Thermodynamic Limit of Crystal Defects with Finite Temperature Tight Binding

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Abstract

We consider a tight binding model for localised crystalline defects with electrons in the *canonical ensemble* (finite Fermi temperature) and nuclei positions relaxed according to the Born–Oppenheimer approximation. We prove that the limit model as the computational domain size grows to infinity is formulated in the *grand-canonical ensemble* for the electrons. The Fermi-level for the limit model is fixed at a homogeneous crystal level, independent of the defect or electron number in the sequence of finite-domain approximations. We quantify the rates of convergence for the nuclei configuration and for the Fermi-level.

1 Introduction

Electronic structure calculations based on density functional theory and related models have been established as a predictive approach to model a wide range of systems with important scientific and engineering applications [23, 33]. Unlike empirical interatomic potentials, electronic structure models assume no prior information on the chemical environment or atomic configuration, which makes them a popular tool to model materials with defects [24].

It is most natural to think of crystalline materials with defects (vacancies, interstitials, dislocations, etc.) as an extended system with an infinite number of atoms and electrons, however, in practical computations only finite systems may be treated. It is therefore important to understand the approximation error due to the choice of computational domain. In this paper we start from the most common model for finite crystalline systems with defects, characterise the limit model, and quantify the rate of convergence.

Thermodynamic limit problems have been studied at great length in the analysis literature. The perfect lattice was studied in [10] for the Thomas–Fermi–von

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Weizsäcker (TFW) model and in [11] for the reduced Hartree–Fock (rHF) model. Results on local defects in crystals in the framework of the TFW and rHF models are [4, 5, 6, 7, 8, 26, 31]. These discussions are restricted to the case where the nuclei are fixed on a periodic lattice (or with a given local defect). Considering the simultaneous relaxation of nuclei positions is a case of great physical and mathematical interest. First steps in this direction have been taken in [35] for the Thomas–Fermi–von Weizsäcker model and in [14] for a tight binding model under the simplifying assumption of a "fixed Fermi level".

A related problem is the continuum limit of quantum models. The TFW models are studied in [3] where it is shown that, in the continuum limit, the difference between the energies of the atomistic and continuum models obtained using the Cauchy–Born rule tends to zero. The tight binding and Kohn–Sham models are studied in a series of papers [17, 18, 19, 20], which establish the extension of the Cauchy–Born rule to electronic structure for smoothly deformed crystals. The macroscopic dielectric properties in the thermodynamic limit are studied in the rHF model in [9].

For electronic structure models of defects, not only do we need to consider the truncation of nuclei degrees of freedom and the associated boundary conditions applied on atom positions, but more importantly, we also have to restrict to finite number of electrons on a finite domain. In particular, for systems with defects, it is a priori unclear how many electrons should be imposed on the computational domain, due to the relaxation of the electronic structure. This can become a subtle issue especially when charged defects are considered. (However, we do not treat charged defects in the present work.)

In the present work, we investigate material defects in the context of tight binding models, which are minimalist models for electronic structure calculations. We assume that the electrons are in finite temperature, whereas we adopt the Born-Oppenheimer approximation for the nuclei (i.e., the nuclei degrees of freedom are under zero temperature). Thus, the relaxation of electronic structure is formulated in the canonical ensemble, while atom positions are determined by minimizing the free energy associated with the electrons; see (2.8). For the electronic degree of freedom, vacuum boundary condition with a buffer zone is assumed; while a Dirichlet (clamped) boundary condition is employed for the atom positions. Alternatively, periodic boundary conditions are considered in Appendix A.

Our main results, formulated in Theorems 3.2 and 3.3, state that the limiting problem is formulated in the *grand-canonical ensemble* for the electrons, with the Fermi-level of a homogeneous crystalline solid. Thus, the limit problem is independent of the details of the defect and it is in particular independent of how many electrons we impose on the finite domain.

Our results partially justify the "fixed Fermi level" approach for the finite system that has been widely used, e.g., in [6, 26] for the reduced Hartree–Fock model, in [14, 30] for the tight binding model, and in [16] for density functional theory. We may take the grand canonical ensemble for the finite system with Fermi level given by the perfect crystal. In the thermodynamic limit, the finite systems with fixed Fermi level converge to the same infinite system. We use the qualifier *partially* because the models mentioned above (except [14, 30]) are formulated at zero Fermi

temperature, whereas our results treat the case of finite Fermi temperature; see the Conclusion for further discussion.

A key ingredient in our analysis is a notion of locality of the electronic structure model, which was also used in [14] to exhibit locality of the potential energy, and which we extend here to other physical quantities, specifically the number of electrons. Roughly speaking, the dependence of a local physical property such as the local density of states and hence local physical quantities on the environment decays exponentially fast away from the physical location of interest. Therefore, away from the boundary of the finite domain, the electronic structure behaves as that of the infinite problem. A subtlety arises for the canonical ensemble as the Fermi level for the finite system depends globally on the atom configuration, which would destroy the locality. The key idea to overcome this difficulty is to view the Fermi-level as an independent variable, which together with the nuclei positions, solves the constraint for the number of electrons together with the force balance equation. The thermodynamic limit can then be viewed as the convergence of the solution to the coupled system as the domain tends to infinity.

Outline

In Section 2 we introduce the tight binding model for finite systems. We discuss a 'two-centre' tight binding model, set in the canonical ensemble and the grand-canonical ensemble respectively, and establish the strong locality of the local density of states. In Section 3 we consider an infinite lattice with a local point defect. We first derive the thermodynamic limits of the local density of states by fixing the Fermi level, then present the convergence of the Fermi level, and finally justify the thermodynamic limits of the finite problem with certain boundary conditions. In Section 4, we make concluding remarks and discuss future perspectives. All the proofs are gathered in Section 5.

In Appendix A we extend the analysis to point defects with periodic boundary conditions and in Appendix B to a straight dislocation line with clamped boundary conditions.

Notation

We will use the symbol $\langle \cdot, \cdot \rangle$ to denote an abstract duality pairing between a Banach space and its dual. We will use the Dirac bra-ket notation, which is widely used in quantum mechanics. The notation defines the "ket" vector $|\psi\rangle$, and its conjugate transpose called the "bra" vector $\langle\psi|$.

The symbol $|\cdot|$ normally denotes the Euclidean or Frobenius norm, while $\|\cdot\|$ denotes an operator norm. For the sake of brevity of notation, we will denote $A\backslash\{a\}$ by $A\backslash a$, and $\{b-a \mid b \in A\}$ by $A-a$. For $E \in C^2(X)$, the first and second variations are denoted by $\langle \delta E(u), v\rangle$ and $\langle \delta^2 E(u)w, v\rangle$ for $u, v, w \in X$.

The symbol C denotes a generic positive constant that may change from one line of an estimate to the next. When estimating rates of decay or convergence, C will always remain independent of the system size, of lattice position or of test functions. The dependencies of C will normally be clear from the context or stated explicitly.

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2 The Tight Binding Model

2.1 Free energy

Consider a many particle system consisting of N_Ω nuclei and N_e electrons. Let $d \in \{1,2,3\}$ be the space dimension and $\Omega \subset \mathbb{R}^d$ be an *index set* or *reference configuration* with $\#\Omega = N_\Omega$. An (atomic) *configuration* is a map $y : \Omega \to \mathbb{R}^d$ satisfying

$$|y(\ell) - y(k)| \geq \mathfrak{m}|\ell - k| \qquad \forall\, \ell, k \in \Omega \tag{2.1}$$

with *accumulation parameter* $\mathfrak{m} > 0$. In the following, we use $r_{\ell m} := |y(\ell) - y(m)|$ for brevity of notation.

The tight binding model is a minimalist electronic structure model, which enables the investigation and prediction of properties of molecules and materials. For simplicity of presentation, we consider a 'two-centre' tight binding model [27, 36] (where the off-diagonal entries of the Hamiltonian are given by a pair potential) with the identity overlap matrix, and a single atomic orbital per atom. (The latter restriction requires us also to assume that $0 < N_\mathrm{e} < 2N_\Omega$.) Our results can be extended directly to general non-self-consistent tight binding models with multiple atomic orbitals per atom [14, § 2 and App. A].

The 'two-centre' tight binding model is formulated in terms of a discrete Hamiltonian, with the matrix elements

$$\Big(\mathcal{H}(y)\Big)_{\ell k} = \begin{cases} h_\mathrm{ons}\Big(\sum_{j\neq\ell} \varrho(r_{\ell j})\Big) & \text{if } \ell = k; \\ h_\mathrm{hop}(r_{\ell k}) & \text{if } \ell \neq k, \end{cases} \tag{2.2}$$

where $h_\mathrm{ons} \in C^\nu((0,\infty))$ is the on-site term, $\varrho \in C^\nu((0,\infty))$ with $\varrho = 0$ in $[R_\mathrm{c}, \infty)$, where R_c a cut-off, $h_\mathrm{hop} \in C^\nu((0,\infty))$ is the hopping term with $h_\mathrm{hop} = 0$ in $[R_\mathrm{c}, \infty)$ and $\nu \geq 3$. Note that h_ons and h_hop are independent of ℓ and k, which indicates that all atoms of the system belong to the same species.

