minimizer of the outer minimization problem in (4),

$$\mathbf{F}^*(\mathbf{x}_0) = \nabla_{\mathbf{x}_0} \mathbf{y}^*(\mathbf{x}_0) \quad \forall \mathbf{x}_0 \in Y_0, \quad \hat{\mathbf{F}}^*(\mathbf{x}) = \mathbf{F}^*(\mathbf{y}^{*-1}(\mathbf{x})) \quad \forall \mathbf{x} \in Y,$$

and, parallel to equation (20), let

$$\mathbf{y}^\varepsilon = \mathbf{y}^* + \varepsilon \mathbf{y}_c \quad (40)$$

with  $\mathbf{y}^\varepsilon \in \mathcal{Y}$  being the minimizer of the outer minimization problem in (19). As we are interested in the elastic fields created in response to the perturbation  $b_c$ , and not the configurational force on  $b_c$ , we hold the pull back of  $b_c$  on to the reference configuration fixed. To this end, we define  $\tilde{b}_c(\mathbf{x}_0) = b_c(\mathbf{y}^*(\mathbf{x}_0)) \forall \mathbf{x}_0 \in Y_0$  as the pull back before introducing the perturbation in the deformation field. Subsequently, for any infinitesimal perturbation of the deformation given by equation (40),  $b_c$  in the current configuration is given by  $b_c(\mathbf{x}) = \tilde{b}_c(\mathbf{y}^{\varepsilon^{-1}}(\mathbf{x})) \forall \mathbf{x} \in Y$ . Further, let

$$\mathbf{F}^\varepsilon(\mathbf{x}_0) = \nabla_{\mathbf{x}_0} \mathbf{y}^\varepsilon(\mathbf{x}_0) \quad \forall \mathbf{x}_0 \in Y_0, \quad \hat{\mathbf{F}}^\varepsilon(\mathbf{x}) = \mathbf{F}^\varepsilon(\mathbf{y}^{\varepsilon^{-1}}(\mathbf{x})) \quad \forall \mathbf{x} \in Y,$$

and

$$[\mathbf{C}(\nabla_{\mathbf{x}_0} \mathbf{y}^*)]_{piqj} := \frac{\partial^2 JW}{\partial \mathbf{F}_{pi} \partial \mathbf{F}_{qj}}(\nabla_{\mathbf{x}_0} \mathbf{y}^*), \quad [\mathbf{B}(\nabla_{\mathbf{x}_0} \mathbf{y}^*)]_{pi} := \frac{\partial J\beta}{\partial \mathbf{F}_{pi}}(\nabla_{\mathbf{x}_0} \mathbf{y}^*). \quad (41)$$

Since

$$\int_Y W(\hat{\mathbf{F}}^\varepsilon(\mathbf{x})) d\mathbf{x} = \int_{Y_0} J(\mathbf{F}^\varepsilon(\mathbf{x}_0)) W(\mathbf{F}^\varepsilon(\mathbf{x}_0)) d\mathbf{x}_0,$$

we have

$$\begin{aligned} \int_Y W(\hat{\mathbf{F}}^\varepsilon(\mathbf{x})) d\mathbf{x} &= \int_{Y_0} J(\nabla_{\mathbf{x}_0} \mathbf{y}^*) W(\nabla_{\mathbf{x}_0} \mathbf{y}^*) d\mathbf{x}_0 + \varepsilon \int_{Y_0} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{S}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) d\mathbf{x}_0 \\ &\quad + \varepsilon^2 \int_{Y_0} \frac{1}{2} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{C}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) \cdot \nabla_{\mathbf{x}_0} \mathbf{y}_c d\mathbf{x}_0 + o(\varepsilon^2). \end{aligned} \quad (42)$$

Further, by equations (27) and (13) we have

$$\begin{aligned} \int_Y b_c \phi_{\mathbf{y}^\varepsilon} d\mathbf{x} &\approx \int_Y b_c(\mathbf{x}) \oint_{\hat{\mathbf{F}}^\varepsilon(\mathbf{x}) U_0} \phi_p(\hat{\mathbf{F}}^\varepsilon(\mathbf{x}), \tilde{\mathbf{x}}) d\tilde{\mathbf{x}} d\mathbf{x} = \int_{Y_0} \tilde{b}_c(\mathbf{x}_0) J(\mathbf{F}^\varepsilon) \beta(\mathbf{F}^\varepsilon) d\mathbf{x}_0 \\ &= \int_{Y_0} \tilde{b}_c(\mathbf{x}_0) J(\nabla_{\mathbf{y}^*}) \beta(\nabla_{\mathbf{y}^*}) d\mathbf{x}_0 + \varepsilon \int_{Y_0} \tilde{b}_c(\mathbf{x}_0) \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{B}(\nabla_{\mathbf{y}^*}) d\mathbf{x}_0 + o(\varepsilon) \\ &\approx \int_Y b_c \phi_{\mathbf{y}^*} d\mathbf{x} + \varepsilon \int_{Y_0} \tilde{b}_c \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{B}(\nabla_{\mathbf{y}^*}) d\mathbf{x}_0. \end{aligned} \quad (43)$$

Replacing  $\mathbf{y}$  in equation (39) by  $\mathbf{y}^\varepsilon$  given by equation (40), expanding and keeping terms up to  $\varepsilon^2$ , by equations (42) and (43) we obtain

$$\begin{aligned} \mathcal{E}^\varepsilon(\mathbf{y}^* + \varepsilon \mathbf{y}_c; b_c) &\approx \int_{Y_0} J(\nabla_{\mathbf{x}_0} \mathbf{y}^*) W(\nabla_{\mathbf{x}_0} \mathbf{y}^*) d\mathbf{x}_0 + \varepsilon \int_{Y_0} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{S}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) d\mathbf{x}_0 + \varepsilon \int_Y b_c \phi_{\mathbf{y}^*} d\mathbf{x} \\ &\quad + \varepsilon^2 \int_{Y_0} \left\{ \frac{1}{2} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{C}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) \cdot \nabla_{\mathbf{x}_0} \mathbf{y}_c + \tilde{b}_c \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{B}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) \right\} d\mathbf{x}_0 \\ &\quad + \varepsilon^2 \mathcal{E}_2(\mathbf{y}^*; b_c) + o(\varepsilon^2), \end{aligned} \quad (44)$$