For future reference, we remark that the spectrum of $\mathcal{H}(y)$ is uniformly bounded in an interval $[\underline{\lambda}, \overline{\lambda}]$, where $\underline{\lambda}, \overline{\lambda}$ depend only on $\mathfrak{m}$ but are independent of Ω or y [14, Lemma 2.1].

The *Helmholtz free energy* (or *Mermin free energy*) of a system at absolute temperature $T > 0$, as a function of configuration y, is [34]

$$\begin{aligned} E(y) := \min\Big\{ \mathfrak{F}\big(y, \{\psi_s\}_{s=1}^{N_\Omega}, \{f_s\}_{s=1}^{N_\Omega}\big) \;:\; \psi_s : \Omega \to \mathbb{R},\ \psi_i^\mathrm{T}\psi_j = \delta_{ij}, \\ 0 \leq f_s \leq 1,\ 2\textstyle\sum_{s=1}^{N_\Omega} f_s = N_\mathrm{e} \Big\} \end{aligned} \tag{2.3}$$

where

$$\begin{aligned} \mathfrak{F}\Big(y, \{\psi_s\}_{s=1}^{N_\Omega}, \{f_s\}_{s=1}^{N_\Omega}\Big) &:= \sum_{s=1}^{N_\Omega} \Big(2f_s\langle\psi_s|\mathcal{H}(y)|\psi_s\rangle + 2k_\mathrm{B}TS(f_s)\Big), \\ S(f) &:= f\ln f + (1-f)\ln(1-f), \end{aligned}$$

$k_{\rm B}$ is Boltzmann's constant, and the factor 2 comes from spin degeneracy. For simplicity, we will write $\beta := (k_{\rm B}T)^{-1}$ for the inverse temperature. In the Helmholtz free energy (2.3), f_s is understood as the occupation number of the electronic state with orbital function ψ_s. Thus the occupation number is between 0 and 1 according to Pauli's exclusion principle and the total number of electrons is given by N_e (counting spin degeneracy).

A straightforward calculation implies that there exists a minimizer $\{\psi_s\}, \{f_s\}$ satisfying

$$\mathcal{H}(y)\psi_s = \lambda_s\psi_s \qquad \text{and} \qquad f_s = \frac{1}{1+e^{\beta(\lambda_s-\mu)}} \qquad \text{for } s = 1, \cdots, N_\Omega, \tag{2.4}$$

where the Lagrange multiplier μ, known as the *chemical potential*, is chosen such that

$$2\sum_{s=1}^{N_\Omega} f_s = N_{\rm e}. \tag{2.5}$$

Since the ordered eigenvalues $\{\lambda_s\}_{s=1}^{N_\Omega}$ are fixed with given y and the functional

$$N(y,\tau) := 2\sum_{s=1}^{N_\Omega} \big(1+e^{\beta(\lambda_s-\tau)}\big)^{-1}$$

is strictly monotone and continuous in τ with $N(y,\tau) \to 0$ (resp. $2N_\Omega$), as $\tau \to -\infty$ (resp. $+\infty$), it follows that μ is uniquely defined. Note that $\{\lambda_s\}, \{\psi_s\}, \{f_s\}$ and μ given above all depend on y, however we suppress this dependence in the notation.

With $f(x) := 1/(1+e^{\beta x})$ we can now rewrite the Helmholtz free energy (2.3) as

$$E(y) = \sum_{s=1}^{N_\Omega} \mathfrak{e}(\lambda_s, \mu) \qquad \text{with} \tag{2.6}$$

$$\begin{aligned}\mathfrak{e}(x,\tau) &:= 2xf(x-\tau) + \frac{2}{\beta}S\big(f(x-\tau)\big) \\ &= 2\tau f(x-\tau) + \frac{2}{\beta}\ln\big(1-f(x-\tau)\big),\end{aligned} \tag{2.7}$$

where $\{\lambda_s\}_{s=1}^{N_\Omega}$ are eigenvalues of $\mathcal{H}(y)$ and μ satisfies (2.5) (the last equality is easily verfied; see also [1]). In particular, we have from the regularity assumptions on $h_{\rm ons}$ and $h_{\rm hop}$ that E is ν times continuously differentiable (in the sense of Fréchet) on the set of configurations y satisfying (2.1). To see this, we refer to (5.14) for the first order derivative calculation (see similar calculations for higher order derivatives in [14, (42)]).

Remark 2.1. *While the solution to the variational problem* (2.3) *in the case of the tight binding model is straightforward, the variational problem associated to the Helmholtz free energy in the continuous case is in fact quite subtle. The difficulty arises when the spectrum of the Hamiltonian operator contains a continuous spectrum part, such as the Hamiltonians for atoms, molecules and solids. (This is of course impossible for the discrete tight binding model.) Since there exists an infinite number of states below an energy level λ_0, by occupying M such states with*

occupation number $\frac{1}{M}$ *for each state, the Helmholtz free energy is then smaller than* $\lambda_0 - \ln M$*, which goes to negative infinity as* $M \to \infty$*. Therefore, even for systems as simple as an atom, some renormalization is needed to make the variational formulation well-posed in the continuous case.*

2.2 Equilibration of nuclei

We consider stable equilibria (local minima) of E under a boundary condition: for some $\Omega^{\rm D} \subset \Omega$ we seek

$$\bar{y} \in \arg\min \big\{ E(y) \ : \ y(\ell) = \ell \text{ for } \ell \in \Omega^{\rm D} \big\}. \tag{2.8}$$

Specifically, we are interested in determining the limiting model of (2.8) as $N_\Omega \to \infty$. To that end, in the remainder of § 2 we assemble some useful observations about the finite-N_Ω model, for which the precise choices of Ω and $\Omega^{\rm D}$ are unimportant, see Remark 2.2.

Abusing notation, we write

$$E(y, \tau) := \sum_{s=1}^{N_\Omega} \mathfrak{e}(\lambda_s, \tau),$$

then the constrained minimisation problem

$$(\bar{y}, \bar{\mu}) \in \arg\min \Big\{ E(y, \tau) \ : \ N(y, \tau) = N_{\rm e}, \ y(\ell) = \ell \text{ for } \ell \in \Omega^{\rm D} \Big\} \tag{2.9}$$

is fully equivalent to (2.8). We will see in § 2.4 that this formulation is analytically convenient due to the fact that $E(y, \tau)$ and $N(y, \tau)$ are separable as functions of y, while $E(y) = E(y, \mu(y))$ contains a small amount of non-local interaction due to the global dependence of μ on y.

Remark 2.2. *The choice of* $\Omega^{\rm D}$ *is not unique, for example, one can even choose* $\Omega^{\rm D}$ *to be empty set. In later sections, we will take* $\Omega^{\rm D}$ *as an outer "buffer layer" sourrounding the atoms to be relaxed. For a given finite system* Ω*, the minima* $\bar{y}$ *of* (2.8) *depend on the choice of* $\Omega^{\rm D}$*. However, the limiting problem (as* $N_\Omega \to \infty$*) will be independent of the choice of (sequence of)* $\Omega^{\rm D}$*. To pass to the limit we will specify a concrete relation between* Ω *and* $\Omega^{\rm D}$ *in §3.5.*

2.3 The grand potential and other quantities of interest

The problem (2.8) is set on the *canonical ensemble*, where the Helmholtz energy is minimized at equilibrium with constant temperature and particle number. By contrast we can also define an analogous problem in the *grand-canonical ensemble*, where the chemical potential μ is a fixed model parameter while the particle number $N_{\rm e}$ is variable.

For this situation, E is replaced with the *grand potential*,

$$G(y, \mu) := E(y, \mu) - \mu N(y, \mu) = \sum_{s=1}^{N_\Omega} \mathfrak{g}(\lambda_s, \mu) \qquad \text{with} \tag{2.10}$$

$$\mathfrak{g}(x, \tau) := \mathfrak{e}(x, \tau) - 2\tau f(x - \tau) = \frac{2}{\beta} \ln\big(1 - f(x - \tau)\big).$$

The energies E, G and the particle number N are the three main quantities of interest for our work. Upon defining $\mathfrak{n}(x,\tau) := 2f(x-\tau)$ the three quantities E, G, and N are of the form

$$O(y,\tau) = \sum_{s=1}^{N_\Omega} \mathfrak{o}(\lambda_s, \tau). \tag{2.11}$$

We call O an analytic *quantity of interest (QoI)* if there exists a strip $U = \{a + ib \ : \ |b| < \mathfrak{d}, \text{ for some } \mathfrak{d} > 0\}$ such that $\mathfrak{o}(\cdot,\tau)$ is analytic on U for all $\tau \in \mathbb{R}$ and $\partial_z^j \mathfrak{o}(z,\tau)$ is continuous on $U \times \mathbb{R}$. This is satisfied for $O = E, N, G$ with $\mathfrak{d} = \pi/\beta$.