Since  $\mathbf{y}^*$  is a local minimizer satisfying equation (18), it follows that  $\int_{Y_0} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{S}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) d\mathbf{x}_0 = 0$ . We further neglect  $o(\varepsilon^2)$ -term in equation (44). Finally, the outer minimization problem given by equation (19) reduces to a minimization problem on  $\mathbf{y}_c$  and is given by

$$\mathcal{E}_{el}(b_c) := \min_{\mathbf{y}_c \in \mathcal{Y}} \int_{Y_0} \left\{ \frac{1}{2} \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{C}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) \nabla_{\mathbf{x}_0} \mathbf{y}_c + \tilde{b}_c \nabla_{\mathbf{x}_0} \mathbf{y}_c \cdot \mathbf{B}(\nabla_{\mathbf{x}_0} \mathbf{y}^*) \right\} d\mathbf{x}_0. \quad (45)$$

Thus, a minimizer  $\mathbf{y}_c$  satisfies the following Euler-Lagrange equation which constitutes the governing equation for the elastic response in the presence of a defect

$$\text{Div}[\mathbf{C}(\nabla_{\mathbf{x}_0}\mathbf{y}^*)\nabla_{\mathbf{x}_0}\mathbf{y}_c + \tilde{b}_c\mathbf{B}(\nabla_{\mathbf{x}_0}\mathbf{y}^*)] = 0 \quad \text{on } Y_0. \quad (46)$$

An important quantity in the study of defects is the defect formation energy, which is defined as the excess energy in the system with a defect measured from a reference state of a perfect crystal consisting of same number of particles—in this case the number of electrons and nuclei. In the framework of the present study, it is given by

$$\mathcal{E}_d(b_c) := [\mathcal{E}_{tot}(b_c) - \mathcal{E}_{tot}(0) - \varepsilon \int_Y b_c \phi_{\mathbf{y}^*} d\mathbf{x}] / \varepsilon^2.$$

From the previous discussions, the defect formation energy (defect energy) can be expressed, to the leading order, as the following min-min-max (saddle point) problem:

$$\begin{aligned} \mathcal{E}_d(b_c) \approx & \min_{\mathbf{y}_c} \min_{u_c^0} \max_{\phi_c^0} \int_{Y_0} \left\{ \frac{1}{2} \nabla_{\mathbf{x}_0}\mathbf{y}_c \cdot \mathbf{C}(\nabla_{\mathbf{x}_0}\mathbf{y}^*) \nabla_{\mathbf{x}_0}\mathbf{y}_c + \tilde{b}_c \nabla_{\mathbf{x}_0}\mathbf{y}_c \cdot \mathbf{B}(\nabla_{\mathbf{x}_0}\mathbf{y}^*) \right\} d\mathbf{x}_0 \\ & + \int_Y \left\{ \gamma(\hat{\mathbf{F}}^*) |u_c^0|^2 + \frac{\lambda}{2} |\nabla_{\mathbf{x}} u_c^0|^2 - \frac{1}{8\pi} |\nabla_{\mathbf{x}} \phi_c^0|^2 + 2\alpha(\hat{\mathbf{F}}^*) u_c^0 \phi_c^0 + b_c \phi_c^0 \right\} d\mathbf{x} \end{aligned} \quad (47)$$

subject to

$$\phi_c^0 \in H_{per}^1(Y), \quad u_c^0 \in H_{per}^1(Y), \quad \int_Y (2\alpha(\hat{\mathbf{F}}^*) u_c^0 + b_c) d\mathbf{x} = 0, \quad \mathbf{y}_c \in \mathcal{Y}. \quad (48)$$

Associated with the above min-min-max problem, the Euler-Lagrange equations are the elasticity equation (46) for  $\mathbf{y}_c$  on the reference configuration  $Y_0$  and

$$\begin{cases} \Delta \phi_c^0 + 4\pi[2\alpha(\hat{\mathbf{F}}^*) u_c^0 + b_c] = 0 & \text{on } Y, \\ -\lambda \Delta u_c^0 + 2\gamma(\hat{\mathbf{F}}^*) u_c^0 + 2\alpha(\hat{\mathbf{F}}^*) \phi_c^0 = 0 & \text{on } Y \end{cases} \quad (49)$$

for  $(\phi_c^0, u_c^0)$  on the current configuration  $Y$ . Note that the elasticity problem (46) for  $\mathbf{y}_c$  is not coupled with the equations for  $(\phi_c^0, u_c^0)$ . In terms of the solutions  $(\mathbf{y}_c, \phi_c^0, u_c^0)$  to equations (46) and (49), the defect energy can be written as

$$\mathcal{E}_d(b_c) \approx \frac{1}{2} \int_{Y_0} \tilde{b}_c \nabla \mathbf{y}_c \cdot \mathbf{B}(\nabla \mathbf{y}^*) + \frac{1}{2} \int_Y b_c \phi_c^0. \quad (50)$$

## 5 Far fields

In this section we determine the far-field behavior of the fields  $(\phi_c^0, u_c^0, \mathbf{y}_c)$  from the governing equations in (49) that will aid in determining the optimal coarse-graining rates for these fields. In this analysis, we assume  $b_c$  is continuous, bounded and supported within the ball  $B_{r_0} = \{\mathbf{x} : |\mathbf{x}| \leq r_0\}$ . Although the analysis in the previous section was performed on the supercells  $Y_0$  and  $Y$ , we note that the results of the analysis are independent of the supercells and thus to determine the asymptotic behavior of the corrector fields we assume

$Y_0 = Y = \mathbb{R}^3$ . We first calculate the far field behavior of  $(\phi_c^0, u_c^0)$  for a homogeneous deformation with  $\nabla_{\mathbf{x}_0} \mathbf{y}^* = \mathbf{F}_0 \in \mathbb{R}^{3 \times 3}$  on  $\mathbb{R}^3$ . In this case,  $\hat{\mathbf{F}}^* = \mathbf{F}_0$  on  $\mathbb{R}^3$  as well;  $\mathbf{C}(\nabla_{\mathbf{x}_0} \mathbf{y}^*)$ ,  $\mathbf{B}(\nabla_{\mathbf{x}_0} \mathbf{y}^*)$ ,  $\alpha(\hat{\mathbf{F}}^*)$ ,  $\gamma(\hat{\mathbf{F}}^*)$  are constants on  $\mathbb{R}^3$  and we drop their dependence on  $\mathbf{F}_0$  in notation. Further, the periodic boundary conditions in equation (48) shall be replaced by appropriate decay conditions at the infinity. Dropping the subscript  $c$  and superscript  $0$  in  $(\phi_c^0, u_c^0, \mathbf{y}^c)$  in equations (49) and (46), we rewrite our problem for  $(\phi, u, \mathbf{y})$  as