Remark 2.3. *Using the fact $\partial_x \mathfrak{g}(x,\tau) = 2f(x-\tau)$ (see [1]), we have*

$$\frac{\partial G(y,\tau)}{\partial y(\ell)} = 2\sum_{s=1}^{N_\Omega} f(\lambda_s - \tau) \left\langle \psi_s \middle| \frac{\partial \mathcal{H}(y)}{\partial y(\ell)} \middle| \psi_s \right\rangle \tag{2.12}$$

from a similar calculation as that in (5.14)*. Thus, if $\tau = \mu$ is the chemical potential satisfying* (2.5)*, then a straightforward calculation (c.f.* (5.14) *or [23, §7.6.2]) implies that*

$$\frac{\partial G(y,\tau)}{\partial y(\ell)}\Big|_{\tau=\mu} = \frac{\partial E(y)}{\partial y(\ell)}, \tag{2.13}$$

This connection between E and G is a key observation in our derivation of the thermodynamic limit of (2.8)*.*

2.4 Spatial decomposition of analytic quantities of interest

Assuming we have the eigenpairs $\{\lambda_s, \psi_s\}_{s=1}^{N_\Omega}$ of the Hamiltonian $\mathcal{H}(y)$, it is useful to define the (total) *density of states* [23] of the system by

$$\mathcal{D}(y,\epsilon) = \sum_{s=1}^{N_\Omega} \delta(\epsilon - \lambda_s). \tag{2.14}$$

This should be understood in the operational sense, i.e.,

$$\big\langle \mathcal{D}(y), g \big\rangle = \int g(\epsilon)\mathcal{D}(y,\epsilon)\, \mathrm{d}\epsilon = \sum_{s=1}^{N_\Omega} g(\lambda_s) \qquad \text{for } g \in C(\mathbb{R}).$$

If $O = O(y,\tau)$ is an analytic QoI (in particular, $O = E, G, N$), we can write

$$O(y,\tau) = \langle \mathcal{D}(y), \mathfrak{o}(\cdot,\tau) \rangle$$

A spatial decomposition of $\mathcal{D}$ would automatically lead to a spatial decomposition of O, which will be a powerful analytical tool. Following [14, 22, 23], we can introduce the *local density of states* (or, *projected density of states*),

$$\mathcal{D}_\ell(y,\epsilon) := \sum_{s=1}^{N_\Omega} \delta(\epsilon - \lambda_s) \big[\psi_s\big]_\ell^2, \tag{2.15}$$

where $[\psi_s]_\ell$ is the ℓ-th entry of ψ_s. Thus, we obtain a local variant of the analytic QoI O,

$$O_\ell(y,\tau) := \big\langle \mathcal{D}_\ell(y), \mathfrak{o}(\cdot,\tau)\big\rangle = \sum_{s=1}^{N_\Omega} \mathfrak{o}(\lambda_s,\tau)\big[\psi_s\big]_\ell^2. \tag{2.16}$$

It is easy to verify that

$$\mathcal{D}(y) = \sum_{\ell=1}^{N_\Omega} \mathcal{D}_\ell(y) \qquad \text{and hence} \qquad O(y,\tau) = \sum_{\ell=1}^{N_\Omega} O_\ell(y,\tau).$$

The next lemma states the locality of $\mathcal{D}_\ell(y,\cdot)$, which is the backbone of our analysis.

Lemma 2.1. *Let y be an atomistic configuration with accumulation parameter $\mathfrak{m}$, and let O be an analytic QoI. Then, for $1 \le j \le \nu$, there exist positive constants C_j and γ_j depending only on d, $\mathfrak{m}$, $R_{\rm c}$, $h_{\rm hop}$, $h_{\rm ons}$, $\mathfrak{o}$ and τ, such that*

$$\left| \frac{\partial^j O_\ell(y,\tau)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} \right| \le C_j e^{-\gamma_j \sum_{t=1}^j r_{\ell m_t}} \tag{2.17}$$

for any $1 \le \ell \le N_\Omega$, $1 \le m_1, \cdots, m_j \le N_\Omega$ and $1 \le i_1, \cdots, i_j \le d$.

The constants C_j are bounded above and γ_j are bounded away from zero on bounded intervals for τ.

Proof. The proof is analogous to that of [14, Lemma 2.3], but for the sake of completeness, we present it in § 5.1. □

Remark 2.4. *We emphasize that it is crucial to keep τ fixed to obtain this locality result. A y-dependent chemical potential would introduce a small amount of non-locality in O_ℓ, which is not easy to control directly. Note how in* (2.9) *we have split off this non-locality at the expense of adding a constraint to the system, cf.* (2.8)*. However, since that constraint is given as a sum of local quantities it is convenient to treat analytically.*

Remark 2.5. *With the definition of Hamiltonian* (2.2)*, we have isometry and permutation invariance of $\mathcal{D}_\ell$ and hence of the quantities O_ℓ (for an analogous proof see [14, Lemma 2.4]): if $\mathcal{I} : \mathbb{R}^d \to \mathbb{R}^d$ is an isometry, then $O_\ell(y,\tau) = O_\ell(\mathcal{I}(y),\tau)$; if Π is a permutation of Ω, then $O_\ell(y,\tau) = O_{\Pi^{-1}(\ell)}(y \circ \Pi, \tau)$.*

Remark 2.6. *As shown in the proofs of Lemma 2.1, we can alternatively use a matrix-trace representation for the analytic QoIs. Instead of using the eigenpair formulations* (2.11) *and* (2.16)*, we can also write (c.f.* (5.1) *and* (5.3)*)*

$$O(y,\tau) = \mathrm{Tr}\Big[\mathfrak{o}\big(\mathcal{H}(y),\tau\big)\Big] \quad \text{and} \quad O_\ell(y,\tau) = \Big[\mathfrak{o}\big(\mathcal{H}(y),\tau\big)\Big]_{\ell\ell}. \tag{2.18}$$

Indeed, this formulation will bring a lot of convenience to our analysis.

3 Thermodynamic limit of a crystal defect

While, in § 2, we considered general atomistic configurations y, we now focus on crystalline defects. For the sake of clarity of presentation the main text concentrates on point defects. An extension to straight dislocation lines is briefly discussed in Appendix B.

Employing the separability of the various physical quantities established in Lemma 2.1 we will formulate a model for a crystalline defect in an infinite lattice and then prove that solutions of (2.9) converge to a solution of the infinite lattice model. Again, for the sake of clarity of presentation, the main text concentrates on clamped boundary condition (Dirichlet boundary condition) for the finite size systems, while periodic boundary conditions are discussed in Appendix A.

3.1 Reference configuration

We consider a single defect embedded in an infinite homogeneous crystalline bulk. A homogeneous crystal reference configuration is given by the Bravais lattice $\Lambda^{\rm hom} = A\mathbb{Z}^d$, for some non-singular matrix $A \in \mathbb{R}^{d\times d}$. A *point defect reference configuration* is a set $\Lambda \subset \mathbb{R}^d$ satisfying

(R) $\exists\ R_{\rm def} > 0$, such that $\Lambda \backslash B_{R_{\rm def}} = \Lambda^{\rm hom} \backslash B_{R_{\rm def}}$ and $\Lambda \cap B_{R_{\rm def}}$ is finite.

Then the set of possible (atomic) *configurations* is

$$\begin{aligned} \mathscr{A}_0(\Lambda) &:= \bigcup_{\mathfrak{m}>0} \mathscr{A}_{\mathfrak{m}}(\Lambda), \qquad \text{where} \\ \mathscr{A}_{\mathfrak{m}}(\Lambda) &:= \left\{ y : \Lambda \to \mathbb{R}^d,\ |y(\ell) - y(m)| > \mathfrak{m}|\ell - m| \quad \forall\ \ell, m \in \Lambda \right\}, \end{aligned}$$

where we have again imposed accumulation parameter $\mathfrak{m}$.

3.2 Limit of the local density of states

We first study pointwise thermodynamic limits with a fixed chemical potential. For $y \in \mathscr{A}_0$ and a finite subset $\Omega \subset \Lambda$, we define $y^\Omega : \Omega \to \mathbb{R}^d$, $y^\Omega(\ell) := y(\ell)$, $\forall\, \ell \in \Omega$. The local density of states and local analytic QoIs associated with y^Ω will be denoted by $\mathcal{D}_\ell(y^\Omega, \cdot)$, $O_\ell(y^\Omega, \tau)$, where the dependence on Ω is implicitly assumed.

The following lemma establishes the existence of the (thermodynamic) limit of $\mathcal{D}_\ell(y^\Omega)$ as $\Omega \uparrow \Lambda$, via local analytic QoI O_ℓ. This result is closely related to the locality result in Lemma 2.1. We will skip the details of the proofs and refer to [14, Theorem 3.1] for an analogous argument.

Lemma 3.1 (pointwise thermodynamic limit)**.** *If Λ satisfies* **(R)** *and $y \in \mathscr{A}_0(\Lambda)$, then for any $\ell \in \Lambda$ and for any sequence of bounded sets $\Omega_R \supseteq B_R(\ell)$, the limit*

$$O_\ell(y, \tau) := \lim_{R\to\infty} O_\ell(y^{\Omega_R}, \tau)$$

exists with a fixed $\tau \in \mathbb{R}$ *and is independent of the choice of sets* Ω_R*. Moreover, there exist constants* C_j *and* η_j *for* $0 \le j \le \nu$ *such that*

$$\left|O_\ell(y,\tau) - O_\ell(y^{\Omega_R},\tau)\right| \le C_0 e^{-\eta_0 R} \qquad \text{and} \tag{3.1}$$

$$\left|\frac{\partial^j O_\ell(y,\tau)}{\partial[y(m_1)]_{i_1}\cdots\partial[y(m_j)]_{i_j}} - \frac{\partial^j O_\ell(y^{\Omega_R},\tau)}{\partial[y(m_1)]_{i_1}\cdots\partial[y(m_j)]_{i_j}}\right| \le C_j e^{-\eta_j\left(R+\sum_{k=1}^j r_{\ell m_k}\right)}$$
$$\forall\ m_k \in \Lambda\cap\Omega_R \quad 1\le k\le j, \quad \forall\ 1\le i_1,\cdots,i_j\le d. \tag{3.2}$$

Similar to Lemma 2.1, the constants in Lemma 3.1 depend only on d, $\mathfrak{m}$, $R_{\rm c}$, $h_{\rm hop}$, $h_{\rm ons}$, $\mathfrak{o}$ and τ, but C_j are bounded above and η_j are bounded away from 0 on bounded intervals for τ.

From (3.2) and the locality (2.17), we can derive the locality of the thermodynamic limits: if $\tau \in \mathbb{R}$ is fixed, then

$$\left|\frac{\partial^j O_\ell(y,\tau)}{\partial[y(m_1)]_{i_1}\cdots\partial[y(m_j)]_{i_j}}\right| \le C_j e^{-\gamma_j \sum_{l=1}^j r_{\ell m_l}} \tag{3.3}$$

for any $\ell \in \Lambda$ and $1 \le i_1,\cdots,i_j \le d$.

Remark 3.1. *From the isometry and permutation invariance of* $O_\ell(y^{\Omega_R},\tau)$*, we can also derive the isometry and permutation invariance of their thermodynamic limits: if* $\mathcal{I}:\mathbb{R}^d\to\mathbb{R}^d$ *is an isometry, then* $O_\ell(y,\tau) = O_\ell(\mathcal{I}(y),\tau)$*; if* Π *is a permutation of* Λ*, then* $O_\ell(y,\tau) = O_{\Pi^{-1}(\ell)}(y\circ\Pi,\tau)$*.*

3.3 Energy space for displacements

We can decompose the configuration y into

$$y(\ell) = \ell + u(\ell) \qquad \forall\ \ell\in\Lambda, \tag{3.4}$$

where $u:\Lambda\to\mathbb{R}^d$ is called the *displacement*. Since we are considering point defects, it is natural to assume that displacements in the infinite lattice model will belong to an energy space [13, 21], which we define next.

If $\ell, \ell+\rho \in \Lambda$ then we define the finite difference $D_\rho u(\ell) := u(\ell+\rho) - u(\ell)$. The full interaction stencil is defined by $Du(\ell) := (D_\rho u(\ell))_{\rho\in\Lambda-\ell}$. For a stencil $Du(\ell)$ and $\gamma > 0$ we define the (semi-)norms

$$\left|Du(\ell)\right|_\gamma := \left(\sum_{\rho\in\Lambda-\ell} e^{-2\gamma|\rho|}\left|D_\rho u(\ell)\right|^2\right)^{1/2} \quad \text{and} \quad \|Du\|_{\ell^2_\gamma} := \left(\sum_{\ell\in\Lambda}|Du(\ell)|_\gamma^2\right)^{1/2}.$$

We will also use the norm $\|Du\|_{\ell^1_\gamma} := \sum_{\ell\in\Lambda}|Du(\ell)|_\gamma$ in our analysis. For any $\Omega\subset\Lambda$, we define $\|Du\|_{\ell^p_\gamma(\Omega)} := \left(\sum_{\ell\in\Omega}|Du(\ell)|_\gamma^p\right)^{1/p}$ with $p = 1, 2$.

We have from [13] that all (semi-)norms $\|\cdot\|_{\ell^2_\gamma}$ with $\gamma > 0$ are equivalent. Following [13, 21] we can therefore define the function space of finite energy displacements,

$$\dot{\mathscr{W}}^{1,2}(\Lambda) := \left\{u:\Lambda\to\mathbb{R}^d,\ \|Du\|_{\ell^2_\gamma} < \infty\right\},$$

with the associated semi-norm $\|Du\|_{\ell^2_\gamma}$.

Upon defining $x : \Lambda \to \mathbb{R}, x(\ell) := \ell$, the associated class of *admissible displacements* is

$$\mathrm{Adm}(\Lambda) := \big\{ u \in \dot{\mathscr{W}}^{1,2}(\Lambda) \ : \ x + u \in \mathscr{A}_0(\Lambda) \big\}.$$

We now transform local analytic QoIs $O_\ell(y, \tau)$ to become functions of displacements $u = y - x$. Due to the isometry (translation) invariance (Remark 3.1), we may represent O_ℓ as a function of $(Du(\ell), \tau)$, i.e.,

$$\mathcal{O}_\ell(Du(\ell), \tau) := O_\ell(x + u, \tau).$$

Moreover, if $\Lambda = \Lambda^{\rm hom}$, then permutation invariance (Remark 3.1) also removes the dependence on the lattice site, i.e., we can write

$$\mathcal{O}_\ell(Du(\ell), \tau) = \mathcal{O}_\#(Du(\ell), \tau) \qquad \forall\ \ell \in \Lambda^{\rm hom}. \tag{3.5}$$

3.4 Limit of the chemical potential

Before we state the variational problem on the limit lattice Λ we investigate the behaviour of the chemical potentials as $\Omega \uparrow \Lambda$.

With the notation (3.5) we can define the *Fermi level* of a homogeneous crystal, $\mu_\#$, such that

$$\mathcal{N}_\#(\mathbf{0}, \mu_\#) = 1. \tag{3.6}$$

Note that $\mu_\#$ is uniquely defined since the thermodynamic limit $\mathcal{N}_\#(\mathbf{0}, \tau)$ is a strictly monotone continuous function of τ, with $\mathcal{N}_\#(\mathbf{0}, \tau) \to 0$ (resp. 2) as $\tau \to -\infty$ (resp. $+\infty$). See also Remark 3.2.

Theorem 3.1. *Let Λ satisfy* **(R)**, $\Lambda_R := \Lambda \cap B_R \uparrow \Lambda$ *and* $N_R := \#\Lambda_R$. *For each R let $u_R : \Lambda_R \to \mathbb{R}^d$ with $y_R(\ell) := \ell + u_R(\ell)$ a* configuration *with parameter $\mathfrak{m}$ independent of R.*

Let $N_{{\rm e},R} \in \mathbb{R}$ be a prescribed number of electrons in the subsystem Λ_R, chosen such that $|N_R - N_{{\rm e},R}|$ is bounded as $R \to \infty$. Then, for R sufficiently large, the chemical potential μ_R solving $N(y_R, \mu_R) = N_{{\rm e},R}$ is well-defined and satisfies

$$\big|\mu_R - \mu_\#\big| \le C_1 \left(R^{-1} + R^{-d} \|Du_R\|_{\ell^1_\gamma} \right) \le C_2 \left(R^{-1} + R^{-d/2} \|Du_R\|_{\ell^2_\gamma} \right) \tag{3.7}$$

with some constants C_1 and C_2.

Proof. The proof is presented in § 5.2. □

Informally, the chemical potential converges to the Fermi level of the corresponding homogeneous lattice if the displacement norm $\|Du_R\|_{\ell^1_\gamma}$ grows slower than N_R. The interpretation of this result is that the Fermi level only changes through a global (non-rigid) transformation of the lattice structure, such as a change in the lattice constant.

Remark 3.2. *One can alternatively define the Fermi level $\mu_\#$ using Bloch's theorem [29]. Let $y_\# : \Lambda^{\rm hom} \to \mathbb{R}^d$ be such that $y_\#(\ell) = \ell$ and* BZ *be the first Brillouin zone associated with $\Lambda^{\rm hom}$. For any point $k \in$ BZ, we have the associated Hamiltonian (in the simple 'two-centre' tight binding setting* (2.2)*)*

$$\mathcal{H}^{(k)}(y_\#) := h_{\rm ons}\left(\sum_{\ell\in\Lambda^{\rm hom}\setminus\{0\}} \varrho\big(r_{0\ell}\big)\right) + \sum_{\ell\in\Lambda^{\rm hom}\setminus\{0\}} \exp\big(ik\cdot\boldsymbol{r}_{0\ell}\big)\cdot h_{\rm hop}\big(r_{0\ell}\big)$$

with $\boldsymbol{r}_{0\ell} = y_\#(\ell) - y_\#(0)$ and $r_{0\ell} = |\boldsymbol{r}_{0\ell}|$. Note that $\mathcal{H}^{(k)}(y_\#)$ is an 1×1 matrix since there is only one atom in each unit cell and one atomic orbital for each atom. Then we can obtain the corresponding eigenvalue $\lambda^{(k)} = \mathcal{H}^{(k)}(y_\#)$, and the Fermi level $\mu_\#$ is defined such that

$$\int_{\rm BZ} f(\lambda^{(k)} - \mu_\#)\ {\rm d}k = \frac{1}{2}. \tag{3.8}$$

Using (3.8)*, $\mu_\#$ can be efficiently computed numerically. The generalisation to multiple atomic orbitals is straightforward.*

3.5 Main result: the thermodynamic limit

In view of Remark 2.3 and Theorem 3.1 the grand potential with *fixed* Fermi-level $\mu_\#$ is a natural candidate for the limit energy. Thus, for a displacement $u : \Lambda \to \mathbb{R}^d$ we define (formally at first) the *grand potential difference functional* of the infinite system by

$$\mathcal{G}(u) := \sum_{\ell\in\Lambda} \Big(\mathcal{G}_\ell(Du(\ell), \mu_\#) - \mathcal{G}_\ell(\mathbf{0}, \mu_\#)\Big). \tag{3.9}$$

Using locality (3.3) of $\mathcal{G}_\ell$ we can obtain the following result, which states that the difference functional is well-defined. We refer to [13] (see also [21]) for a rigorous proof.