$$\begin{cases} \Delta\phi + 4\pi(2\alpha u + b_c) = 0 & \text{on } \mathbb{R}^3, \\ -\lambda\Delta u + 2\gamma u + 2\alpha\phi = 0 & \text{on } \mathbb{R}^3, \\ \text{Div}[\mathbf{C}\nabla_{\mathbf{x}_0} \mathbf{y} + b_c(\mathbf{F}_0 \mathbf{x}_0)\mathbf{B}] = 0 & \text{on } \mathbb{R}^3, \end{cases} \quad (51)$$

subject to

$$|\phi(\mathbf{x})|, |u(\mathbf{x})|, |\mathbf{y}| \rightarrow 0 \quad \text{as } |\mathbf{x}| \rightarrow +\infty, \quad \int_{\mathbb{R}^3} (2\alpha u + b_c) = 0. \quad (52)$$

We now address the solutions of the first two of equation (51). Taking Laplacian of equation (51)<sub>2</sub> and inserting into equation (51)<sub>1</sub>, we obtain

$$\Delta\Delta u - \frac{2}{l_1^2}\Delta u + \frac{1}{l_0^4}u = b \quad \text{on } \mathbb{R}^3, \quad (53)$$

where  $l_0 > 0$ ,  $\text{Re}(l_1) \geq 0$ ,

$$\frac{1}{l_1^2} = \frac{\gamma}{\lambda}, \quad \frac{1}{l_0^4} = \frac{16\pi\alpha^2}{\lambda} > 0, \quad b = -\frac{8\pi\alpha b_c}{\lambda}. \quad (54)$$

The constants  $l_1, l_0$  determine the asymptotic behavior of the fundamental solution at the infinity. Since equation (53) is linear, we express its solution as

$$u(\mathbf{x}) = (E_u * b)(\mathbf{x}) = \int_{\mathbb{R}^3} E_u(\mathbf{x} - \mathbf{x}')b(\mathbf{x}')d\mathbf{x}', \quad (55)$$

where  $E_u$  is the fundamental solution satisfying

$$(\Delta\Delta - \frac{2}{l_1^2}\Delta + \frac{1}{l_0^4})E_u = \delta(0),$$

and  $\delta(0)$  is the Dirac distribution. We find the fundamental solution  $E_u$  by Fourier analysis. Solving the algebraic equation

$$x^4 + \frac{2}{l_1^2}x^2 + \frac{1}{l_0^4} = 0, \quad (56)$$

we obtain two roots  $\kappa_{\pm}$  with  $\text{Im}(\kappa_{\pm}) \geq 0$  and satisfying

$$\kappa_{\pm}^2 = -\frac{1}{l_1^2} \pm \sqrt{\frac{1}{l_1^4} - \frac{1}{l_0^4}}. \quad (57)$$

The two other roots with  $\text{Im}(\kappa_{\pm}) < 0$  are discarded as they will correspond to exponentially growing solutions in  $(u, \phi)$ , defined subsequently, and do not satisfy the decay conditions imposed in (52). By Fourier analysis, we have

$$\begin{aligned} E_u(\mathbf{x}) &= \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{1}{|\mathbf{k}|^4 + \frac{2}{l_1^2} |\mathbf{k}|^2 + \frac{1}{l_0^4}} \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \\ &= \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{1}{(\kappa_+^2 - \kappa_-^2)} \left[ \frac{1}{|\mathbf{k}|^2 - \kappa_+^2} - \frac{1}{|\mathbf{k}|^2 - \kappa_-^2} \right] \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k}. \end{aligned} \quad (58)$$

We are therefore motivated to consider the fundamental solution of the operator

$$(\Delta + \kappa^2)G = \delta(0) \quad (59)$$

for some  $\kappa \in \mathcal{G}$  with  $\text{Im}(\kappa) \geq 0$ . By the standard method (cf. Jackson (1999) page 243), we have

$$G(\mathbf{x}, \kappa) = \begin{cases} -\frac{\exp(i\kappa|\mathbf{x}|)}{4\pi|\mathbf{x}|} & \text{if } \text{Im}(\kappa) \neq 0, \\ -A\frac{\exp(i\kappa|\mathbf{x}|)}{4\pi|\mathbf{x}|} - B\frac{\exp(-i\kappa|\mathbf{x}|)}{4\pi|\mathbf{x}|} & \text{if } \text{Im}(\kappa) = 0, \end{cases} \quad (60)$$

where  $A + B = 1$ . In Fourier space, equation (59) can be rewritten as

$$G(\mathbf{x}, \kappa) = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{-1}{|\mathbf{k}|^2 - \kappa^2} \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k}. \quad (61)$$

If  $|l_1| \neq l_0$ , i.e.,  $\kappa_+^2 \neq \kappa_-^2$ , from equations (58)-(61) we have

$$E_u(\mathbf{x}) = \frac{-1}{(\kappa_+^2 - \kappa_-^2)} \left[ G(\mathbf{x}, \kappa_+) - G(\mathbf{x}, \kappa_-) \right]. \quad (62)$$

If  $|l_1| = l_0 > 0$ , i.e.,  $\kappa_+^2 = \kappa_-^2 = -\frac{1}{l_1^2}$ , sending  $\kappa_+$  to  $\kappa_-$  in equation (62) we obtain

$$E_u(\mathbf{x}) = \begin{cases} \frac{-1}{2\kappa} \partial_\kappa G(\mathbf{x}, \kappa) = \frac{l_0}{8\pi} \exp(-|\mathbf{x}|/l_0) & \text{if } \gamma > 0, \kappa = i/l_0, \\ \frac{-1}{2\kappa} \partial_\kappa G(\mathbf{x}, \kappa) = \frac{iAl_0}{8\pi} \exp(i|\mathbf{x}|/l_0) + \frac{iBl_0}{8\pi} \exp(-i|\mathbf{x}|/l_0) & \text{if } \gamma < 0, \kappa = 1/l_0. \end{cases} \quad (63)$$

Further, by the second of equation (51), the associated potential is given by

$$\phi(\mathbf{x}) = \frac{\lambda}{2\alpha} \Delta u - \frac{\gamma}{\alpha} u = \int_{\mathbb{R}^3} E_\phi(\mathbf{x} - \mathbf{x}') b(\mathbf{x}') d\mathbf{x}', \quad (64)$$

where

$$E_\phi(\mathbf{x}) = \frac{\lambda}{2\alpha} [\Delta E_u(\mathbf{x}) - \frac{2}{l_1^2} E_u(\mathbf{x})]. \quad (65)$$

We remark that the above formal calculations can be rigorously justified (cf. e. g. Rudin (1991), chapter 7).