Lemma 3.2. *$\mathcal{G}$ is well-defined on $\dot{\mathscr{W}}^{\rm c}(\Lambda) \cap {\rm Adm}(\Lambda)$ where*

$$\dot{\mathscr{W}}^{\rm c}(\Lambda) = \Big\{u \in \dot{\mathscr{W}}^{1,2}(\Lambda),\ \exists\ R > 0\ s.t.\ u = {\rm const}\ in\ \Lambda\backslash B_R\Big\},$$

and continuous with respect to the $\dot{\mathscr{W}}^{1,2}$-topology. In particular, there exists a unique continuous extension to Adm(Λ)*. The extended functional, still denoted by $\mathcal{G}$, is ν times Fréchet differentiable.*

The force equilibration problem associated with $\mathcal{G}$ is

$$\bar{u} \in \arg\min\Big\{\mathcal{G}(u)\ :\ u \in {\rm Adm}(\Lambda)\Big\}, \tag{3.10}$$

where "arg min" is understood in the sense of local minimality. We claim that solutions to (2.9) converge to a solution of (3.10). We will prove two complementary results to establish this.

First, we reformulate (2.9) in terms of displacements, and specify a sequence of domains Ω and $\Omega^{\rm D}$. For each domain radius $R > 0$ we choose a buffer radius $R_{\rm b} = R_{\rm b}(R)$ with $R_{\rm b} \to \infty$ as $R \to \infty$ and define

$$\Lambda_R := \Lambda \cap B_{R+R_{\rm b}} \qquad \text{and} \qquad \Lambda_R^{\rm D} := \Lambda_R \setminus B_R.$$

The associated set of admissible displacements is

$$\mathrm{Adm}(R) := \Big\{ u \in \dot{\mathscr{W}}_R(\Lambda) \;\Big|\; x + u \in \mathscr{A}_0(\Lambda) \Big\},$$
$$\text{with} \qquad \dot{\mathscr{W}}_R(\Lambda) := \Big\{ u : \Lambda \to \mathbb{R}^d \;\Big|\; u = 0 \text{ in } \Lambda \backslash B_R \Big\}.$$

Note that we have extended displacements of Λ_R by zero in order to be able to estimate errors. The resulting finite-domain equilibrium problem corresponding to (2.9) (with $\Omega = \Lambda_R$ and $\Omega^{\rm D} = \Lambda_R^{\rm D}$) is to find $(\bar{u}_R, \bar{\mu}_R) \in \mathrm{Adm}(R) \times \mathbb{R}$ such that

$$(\bar{u}_R, \bar{\mu}_R) \in \arg\min \Big\{ \mathcal{E}^{\Lambda_R}(u_R, \tau) \;:\; \mathcal{N}^{\Lambda_R}(u_R, \tau) = N_{{\rm e},R},\ \tau \in \mathbb{R},\ u_R \in \mathrm{Adm}(R) \Big\}, \tag{3.11}$$

where $\mathcal{E}^{\Lambda_R}(u_R, \tau) := E\big((x+u_R)|_{\Lambda_R}, \tau\big)$, $\mathcal{N}^{\Lambda_R}(u_R, \tau) := N\big((x+u_R)|_{\Lambda_R}, \tau\big)$ and $N_{{\rm e},R}$ is the number of electrons contained in Λ_R.

As indicated above, we present two rigorous justifications of (3.10), the proofs of which are, respectively, given in § 5.3 and § 5.4. We refer to Remark 3.3 for a discussion of the assumptions under which these results hold.

First, we show that, if (3.10) has a solution $\bar{u}$, then there exist solutions $\bar{u}_R$ to (3.11) such that $\|D\bar{u}_R - D\bar{u}\|_{\ell^2_\gamma} \to 0$.

Theorem 3.2. *Assume that $|N_R - N_{{\rm e},R}|$ is bounded as $R \to \infty$. If $\bar{u} \in \mathrm{Adm}(\Lambda)$ is a solution of* (3.10) *which is also strongly stable, i.e.,*

$$\big\langle \delta^2 \mathcal{G}(\bar{u}) v, v \big\rangle \geq \bar{c} \|Dv\|^2_{\ell^2_\gamma} \qquad \forall\ v \in \dot{\mathscr{W}}^{1,2}(\Lambda), \tag{3.12}$$

then there are constants $R_0, c_{\rm b} > 0$ such that, for $R > R_0$ and $R_{\rm b} > c_{\rm b} \log R$, there exists a solution $(\bar{u}_R, \bar{\mu}_R)$ of (3.11) *satisfying*

$$\big\|D\bar{u} - D\bar{u}_R\big\|_{\ell^2_\gamma} + \big|\bar{\mu}_R - \mu_\#\big| \leq C R^{-\min\{1,d/2\}}. \tag{3.13}$$

Our second result reverses the argument: if $\bar{u}_R$ is a bounded sequence of solutions to (3.11), then any accumulation point $\bar{u}$ solves (3.10).

Theorem 3.3. *Let $R_j \uparrow \infty$ and $(\bar{u}_{R_j}, \bar{\mu}_{R_j})$ be solutions to* (3.11) *with $R = R_j$, if $|N_{R_j} - N_{{\rm e},R_j}|$ is bounded and $\sup_{j>0} \|D\bar{u}_{R_j}\|_{\ell^2_\gamma} < \infty$, then there exists a subsequence (not relabelled) and $\bar{u} \in \mathrm{Adm}(\Lambda)$ such that*

$$\bar{\mu}_{R_j} \to \mu_\# \quad \text{and} \quad D_\rho \bar{u}_{R_j}(\ell) \to D_\rho \bar{u}(\ell) \quad \forall\ \ell \in \Lambda,\ \rho \in \Lambda - \ell. \tag{3.14}$$

Moreover, each such accumulation point $\bar{u}$ solves (3.10).

Remark 3.3. *Theorem 3.2 assumes the existence of a stable solution to the limit problem. This assumption is the natural generalisation of phonon stability [29] to defects, and from a physical perspective very mild. However we are not aware of any means to prove it rigorously; even in the context of classical interatomic potentials few results under very stringent assumptions exist [2, 28], and indeed only for the case of anti-plane screw dislocations where a topologically imposed infinite energy barrier makes such an analysis tractable.*

On the other hand, Theorem 3.3 assumes uniform boundedness of approximation solutions, which is a weaker uniform stability assumption placed on the the sequence of approximations. Again, we are unaware of any avenue to establish it rigorously, but it is interesting from a practical perspective since this assumption could be checked a posteriori during a numerical simulation.

4 Conclusions

In this paper, we derive the thermodynamic limit for a coupled electron and geometry relaxation problem in the context of the tight binding model for crystalline defects. In particular, we have seen that the Fermi level of the finite systems converges to the Fermi level of the homogeneous crystal in which the defect is embedded, and that the equilibrium states of the finite system converge to the minimizer of the infinite grand potential.

A key motivation for our analysis is that it lends strong theoretical support to the "fixed Fermi-level" assumption approach in recent analyses of multi-scale methods. The canonical ensemble setting, where the Fermi level depends globally on the atom configuration, we cannot exploit locality of electronic structure [14, 16]. However, Theorems 3.2 and 3.3 indicate that we can approximate the canonical ensemble equilibrium state by minimizing the grand potential with the (fixed) Fermi level of the perfect crystal. The strong locality results arising in this setting then allow the construction and rigorous analysis of linear-scaling, QM/MM multi-scale, and Green's function embedding methods [15, 14, 16, 30].

The "fixed Fermi-level" assumption has also been employed in zero temperature electronic structure models for insulators [6, 16, 26]. In the setting of crystalline defects it is not immediately clear how to choose it. A possible choice would be through the zero temperature limit $\beta \to \infty$. This leads to the interesting issue that the thermodynamic limit most likely does not commute with the zero temperature limit, due to eigenstates in the band-gap which give rise to $O(1)$ changes in the Fermi-level. Thus, the correct choice of Fermi-level at zero (or low) Fermi temperature is an interesting and subtle issue.

A final key question is whether our result can be extended to the more accurate electronic structure models, such as Kohn–Sham density functional theory. The main difficulty is to control the long-range Coulomb interaction, which gives rise to substantial technical and conceptual challenges, in particular the possibility of charged defects [6]. Moreover the variational formulation of the canonical ensemble also becomes subtle in the continuous setting, as mentioned in Remark 2.1.