Note that the last of equation (52) requires

$$\int_{\mathbb{R}^3} \left( \frac{1}{l_0^4} u - b \right) = 0. \quad (66)$$



If  $\int b(\mathbf{x})d\mathbf{x} \neq 0$  and  $b(\mathbf{x})$  has a compact support in a ball around the origin, then for large  $|\mathbf{x}|$  the solution  $u(\mathbf{x})$  is well approximated by the Green's function  $E_u$  in equation (62), which is not integrable if  $\kappa_{\pm}$  are real numbers as  $\int_{\mathbb{R}^3} \frac{\exp(ik|\mathbf{x}|)}{|\mathbf{x}|} d\mathbf{x}$  is not integrable for real  $k$ . We therefore conclude that  $\kappa_{\pm}$  should be both nonreal numbers. This is possible for the following three cases:

1.  $\gamma > 0$  and  $l_0 > l_1$ . In this case, all roots of equation (56) are pure imaginary. By equations (62) and (65), we have

$$\begin{aligned} E_u(\mathbf{x}) &= \frac{1}{4\pi(\kappa_+^2 - \kappa_-^2)|\mathbf{x}|} \left[ \exp(i\kappa_+|\mathbf{x}|) - \exp(i\kappa_-|\mathbf{x}|) \right], \\ E_\phi(\mathbf{x}) &= \frac{1}{4\pi(\kappa_+^2 - \kappa_-^2)|\mathbf{x}|} \left[ C_+ \exp(i\kappa_+|\mathbf{x}|) - C_- \exp(i\kappa_-|\mathbf{x}|) \right], \end{aligned} \quad (67)$$

where

$$C_{\pm} = \frac{\lambda}{2\alpha} \left( -\kappa_{\pm}^2 - \frac{2}{l_1^2} \right) = \frac{\lambda}{2\alpha} \kappa_{\mp}^2. \quad (68)$$

2.  $\gamma > 0$  and  $l_0 = l_1$ . This is the first case in equation (63) and we have

$$E_u(\mathbf{x}) = \frac{l_0}{8\pi} \exp(-|\mathbf{x}|/l_0), \quad E_\phi(\mathbf{x}) = \frac{-\lambda}{16\pi\alpha} \left( \frac{1}{l_0} + \frac{2}{r} \right) \exp(-|\mathbf{x}|/l_0). \quad (69)$$

3.  $l_0 < |l_1|$ . In this case, all roots of equation (56) are nonreal and the fundamental solutions are given by (67) as well.

To verify the constraint (66), we integrate equation (53) on the ball  $B_N$  with radius  $N$ , and by the divergence theorem arrive at

$$\int_{\partial B_N} (\nabla \Delta u - \frac{2}{l_1^2} \nabla u) \cdot \hat{\mathbf{x}} dS + \int_{B_N} \left( \frac{1}{l_0^4} u - b \right) d\mathbf{x} = 0, \quad (70)$$

where  $\hat{\mathbf{x}} = \mathbf{x}/|\mathbf{x}|$ . Sending  $N \rightarrow +\infty$ , we arrive at equation (66) since the first term in the above equation vanishes for expressions in equations (67) or (69).

Finally, we remark that the solution to the last of equation (51) is given by the classic theory of linear elasticity (cf. e. g. Mura (1987), chapter 1).

Equations (55), (64), (67)-(69) and the theory of elasticity determine the far-field behavior of  $(u, \phi, \mathbf{y})$ , where the perturbation  $b_c$  plays the role of a source. For a continuous bounded  $b_c$  supported within the ball  $B_{r_0} = \{\mathbf{x} : |\mathbf{x}| < r_0\}$ , we have that for some  $R > 0$  and some  $C, \kappa > 0$ ,

$$|u(\mathbf{x})| \leq C \exp(-\kappa|\mathbf{x}|), \quad |\phi(\mathbf{x})| \leq C \exp(-\kappa|\mathbf{x}|), \quad |\mathbf{y}(\mathbf{x}_0)| \leq \frac{C}{|\mathbf{x}|^2} \quad \forall |\mathbf{x}| > R. \quad (71)$$

With the above estimates on the far-fields, we continue our solutions to equations (51)-(52) for a particular example in the next section.

## 6 Defect energy and cell-size effects

In this section we study how the defect energy depends on the size of the supercell. For simplicity, we assume that the supercell is the ball  $B_{R_0} = \{\mathbf{x} : |\mathbf{x}| < R_0\}$ , the coefficients  $l_0 > l_1 > 0$  and thus both the roots  $\kappa_{\pm}$  in equation (57) are pure imaginary numbers. We denote by

$$k_{\pm} = -i\kappa_{\pm} = \sqrt{\frac{1}{l_1^2} \mp \sqrt{\frac{1}{l_1^4} - \frac{1}{l_0^4}}} = \sqrt{\frac{\gamma \mp \sqrt{\gamma^2 - 4\alpha^2\lambda}}{\lambda}} > 0. \quad (72)$$

Below we solve equations (51) for the corrector fields  $(u, \phi, \mathbf{y})$  with

$$b(\mathbf{x}) = \begin{cases} \rho & \text{if } |\mathbf{x}| \leq r_0, \\ 0 & \text{if } |\mathbf{x}| > r_0, \end{cases}$$

where  $\rho \in \mathbb{R}$  is a constant,  $r_0 < R_0$  describes the length scale of the defect representative of a vacancy. We apply the Dirichlet boundary condition

$$u(\mathbf{x}) = 0, \quad \phi(\mathbf{x}) = \frac{\lambda}{2\alpha}\Delta u(\mathbf{x}) - \frac{\gamma}{\alpha}u(\mathbf{x}) = \varsigma, \quad \mathbf{y} = 0 \quad \text{on } \partial B_{R_0}, \quad (73)$$

where  $\varsigma \in \mathbb{R}$  is a constant determined by the constraint (66).