5 Proofs

5.1 Proof of Lemma 2.1

The analysis of the locality results in Lemma 2.1 builds on a representation of $O(y,\tau)$ in terms of contour integrals. This technique has been used in quantum chemistry, for example [14, 18, 25] for tight binding models.

For an atomic configuration y, we can rewrite $O(y,\tau)$ as the trace of some operator-valued function of the Hamiltonian

$$O(y,\tau) = \mathrm{Tr}\Big[\mathfrak{o}\big(\mathcal{H}(y),\tau\big)\Big]. \tag{5.1}$$

Following [14], we can find a bounded contour $\mathscr{C} \subset \mathbb{C}$, circling all the eigenvalues λ_s on the real axis and avoiding the intersection with the non-analytic region of $\mathfrak{o}(\cdot,\tau)$ at the same time. Then we have

$$O(y,\tau) = -\frac{1}{2\pi i}\oint_{\mathscr{C}} \mathfrak{o}(z,\tau)\mathrm{Tr}\Big[\big(\mathcal{H}(y) - zI\big)^{-1}\Big]\,\mathrm{d}z. \tag{5.2}$$

We can also derive similar representations for $O_\ell(y,\tau) = \langle \mathcal{D}_\ell(y,\cdot), \mathfrak{o}(\cdot,\tau)\rangle$. Let e_ℓ be the N dimensional canonical basis vector, then we obtain from the definition (2.15) that

$$\begin{aligned} O_\ell(y,\tau) &= \sum_{s=1}^{N_\Omega} \mathfrak{o}(\lambda_s,\tau)(\psi_s,e_\ell)(e_\ell,\psi_s) = \sum_{s=1}^{N_\Omega} \Big(\mathfrak{o}\big(\mathcal{H}(y),\tau\big)\psi_s, e_\ell\Big)(e_\ell,\psi_s) \\ &= \sum_{s=1}^{N_\Omega} (e_\ell,\psi_s)\Big(\psi_s, \mathfrak{o}\big(\mathcal{H}(y),\tau\big)e_\ell\Big) = \Big(e_\ell, \mathfrak{o}\big(\mathcal{H}(y),\tau\big)e_\ell\Big) \\ &= -\frac{1}{2\pi i}\oint_{\mathscr{C}} \mathfrak{o}(z,\tau)\Big[\big(\mathcal{H}(y) - zI\big)^{-1}\Big]_{\ell\ell}\,\mathrm{d}z. \end{aligned} \tag{5.3}$$

Proof of Lemma 2.1. First, we have from the definition (2.2) that the Hamiltonian matrix $\mathcal{H}(y)$ is *banded* in the sense that

$$\Big(\mathcal{H}(y)\Big)_{\ell k} = 0 \qquad \text{if } r_{\ell k} \geq R_{\mathrm{c}}.$$

Denoting the resolvent by $\mathscr{R}_z = \big(\mathcal{H}(y) - zI\big)^{-1}$, we have from [14, Lemma 2.2] and [18, Lemma 12] that there exist constants C_{a} and η_{a} such that

$$\Big|\Big(\mathscr{R}_z(y)\Big)_{\ell k}\Big| \leq C_{\mathrm{a}} e^{-\eta_{\mathrm{a}} r_{\ell k}} \qquad \forall\ z \in \mathscr{C}, \tag{5.4}$$

where C_{a} depends on h_{hop} and h_{ons}, and η_{a} depends on $\mathfrak{m}$, R_{c} and $\mathfrak{o}$ (through $\mathfrak{d}$, which equals π/β for $\mathfrak{o} = \mathfrak{e}, \mathfrak{n}, \mathfrak{g}$). For sake of readability, we will drop the argument (y) in $\mathcal{H}(y)$ and $\mathscr{R}_z(y)$ whenever convenient and possible without confusion.

Denoting the first and second order partial derivatives of Hamiltonians by

$$\Big(\,[\mathcal{H}_{,m}(y)]_i\,\Big)_{\ell k} = \frac{\partial\big(\mathcal{H}(y)\big)_{\ell k}}{\partial [y(m)]_i} \quad \text{and} \quad \Big(\,[\mathcal{H}_{,mn}(y)]_{i_1 i_2}\,\Big)_{\ell k} = \frac{\partial^2\big(\mathcal{H}(y)\big)_{\ell k}}{\partial [y(m)]_{i_1}\partial [y(n)]_{i_2}}$$

with $1 \le i, i_1, i_2 \le d$, we can calculate the first and second order derivatives of $O_\ell(y,\tau)$ based on (5.3),

$$\frac{\partial O_\ell(y,\tau)}{\partial [y(m)]_i} = \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{o}(z,\tau) \Big[\mathscr{R}_z \left[\mathcal{H}_{,m}\right]_i \mathscr{R}_z \Big]_{\ell\ell} \, \mathrm{d}z \qquad \text{and} \tag{5.5}$$

$$\begin{aligned} \frac{\partial^2 O_\ell(y,\tau)}{\partial [y(m)]_{i_1} \partial [y(n)]_{i_2}} = \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{o}(z,\tau) \Big[& \mathscr{R}_z \big[\mathcal{H}_{,mn}\big]_{i_1 i_2} \mathscr{R}_z - \mathscr{R}_z \left[\mathcal{H}_{,m}\right]_{i_1} \mathscr{R}_z \big[\mathcal{H}_{,n}\big]_{i_2} \mathscr{R}_z \\ & - \mathscr{R}_z \left[\mathcal{H}_{,n}\right]_{i_2} \mathscr{R}_z \big[\mathcal{H}_{,m}\big]_{i_1} \mathscr{R}_z \Big]_{\ell\ell} \, \mathrm{d}z. \end{aligned} \tag{5.6}$$

For $j = 1$, we have from the definition (2.2) that

$$\Big| \Big(\left[\mathcal{H}_{,m}\right]_i (y) \Big)_{\ell k} \Big| \le C_{\mathrm{b}} e^{-\eta_{\mathrm{b}}(r_{\ell m} + r_{km})},$$

where the constant C_{b} depends on h_{hop} and h_{ons}, and η_{b} depends on R_{c}. This together with (5.4) implies

$$\begin{aligned} \Big[\mathscr{R}_z \left[\mathcal{H}_{,m}\right]_i \mathscr{R}_z \Big]_{\ell\ell} &= \sum_{1 \le \ell_1, \ell_2 \le N_\Omega} \big[\mathscr{R}_z\big]_{\ell\ell_1} \big(\left[\mathcal{H}_{,m}\right]_i \big)_{\ell_1 \ell_2} \big[\mathscr{R}_z\big]_{\ell_2 \ell} \\ \le C_{\mathrm{a}}^2 C_{\mathrm{b}} \sum_{1 \le \ell_1, \ell_2 \le N_\Omega} & e^{-\min\{\eta_{\mathrm{a}}, \eta_{\mathrm{b}}\} \left(r_{\ell\ell_1} + r_{\ell_1 m} + r_{m\ell_2} + r_{\ell_2 \ell} \right)} \le C_{\mathrm{a}}^2 C_{\mathrm{b}} e^{-\min\{\eta_{\mathrm{a}}, \eta_{\mathrm{b}}\} r_{\ell m}}. \end{aligned} \tag{5.7}$$

We then obtain from (5.5) and (5.7) that

$$\frac{\partial O_\ell(y)}{\partial [y(m)]_i} \le C_{\mathrm{a}}^2 C_{\mathrm{b}} |\mathscr{C}| \left(\sup_{z \in \mathscr{C}} |\mathfrak{o}(z,\tau)| \right) e^{-\min\{\eta_{\mathrm{a}}, \eta_{\mathrm{b}}\} r_{\ell m}} \le C_1 e^{-\eta_1 r_{\ell m}} \qquad \text{for } 1 \le i \le d,$$

where $|\mathscr{C}|$ depends on d, $\mathfrak{m}$, h_{hop}, h_{ons} and R_{c}, and $\sup_{z \in \mathscr{C}} |\mathfrak{o}(z,\tau)|$ depends on $\mathfrak{o}$ and τ. This completes the proof for $j = 1$.

For $j = 2$, we have from the definition (2.2) that

$$\Big| \Big(\left[\mathcal{H}_{,mn}\right]_{i_1 i_2} (y) \Big)_{\ell k} \Big| \le C e^{-\gamma(r_{\ell m} + r_{km} + r_{\ell n} + r_{kn})},$$

which together with (5.4) implies

$$\begin{aligned} & \Big[\mathscr{R}_z \left[\mathcal{H}_{,m}\right]_{i_1} \mathscr{R}_z \left[\mathcal{H}_{,n}\right]_{i_2} \mathscr{R}_z \Big]_{\ell\ell} \le C e^{-\frac{1}{2}\gamma(r_{\ell m} + r_{\ell n})}; \\ & \Big[\mathscr{R}_z \left[\mathcal{H}_{,n}\right]_{i_2} \mathscr{R}_z \left[\mathcal{H}_{,m}\right]_{i_1} \mathscr{R}_z \Big]_{\ell\ell} \le C e^{-\frac{1}{2}\gamma(r_{\ell m} + r_{\ell n})}; \qquad \text{and} \\ & \Big[\mathscr{R}_z \left[\mathcal{H}_{,mn}\right]_{i_1 i_2} \mathscr{R}_z \Big]_{\ell\ell} \le C e^{-\frac{1}{2}\gamma(r_{\ell m} + r_{\ell n})}. \end{aligned}$$

Inserting these three estimates into (5.6) yields the desired result,

$$\frac{\partial^2 O_\ell(y)}{\partial [y(m)]_{i_1} \partial [y(n)]_{i_2}} \le C_2 e^{-\eta_2 \left(r_{\ell m} + r_{\ell n} \right)} \qquad \text{for } 1 \le i_1, i_2 \le d.$$

We will skip the details for the proofs for cases $j \ge 2$, which are analogous but tedious. □

5.2 Proof of Theorem 3.1

Proof of Theorem 3.1. Define a corresponding homogeneous finite system $\Lambda_R^{\rm hom} := \Lambda^{\rm hom} \cap B_R$, which has $N_{\#,R}$ nuclei and $N_{\#,R}$ electrons. Denoting by $\mathcal{N}_\ell^\Omega(Du(\ell),\tau) := \mathcal{N}_\ell(Du|_\Omega(\ell),\tau)$ for the finite system contained in Ω, we have

$$\begin{aligned}
& N(y_R,\mu_R) - N(y_R,\mu_\#) \\
= \;& N_{{\rm e},R} - N_{\#,R} + \sum_{\ell\in\Lambda_R^{\rm hom}} \mathcal{N}_\#(\mathbf{0},\mu_\#) - \sum_{\ell\in\Lambda_R} \mathcal{N}_\ell^{\Lambda_R}(Du(\ell),\mu_\#) \\
= \;& \big(N_{{\rm e},R} - N_{\#,R}\big) + \Big(\sum_{\ell\in\Lambda^{\rm hom}\cap B_{R_{\rm def}}} \mathcal{N}_\#\big(\mathbf{0},\mu_\#\big) - \sum_{\ell\in\Lambda\cap B_{R_{\rm def}}} \mathcal{N}_\ell^{\Lambda_R}\big(Du(\ell),\mu_\#\big)\Big) \\
& + \sum_{\ell\in\Lambda_R^{\rm hom}\setminus B_{R_{\rm def}}} \Big(\mathcal{N}_\#(\mathbf{0},\mu_\#) - \mathcal{N}_\ell^{\Lambda_R^{\rm hom}\setminus B_{R_{\rm def}}}(\mathbf{0},\mu_\#)\Big) \\
& - \sum_{\ell\in\Lambda_R\setminus B_{R_{\rm def}}} \Big(\mathcal{N}_\ell^{\Lambda_R}(Du(\ell),\mu_\#) - \mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(Du(\ell),\mu_\#)\Big) \\
& + \sum_{\ell\in\Lambda_R\setminus B_{R_{\rm def}}} \Big(\mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(\mathbf{0},\mu_\#) - \mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(Du(\ell),\mu_\#)\Big) \\
=: \;& T_1 + T_2 + T_3 + T_4 + T_5. \qquad (5.8)
\end{aligned}$$

The condition $|N_{{\rm e},R} - N_R| < C$ and **(R)** imply that T_1 and T_2 are uniformly bounded. T_3 can be estimated by Lemma 3.1 as

$$|T_3| \le C \sum_{\ell\in\Lambda,\ R_{\rm def}\le|\ell|\le R} \Big(e^{-\eta_0(|\ell|-R_{\rm def})} + e^{-\eta_0(R-|\ell|)}\Big) \le CR^{d-1}. \qquad (5.9)$$

The term $e^{-\eta_0(R-|\ell|)}$ arises due to the presence of the domain boundary where the local geometry is distinct from the bulk geometry. T_4 can be bounded in the same way. To estimate T_5, we have from Lemma 2.1 that

$$\begin{aligned}
|T_5| \;&\le\; C \sum_{\ell\in\Lambda_R\setminus B_{R_{\rm def}}} \Big|\mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(\mathbf{0},\mu_\#) - \mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(Du(\ell),\mu_\#)\Big| \\
&\le\; C \sum_{\ell\in\Lambda_R\setminus B_{R_{\rm def}}} \sum_{\rho\in\Lambda_R\setminus B_{R_{\rm def}}-\ell} \left| \frac{\partial \mathcal{N}_\ell^{\Lambda_R\setminus B_{R_{\rm def}}}(Dw(\ell),\mu_\#)}{\partial D_\rho w(\ell)}\Big|_{Dw=\theta_\ell Du} \right| \cdot |D_\rho u(\ell)| \\
&\le\; C \sum_{\ell\in\Lambda\setminus B_{R_{\rm def}}} \big|Du(\ell)\big|_\gamma \le CN_R^{1/2}\|Du\|_{\ell^2_\gamma} \le CR^{d/2}\|Du\|_{\ell^2_\gamma}, \qquad (5.10)
\end{aligned}$$

where $\theta_\ell \in (0,1)$ depends on ℓ, and the constant C depends on γ and γ_1. Therefore, we have from (5.8), (5.9) and (5.10) that

$$\begin{aligned}
\big|\mathcal{N}(u_R,\mu_R) - \mathcal{N}(u_R,\mu_\#)\big| \;&\le\; C\big(R^{d-1} + \|Du\|_{\ell^1_\gamma}\big) \\
&\le\; C\big(R^{d-1} + R^{d/2}\|Du\|_{\ell^2_\gamma}\big). \qquad (5.11)
\end{aligned}$$

Note that for a finite temperature $T > 0$, there exists a constant c depending only on T such that $f'(\lambda_s - \tau) \ge c \;\forall\; \lambda_s \in [\underline{\lambda}, \bar{\lambda}]$, hence

$$\frac{\partial \mathcal{N}(u_R,\tau)}{\partial \tau} = -\sum_{s=1}^{N_R} f'(\lambda_s - \tau) \ge cN_R \ge CR^d. \qquad (5.12)$$

Since (5.11) is equivalent to

$$\left|\frac{\partial \mathcal{N}(u_R,\tau_\theta)}{\partial \tau}\right| \cdot |\mu_R - \mu_\#| \le C\big(R^{d-1} + \|Du\|_{\ell^1_\gamma}\big) \le C\big(R^{d-1} + R^{d/2}\|Du\|_{\ell^2_\gamma}\big)$$

with $\tau_\theta = \theta\mu_R + (1-\theta)\mu_\#$, which together with (5.12) yields (3.7) and thus completes the proof. □

5.3 Proof of Theorem 3.2

We will first need the following result, which gives us the far-field structure of the minimizers of (3.10). For the proof we refer to [13, 21].

Lemma 5.1. *If $\bar{u} \in \mathrm{Adm}(\Lambda)$ is a strongly stable solution to (3.10) in the sense of (3.12) with some constant $\bar{c} > 0$, then there exists a constant $C > 0$ such that*

$$|D\bar{u}(\ell)|_\gamma \le C(1+|\ell|)^{-d} \qquad \forall \ell \in \Lambda. \tag{5.13}$$

Next, we shall derive a force-balance equation that is equivalent to (2.8) and (2.9). Let y be a configuration with corresponding chemical potential $\mu = \mu(y)$ satisfying (2.5). Then by using (2.6), (5.1), (5.2) and the fact $\partial_x \mathfrak{g}(x,\tau) = 2f(x-\tau)$, we can compute the derivative of $E(y)$ on the ℓ-th atom (ignoring the Cartesian coordinate for simplicity of notations)

$$\begin{aligned}
\frac{\partial E(y)}{\partial y(\ell)} &= \frac{\partial}{\partial y(\ell)} \mathrm{Tr}\big(\mathfrak{e}(\mathcal{H}(y),\mu(y))\big) \\
&= \frac{\partial}{\partial y(\ell)} \Big(\mu(y)\mathrm{Tr}\big(\mathfrak{n}(\mathcal{H}(y),\mu(y))\big)\Big) + \frac{\partial}{\partial y(\ell)} \mathrm{Tr}\big(\mathfrak{g}(\mathcal{H}(y),\mu(y))\big) \\
&= 2\sum_{s=1}^{N_\Omega} f(\lambda_s - \mu) \left\langle \psi_s \middle| \frac{\partial \mathcal{H}(y)}{\partial y(\ell)} \middle| \psi_s \right\rangle,
\end{aligned} \tag{5.14}$$

and we refer to the preprint [12] for more details.

Therefore, any minimiser $(\bar{y}, \bar{\mu})$ of (2.8) and (2.9) satisfies the equations

$$\begin{cases} F_\ell(\bar{y},\bar{\mu}) = 0 & \forall\ \ell \in \Omega\backslash\Omega^{\mathrm{D}}, \\ N(\bar{y},\bar{\mu}) = N_{\mathrm{e}} \end{cases} \tag{5.15}$$

with

$$F_\ell(y,\tau) := -2\sum_{s=1}^{N_\Omega} f(\lambda_s - \tau) \left\langle \psi_s \middle| \frac{\partial \mathcal{H}(y)}{\partial y(\ell)} \middle| \psi_s \right\rangle. \tag{5.16}$$

We remark that (5.15) can also be derived as the associated Euler-Lagrange equation of the constrained minimization problem (2.9).