We first consider the electrostatic contribution of the defect energy, i.e., the second term on the r.h.s. of equation (50). By symmetry, we have  $u = u(r)$  with  $r = |\mathbf{x}|$ . Therefore, equation (53) can be rewritten as

$$\frac{d^4}{dr^4}ru - \frac{2}{l_1^2}\frac{d^2}{dr^2}ru + \frac{1}{l_0^4}ru = rb \quad \forall 0 < |\mathbf{x}| < R_0.$$

From the theory of ordinary differential equation, we obtain

$$ru(r) = \begin{cases} \rho r l_0^4 + C_1 \exp(k_+ r) + C_2 \exp(k_- r) \\ \quad + C_3 \exp(-k_+ r) + C_4 \exp(-k_- r) & \text{if } r \leq r_0, \\ C_5 \exp(k_+ r) + C_6 \exp(k_- r) \\ \quad + C_7 \exp(-k_+ r) + C_8 \exp(-k_- r) & \text{if } r \geq r_0, \end{cases}$$

where the constants  $C_i$  ( $i = 1, \dots, 8$ ) are determined by the analyticity of  $u(\mathbf{x})$  at  $r = 0$  (which implies  $C_1 + C_3 = 0$  and  $C_2 + C_4 = 0$ ), the continuities of  $\frac{d^m}{dr^m}(ru)$  for  $m = 0, 1, 2, 3$  at  $r = r_0$ , the boundary condition (73) and the constraint (66). Direct calculations reveal that these conditions imply

$$\begin{bmatrix} 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ \mathbf{a}(r_0, 0) & & & & -\mathbf{a}(r_0, 0) & & & \\ \mathbf{a}(r_0, 1) & & & & -\mathbf{a}(r_0, 1) & & & \\ \mathbf{a}(r_0, 2) & & & & -\mathbf{a}(r_0, 2) & & & \\ \mathbf{a}(r_0, 3) & & & & -\mathbf{a}(r_0, 3) & & & \\ 0 & 0 & 0 & 0 & \mathbf{a}(R_0, 0) & & & \\ 0 & 0 & 0 & 0 & R_0 \mathbf{a}(R_0, 3) - \mathbf{a}(R_0, 2) & & & \\ & & & & -\frac{2}{l_1^2} R_0 \mathbf{a}(R_0, 1) + \frac{2}{l_1^2} \mathbf{a}(R_0, 0) & & & \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \\ C_7 \\ C_8 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ -\rho r_0 l_0^4 \\ -\rho l_0^4 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (74)$$

where the  $1 \times 4$  row vector  $\mathbf{a}(r, m)$  is given by

$$\mathbf{a}(r, m) = [k_+^m \exp(k_+ r), k_-^m \exp(k_- r), (-k_+)^m \exp(-k_+ r), (-k_-)^m \exp(-k_- r)].$$

Note that the last row of equation (74) follows from setting the ball  $B_N$  to be  $B_{R_0}$  in equation (70) and the constraint (66). Further, from equation (64) we have  $r\phi(r) = \frac{\lambda}{2\alpha} \frac{d^2}{dr^2} ru - \frac{\gamma}{\alpha} ru$  and hence

$$r\phi(r) = \begin{cases} -\frac{\rho\gamma\lambda}{4\alpha^3}r + C_+C_1[\exp(k_+r) - \exp(-k_+r)] \\ \quad + C_-C_2[\exp(k_-r) - \exp(-k_-r)] & \text{if } r \leq r_0, \\ C_+C_5\exp(k_+r) + C_-C_6\exp(k_-r) \\ \quad + C_+C_7\exp(-k_+r) + C_-C_8\exp(-k_-r) & \text{if } r > r_0, \end{cases} \quad (75)$$

where, by equations (68) and (72),  $C_\pm = -\lambda k_\pm^2/2\alpha$ . Therefore, the electrostatic contribution to the defect energy is given by

$$\mathcal{E}_d^{es}(R_0) := \frac{1}{2} \int_{\mathbb{R}^3} \left(-\frac{\lambda}{2\alpha} b\right) \phi = \frac{-\lambda}{4\alpha} \left\{ \frac{-\pi\gamma\lambda\rho r_0^3}{3\alpha^3} + C_+C_1 \frac{8\pi[k_+r_0 \cosh(k_+r_0) - \sinh(k_+r_0)]}{k_+^2} \right. \\ \left. + C_-C_2 \frac{8\pi[k_-r_0 \cosh(k_-r_0) - \sinh(k_-r_0)]}{k_-^2} \right\}. \quad (76)$$

We remark that the algebraic equations (74) determine the constants  $[C_1, \dots, C_8]$  uniquely. Analytical expressions of these constants are desirable but impractical to write them down. In the limit  $R_0 \rightarrow +\infty$ , we find

$$C_1 = \frac{\rho l_0^4 k_-^2 (1 + k_+ r_0) \exp(-k_+ r_0)}{2k_+(k_+^2 - k_-^2)}, \quad C_2 = \frac{-\rho l_0^4 k_+^2 (1 + k_- r_0) \exp(-k_- r_0)}{2k_-(k_+^2 - k_-^2)} \\ C_5 = C_6 = 0, \quad C_7 = \frac{\rho l_0^4 k_-^2 [k_+ r_0 \cosh(k_+ r_0) - \sinh(k_+ r_0)]}{k_+(k_+^2 - k_-^2)}, \quad (77) \\ C_8 = \frac{\rho l_0^4 k_+^2 [k_- r_0 \cosh(k_- r_0) - \sinh(k_- r_0)]}{k_-(k_+^2 - k_-^2)}.$$

For general cases with finite  $R_0$ , which represent computations on a finite simulation cell, we resort to numerical solutions. In particular, we are interested in estimating the error incurred in the defect energy from using a simulation cell, and its dependence on the cell-size. To this end, we have conducted a periodic calculation on a unit cell of FCC lattice for aluminum using a real-space formulation for OFDFT and a finite-element discretization of the formulation (Gavini et al., 2007b). In our simulation, we used the TFW family of kinetic energy functionals with  $\lambda = \frac{1}{6}$  and a modified form of Heine-Abarenkov pseudopotential for aluminium (Goodwin et al., 1990). We subsequently estimate the constants  $\alpha, \beta, \gamma$  from our numerical calculations to be

$$\alpha = 0.1629 \text{ a.u.}, \quad \beta = -0.0509 \text{ a.u.}, \quad \gamma = 0.9449 \text{ a.u.} \quad .$$

We now estimate the cell-size effects in the electrostatic contribution to the energy of a defect that is representative of a vacancy. A reasonable choice for the length scale of a vacancy is

$r_0 = a_0/\sqrt{2}$ , corresponding to the nearest neighbor distance in a face-centered cubic lattice, where  $a_0$  is the lattice parameter for aluminum which is computed to be 7.5 a.u. Using equations (74)-(76), we numerically solve for the electrostatic contribution to defect energy. Figure 1 shows our estimate of cell-size effects from finite cell simulations. As is evident from these results,  $R_0 \approx 4r_0 \approx 3a_0$  is necessary for the approximation errors from finite cell-size studies to be within 1% of the defect energy—a threshold representative of chemical accuracy. In typical electronic structure simulations this  $R_0$  corresponds to a simulation cell with  $6 \times 6 \times 6$  FCC unit cells containing 864 aluminum atoms. This estimate is in close agreement with recent cell-size studies on vacancy formation energies conducted in Gavini et al. (2007a); Radhakrishnan & Gavini (2010), where about  $10^3$  atoms were required for the cell-size effects in defect formation energy to be within 0.01eV. We note that despite the exponential decay in the electronic fields, cell-size effects are significant, even for a simple defect like vacancy. In the more accurate models of density functional theory, like the Kohn-Sham formulation, the decay in electronic fields is known to be slower and hence cell-sizes beyond those considered in previous electronic structure studies may be needed for an accurate study of defects.

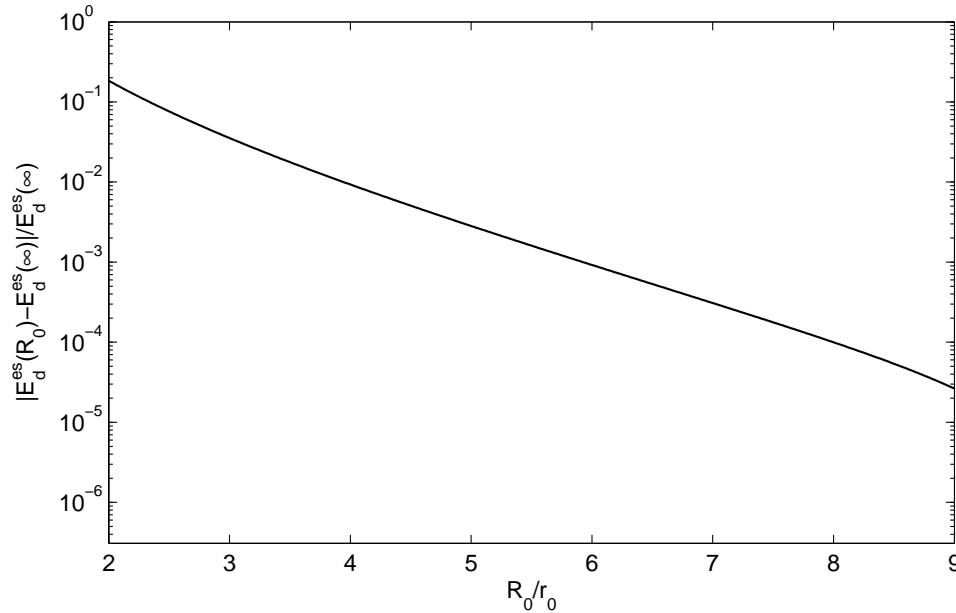


Figure 1: Cell-size effects showing relative error in the electrostatic contribution to the defect energy from finite cell calculations.

We now consider the elastic contribution of the defect energy, i.e., the first term on the r.h.s. of equation (50), which is a standard calculation and provide it for the sake of completeness. For simplicity, we assume that the stiffness tensor of the crystal, defined by (41), is isotropic and that the “eigenstress”  $\mathbf{B}$  is dilatational. Let  $\mu$  be the shear modulus,  $\kappa$  be the bulk modulus, and  $\mathbf{B} = \sigma_0 \mathbf{I}$  ( $\mathbf{I}$  is the identity matrix). Based on the Eshelby’s solution

(Eshelby, 1957), we find that the displacement is given by

$$\mathbf{y} = \nabla \xi, \quad \xi = \begin{cases} \frac{1}{2}\Theta_1 r^2 + \Theta_0 & \text{if } |\mathbf{x}| \leq r_0, \\ \frac{1}{2}\Theta_2 r^2 + \Theta_3 \frac{1}{r} & \text{if } r_0 < |\mathbf{x}| < R_0, \end{cases}$$

where  $\Theta_1, \Theta_2, \Theta_3 \in \mathbb{R}$  are constants to be determined. Indeed, by direct calculations we verify that the function  $\mathbf{y}$  given by the above expression satisfies the last of equation (51) inside the ball  $r < r_0$  and inside the annulus region  $r_0 < r < R_0$ . Across the interface  $r = r_0$ , the continuity of  $\mathbf{y}$ , the continuity of traction and the boundary condition  $\mathbf{y} = 0$  at  $r = R_0$  imply

$$\Theta_1 = \Theta_2 - \Theta_3/r_0^3, \quad \rho\sigma_0 + 3\kappa\Theta_1 = 3\kappa\Theta_2 + 4\mu\Theta_3/r_0^3, \quad \Theta_2 - \Theta_3/R_0^3 = 0.$$

Direct calculation reveals that

$$\Theta_1 = \frac{\rho\sigma_0}{4\mu + 3\kappa} \left( \frac{r_0^3}{R_0^3} - 1 \right).$$

Therefore, the elastic contribution to the defect energy is given by

$$\mathcal{E}_d^{el}(R_0) := \frac{1}{2} \int_{r \leq r_0} \rho \nabla \mathbf{y} \cdot \sigma_0 \mathbf{I} = \frac{3\rho\sigma_0}{2} \Theta_1 = \frac{3\rho^2\sigma_0^2}{2(4\mu + 3\kappa)} \left( \frac{r_0^3}{R_0^3} - 1 \right).$$

The elastic contribution of the defect energy has a slower asymptotic decay ( $O(\frac{1}{R_0^3})$ ) in comparison to the electronic contribution and is one other reason to consider large cell-sizes to ensure the accurate computation of the energetics of defects.

## 7 Extensions

The form of OFDFT energy we considered for the multiple scale analysis in prior sections represents an orbital-free model with TFW kinetic energy functionals without exchange and correlation terms. In this section we comment on other general forms of energies that are widely used in OFDFT computations. We remark that the multiple scale analysis is independent of the form of the non-linear term  $f(u)$  appearing in equation (3), and thus including the exchange and correlation energies does not affect the analysis or the derived expressions. However, the non-local kernel energies can not be represented by a local function of the form  $f(u)$ , and we now present the extension of our analysis to these commonly used kinetic energy functional forms.

The OFDFT formulations employed in numerical studies widely use functional forms for kinetic energy that are non-local in real-space, called *kernel energies*, which are considered to be more accurate than the local TFW functionals (cf. equation (2)). We refer to Wang & Teter (1992); Smargiassi & Madden (1994); Wang et al. (1998, 1999) for further details on these models. We also remark that recent analysis (Blanc & Cancés, 2005) has shown that some of the proposed models lack global stability and can pose serious numerical issues. For the sake of completeness, we briefly discuss the multiple scale analysis of these non-local kernel energies. The functional form of these kernel energies is given by

$$E^{Ker}(u) = \int_Y \int_Y p(u(\mathbf{x})) K(|\mathbf{x} - \mathbf{x}'|) q(u(\mathbf{x}')) d\mathbf{x} d\mathbf{x}', \quad (78)$$

where  $p(u), q(u)$  are functions whose specific form depends on the particular flavor of the OFDFT model, and the total energy is given by

$$E(\phi, u; b_{\mathbf{y}}) = \int_Y \left[ f(u) + \frac{1}{2} |\nabla u|^2 - \frac{1}{2} |\nabla \phi|^2 + (u^2 + b_{\mathbf{y}}) \phi \right] d\mathbf{x} + E^{Ker}(u). \quad (79)$$

We define the following potentials which will be used to reformulate the non-local kernel energy given by equation (78) into a local variational problem:

$$V_p(\mathbf{x}) = \int_Y K(|\mathbf{x} - \mathbf{x}'|) p(u(\mathbf{x}')) d\mathbf{x}', \quad V_q(\mathbf{x}) = \int_Y K(|\mathbf{x} - \mathbf{x}'|) q(u(\mathbf{x}')) d\mathbf{x}'. \quad (80)$$

Taking the Fourier transform of the above expressions we obtain

$$\hat{V}_p(\mathbf{k}) = \hat{K}(|\mathbf{k}|) \hat{p}(\mathbf{k}), \quad \hat{V}_q(\mathbf{k}) = \hat{K}(|\mathbf{k}|) \hat{q}(\mathbf{k}). \quad (81)$$

Following the ideas developed in [Choly & Kaxiras \(2002\)](#),  $\hat{K}$  can be modeled to good accuracy using a sum of partial fractions of the form,

$$\hat{K}(|\mathbf{k}|) \approx \sum_{j=1}^m \frac{P_j |\mathbf{k}|^2}{|\mathbf{k}|^2 + Q_j} \quad (82)$$

where  $P_j, Q_j, j = 1 \dots m$  are constants which are fitted to best reproduce  $\hat{K}(|\mathbf{k}|)$ . These constants can possibly be complex, but appear in pairs with complex conjugates. Substituting this approximation for  $\hat{K}$  in equation (81) and taking the inverse Fourier transforms, we obtain a system of partial differential equations with possibly complex coefficients given by

$$\begin{cases} -\Delta V_{pj} + Q_j V_{pj} + P_j \Delta p(u) = 0 & j = 1 \dots m, \\ -\Delta V_{qj} + Q_j V_{qj} + P_j \Delta q(u) = 0 & j = 1 \dots m. \end{cases} \quad (83)$$

where  $V_{pj}$  and  $V_{qj}$  are the inverse Fourier transforms of  $\frac{P_j |\mathbf{k}|^2}{|\mathbf{k}|^2 + Q_j} \hat{p}(\mathbf{k})$  and  $\frac{P_j |\mathbf{k}|^2}{|\mathbf{k}|^2 + Q_j} \hat{q}(\mathbf{k})$  respectively for  $j = 1 \dots m$ . Further,  $V_p \approx \sum_j V_{pj}, V_q \approx \sum_j V_{qj}$ . By defining  $\varphi_{pj} = V_{pj} - P_j p(u)$  and  $\varphi_{qj} = V_{qj} - P_j q(u)$  for  $j = 1 \dots m$ , equation (83) can be rewritten as

$$\begin{cases} -\Delta \varphi_{pj} + Q_j \varphi_{pj} + P_j Q_j p(u) = 0 & j = 1 \dots m, \\ -\Delta \varphi_{qj} + Q_j \varphi_{qj} + P_j Q_j q(u) = 0 & j = 1 \dots m. \end{cases} \quad (84)$$

The kernel energy,  $E^{Ker}$ , can now be expressed in a local form in terms of the potentials  $\varphi_{pj}, \varphi_{qj}$ , or equivalently as a local saddle point problem:

$$\begin{aligned} E^{Ker}(u) = \min_{\varphi_{pj}} \max_{\varphi_{qj}} \left\{ \sum_{j=1}^m \frac{1}{P_j Q_j} \int_Y \nabla \varphi_{pj} \cdot \nabla \varphi_{qj} d\mathbf{x} + \frac{1}{P_j} \int_Y \varphi_{pj} \varphi_{qj} d\mathbf{x} \right. \\ \left. + \int_Y \varphi_{qj} p(u) d\mathbf{x} + \int_Y \varphi_{pj} q(u) d\mathbf{x} + P_j \int_Y p(u) q(u) d\mathbf{x} \right\}. \end{aligned} \quad (85)$$

We note that variations with respect to  $\varphi_{pj}$  and  $\varphi_{qj}$  return the Euler-Lagrange equations given by equation (84), and the saddle point problem correctly represents, within the approximation (82), the kernel energy and its functional derivatives.

We now decompose the potential fields  $(\varphi_{pj}, \varphi_{qj})$  into a predictor  $(\varphi_{pj_p}, \varphi_{qj_p})$  and a corrector  $(\varphi_{pj_c}, \varphi_{qj_c})$ , and expand the corrector fields using a two-scale expansion given by

$$\begin{cases} \varphi_{pj_c}(\mathbf{x}) = \varphi_{pj_c}^0(\mathbf{x}, \tilde{\mathbf{x}}) + \eta \varphi_{pj_c}^1(\mathbf{x}, \tilde{\mathbf{x}}) + \dots, \\ \varphi_{qj_c}(\mathbf{x}) = \varphi_{qj_c}^0(\mathbf{x}, \tilde{\mathbf{x}}) + \eta \varphi_{qj_c}^1(\mathbf{x}, \tilde{\mathbf{x}}) + \dots. \end{cases} \quad (86)$$

Following on similar lines as in section 4, we obtain the following expressions for  $j = 1 \dots m$  from the leading order terms of the expansion in equation (86):

$$\nabla_{\tilde{\mathbf{x}}} \varphi_{pj_c}^0(\mathbf{x}, \tilde{\mathbf{x}}) = 0 \quad \text{and} \quad \nabla_{\tilde{\mathbf{x}}} \varphi_{qj_c}^0(\mathbf{x}, \tilde{\mathbf{x}}) = 0, \quad (87)$$

$$\nabla_{\tilde{\mathbf{x}}} \varphi_{pj_c}^1(\mathbf{x}, \tilde{\mathbf{x}}) = 0 \quad \text{and} \quad \nabla_{\tilde{\mathbf{x}}} \varphi_{qj_c}^1(\mathbf{x}, \tilde{\mathbf{x}}) = 0. \quad (88)$$

Thus, the corrector fields in their leading and first order are independent of the fast variable representing the lattice length scale. The governing equations for  $\varphi_{pj_c}^0(\mathbf{x})$  and  $\varphi_{qj_c}^0(\mathbf{x})$  are given by,

$$\begin{cases} -\Delta \varphi_{pj_c}^0 + Q_j \varphi_{pj_c}^0 + \xi_p(\hat{\mathbf{F}}^*) u_c^0 = 0 & \text{on } Y, \\ -\Delta \varphi_{qj_c}^0 + Q_j \varphi_{qj_c}^0 + \xi_q(\hat{\mathbf{F}}^*) u_c^0 = 0 & \text{on } Y, \end{cases} \quad (89)$$

where

$$\xi_p(\hat{\mathbf{F}}^*) = \oint_{\hat{\mathbf{F}}^* U_0} p'(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) d\tilde{\mathbf{x}}, \quad \xi_q(\hat{\mathbf{F}}^*) = \oint_{\hat{\mathbf{F}}^* U_0} q'(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) d\tilde{\mathbf{x}}.$$

Further, the governing equations for  $(\phi_c^0, u_c^0)$  are given by

$$\begin{cases} \Delta \phi_c^0 + 2\alpha(\hat{\mathbf{F}}^*) u_c^0 + b_c = 0 & \text{on } Y, \\ -\Delta u_c^0 + 2\tilde{\gamma}(\hat{\mathbf{F}}^*) u_c^0 + 2\alpha(\hat{\mathbf{F}}^*) \phi_c^0 + \sum_{j=1}^m (\xi_p(\hat{\mathbf{F}}^*) \varphi_{pj_c}^0 + \xi_q(\hat{\mathbf{F}}^*) \varphi_{qj_c}^0) = 0 & \text{on } Y, \end{cases} \quad (90)$$

where

$$\begin{aligned} \tilde{\gamma}(\hat{\mathbf{F}}^*) &= \gamma(\hat{\mathbf{F}}^*) + \frac{1}{2} \sum_{j=1}^m (\chi_{pj}(\hat{\mathbf{F}}^*) + \chi_{qj}(\hat{\mathbf{F}}^*) + \psi_j(\hat{\mathbf{F}}^*)), \\ \chi_{pj}(\hat{\mathbf{F}}^*) &= \oint_{\hat{\mathbf{F}}^* U_0} p''(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) \varphi_{qj_p}(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}}) d\tilde{\mathbf{x}}, \\ \chi_{qj}(\hat{\mathbf{F}}^*) &= \oint_{\hat{\mathbf{F}}^* U_0} q''(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) \varphi_{pj_p}(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}}) d\tilde{\mathbf{x}}, \\ \psi_j(\hat{\mathbf{F}}^*) &= \oint_{\hat{\mathbf{F}}^* U_0} \left[ p''(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) q(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) + 2p'(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) q'(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) \right. \\ &\quad \left. + p(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) q''(u_p(\hat{\mathbf{F}}^*, \tilde{\mathbf{x}})) \right] d\tilde{\mathbf{x}}. \end{aligned}$$

Finally, we comment that the results obtained with OFDFT as the model theory are equally valid for the field formulations that describe empirical interatomic potentials presented in [Iyer & Gavini \(2011\)](#). We note that the field formulation presented in [Iyer & Gavini \(2011\)](#) result in a system of coupled linear partial differential equations which represent a special case of the non-linear governing equations describing OFDFT.



## 8 Summary

The main idea behind the quasi-continuum reduction of field theories is the coarse-graining of corrector fields in the formulation using an unstructured finite-element triangulation. In this work we have presented a formal mathematical justification that supports such a coarse-graining, and places the quasi-continuum reduction of field theories on a firm mathematical footing. In particular, we have demonstrated using perturbation method and multiple scale analysis that the corrector fields do not exhibit fine-scale (atomic-scale) oscillations in the leading order, which allows for the coarse-graining of these fields. Further, we have derived the homogenized equations that govern the macroscopic far-field nature of these corrector fields, and using Fourier analysis we have estimated their far-field asymptotic behavior. In the case of orbital-free density functional theory with TFW kinetic energy functionals, the electronic fields comprising of the electrostatic potential and electron density are found to exhibit an exponential decay.

Using the computed asymptotic behavior of these corrector fields, we have estimated the errors incurred in the computation of defect energies using finite cell simulations. Although the electronic fields exhibit an exponential decay, our analysis shows that cell-sizes of the order of  $10^3$  atoms are required for an accurate computation of defect energies, which is in keeping with recent cell-size studies conducted in [Gavini et al. \(2007a\)](#); [Radhakrishnan & Gavini \(2010\)](#). We note that in the more accurate versions of density functional theory, like the Kohn-Sham formulation, the decay in electronic fields is known to be slower. Further, the asymptotic decay in elastic fields is much slower than electronic fields and this effect can become very significant for stronger defects like dislocations. This suggests that larger cell-sizes than those that are typically used in electronic structure calculations ( $\sim 100$  atoms) are needed for an accurate study of defects in materials.

*A priori* estimates on the asymptotic behavior of corrector fields from this work can be used to determine the optimal coarse-graining rates for finite-element triangulations in the quasi-continuum formulation of field theories, and presents itself as a worthwhile future direction to pursue. Further, developing the quasi-continuum reduction of Kohn-Sham density functional theory and an analysis of this formulation is an important open problem, which is the focus of our future work.

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