We now consider the sequence of problems (3.11) with parameter R. For $(u_R,\tau) \in \dot{\mathscr{W}}_R(\Lambda) \times \mathbb{R}$, we define

$$\mathcal{F}_\ell^{\Lambda_R}(u_R,\tau) := F_\ell((x+u_R)|_{\Lambda_R},\tau)$$

and $\mathcal{F}(u_R,\tau)\in \dot{\mathscr{W}}_R(\Lambda)'$ with

$$\big\langle \mathcal{F}^{\Lambda_R}(u_R,\tau), v\big\rangle = \sum_{\ell\in\Lambda_R} \mathcal{F}_\ell^{\Lambda_R}(u_R,\tau)\cdot v(\ell) \qquad \forall\ v\in \dot{\mathscr{W}}_R(\Lambda). \tag{5.17}$$

Here $\dot{\mathscr{W}}_R(\Lambda)'$ is the dual space of $\dot{\mathscr{W}}_R(\Lambda)$.

Define $\mathcal{T}_R : \dot{\mathscr{W}}_R(\Lambda)\times\mathbb{R}\to \dot{\mathscr{W}}_R(\Lambda)'\times\mathbb{R}$ by (recall the definition of $\mathcal{N}^{\Lambda_R}$ below (3.11))

$$\mathcal{T}_R(u_R,\tau) := \Big(-\mathcal{F}^{\Lambda_R}(u_R,\tau), N_{\mathrm{e},R}^{-1}\mathcal{N}^{\Lambda_R}(u_R,\tau)-1\Big) \quad \text{for } (u_R,\tau)\in \dot{\mathscr{W}}_R(\Lambda)\times\mathbb{R}.$$

We have from (5.15) that (3.11) is equivalent to

$$\mathcal{T}_R(\bar u_R,\bar\mu_R)=\mathbf{0}. \tag{5.18}$$

We can further compute the Jacobian matrix of $\mathcal{T}$ at $(u_R,\tau)\in\dot{\mathscr{W}}_R(\Lambda)\times\mathbb{R}$,

$$\mathcal{J}_R(u_R,\tau) := \begin{bmatrix} -\delta_u\mathcal{F}^{\Lambda_R}(u_R,\tau) & -\delta_\tau\mathcal{F}^{\Lambda_R}(u_R,\tau)\\ N_{\mathrm{e},R}^{-1}\delta_u\mathcal{N}^{\Lambda_R}(u_R,\tau) & N_{\mathrm{e},R}^{-1}\delta_\tau\mathcal{N}^{\Lambda_R}(u_R,\tau)\end{bmatrix}, \tag{5.19}$$

which will be heavily used in the proof.

Proof of Theorem 3.2. Step 1. Quasi-best approximation. Following [21, Lemma 7.3], we can construct $T_R\bar u\in \mathrm{Adm}(R)$ such that for R sufficiently large,

$$\|DT_R\bar u - D\bar u\|_{\ell^2_\gamma} \le C\|D\bar u\|_{\ell^2_\gamma(\Lambda\setminus B_{R/2})} \le CR^{-d/2}$$

where Lemma 5.1 is used for the last inequality. We now fix some $r>0$ such that $x+B_r(\bar u)\subset \mathscr{A}_{\mathfrak{m}}$ for some $\mathfrak{m}>0$. Then, for R sufficiently large, we have that $T_R\bar u\in B_{r/2}(\bar u)$ and hence $x+B_{r/2}(T_R\bar u)\subset\mathscr{A}_{\mathfrak{m}}$.

Since $\mathcal{G}\in C^3(\mathrm{Adm}(R))$, $\delta\mathcal{G}$ and $\delta^2\mathcal{G}$ are Lipschitz continuous in $B_r(\bar u)\cap\mathrm{Adm}(R)$ with Lipschitz constants L_1 and L_2, that is,

$$\|\delta\mathcal{G}(\bar u)-\delta\mathcal{G}(T_R\bar u)\| \le L_1\|D\bar u - DT_R(\bar u)\|_{\ell^2_\gamma}\le CR^{-d/2}, \qquad \text{and} \tag{5.20}$$

$$\|\delta^2\mathcal{G}(\bar u)-\delta^2\mathcal{G}(T_R\bar u)\| \le L_2\|D\bar u - DT_R(\bar u)\|_{\ell^2_\gamma}\le CR^{-d/2}. \tag{5.21}$$

Step 2. Consistency. Let $\mathcal{G}^{\Lambda_R}(u,\tau) := G\big((x+u)|_{\Lambda_R},\tau\big)$. We have from (2.12) and (5.16) that

$$\mathcal{F}_\ell^{\Lambda_R}(T_R\bar u,\mu_\#) = -\frac{\partial\mathcal{G}^{\Lambda_R}(T_R\bar u,\mu_\#)}{\partial T_R\bar u(\ell)}, \tag{5.22}$$

which implies that for any $v\in\dot{\mathscr{W}}_R(\Lambda)$,

$$\begin{aligned}\big\langle -\mathcal{F}^{\Lambda_R}(T_R\bar u,\mu_\#), v\big\rangle &= -\sum_{\ell\in\Lambda\cap B_{R+R_0}} \mathcal{F}_\ell^{\Lambda_R}(T_R\bar u,\mu_\#)v_\ell\\ &= \big\langle \delta_u\mathcal{G}^{\Lambda_R}(T_R\bar u,\mu_\#), v\big\rangle = \sum_{\ell\in\Lambda_R}\big\langle \delta_u\mathcal{G}_\ell^{\Lambda_R}(D(T_R\bar u)(\ell),\mu_\#), Dv(\ell)\big\rangle.\end{aligned} \tag{5.23}$$

Using Lemma 3.1 and the facts that $v = 0$ and $T_R\bar{u} = 0$ outside Λ_R, we have that there exists a constant $\gamma_{\rm c}$, such that

$$\left|\left\langle \delta_u \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - \delta_u \mathcal{G}(T_R\bar{u}, \mu_\#), v\right\rangle\right| \leq Ce^{-\gamma_{\rm c} R_{\rm b}} R^{d-1/2} \|Dv\|_{\ell^2_\gamma}. \tag{5.24}$$

The proof of this estimate is relatively straightforward and we refer to [14, Proof of (4.12)] for an analogous one. In order to balance the error, we must choose $R_{\rm b}$ such that $e^{-\gamma_{\rm c} R_{\rm b}} R^{d-1/2} \leq CR^{-d/2}$, or equivalently, $e^{-\gamma_{\rm c} R_{\rm b}} \leq CR^{-(3d+1)/2}$. On taking logarithms, we observe that this is true provided that $R_{\rm b} \geq c_{\rm b} \log R$ for $c_{\rm b}$ sufficiently large.

Then we obtain from (5.20), (5.23), (5.24) and $\delta\mathcal{G}(\bar{u}) = 0$ that $\forall\ v \in \dot{\mathscr{W}}_R(\Lambda)$,

$$\begin{aligned} & \left\langle -\mathcal{F}^{\Lambda_R}(T_R\bar{u}, \mu_\#), v\right\rangle \\ = \ & \left\langle \delta_u \mathcal{G}(T_R\bar{u}, \mu_\#) - \delta_u \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#), v\right\rangle + \left\langle \delta_u \mathcal{G}(\bar{u}, \mu_\#) - \delta_u \mathcal{G}(T_R\bar{u}, \mu_\#), v\right\rangle \\ \leq \ & C\big(e^{-\gamma_{\rm c} R} R^{d-1/2} + R^{-d/2}\big)\|Dv\|_{\ell^2_\gamma} \ \leq \ CR^{-d/2}\|Dv\|_{\ell^2_\gamma} \end{aligned} \tag{5.25}$$

for sufficiently large R and appropriate $c_{\rm b}$.

To proceed, we recall from (3.5) the definition of local analytic QoIs $\mathcal{O}_\#$ (in particular $\mathcal{N}_\#$) associated with the homogeneous lattice.

We still have to estimate the residual of $N_{{\rm e},R}^{-1}\mathcal{N}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - 1$. We first construct a corresponding homogeneous finite system $\Lambda^{\rm hom} \cap B_{R+R_{\rm b}}$ with $N_{\#,\Lambda_R}$ electrons, and then obtain from an argument similar to (5.8)-(5.11) that

$$\begin{aligned} & \left|\mathcal{N}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - N_{{\rm e},R}\right| \\ \leq \ & \left|\mathcal{N}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - \sum_{\ell \in \Lambda^{\rm hom} \cap B_{R+R_{\rm b}}} \mathcal{N}_\#(\mathbf{0}, \mu_\#)\right| + \left|N_{{\rm e},R} - N_{\#,\Lambda_R}\right| \\ \leq \ & C\big(R^{d-1} + R^{d/2}\big), \end{aligned}$$

where C depends on $\|DT_R\bar{u}\|_{\ell^2_\gamma}$ (which is bounded by $\|D\bar{u}\|_{\ell^2_\gamma}$ and is hence independent of R). Therefore, we have

$$\left|N_{{\rm e},R}^{-1}\mathcal{N}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - 1\right| \leq CR^{-\min\{1,d/2\}}. \tag{5.26}$$

Then we have the following consistency estimate from (5.25) and (5.26)

$$\left\|\mathcal{T}_R\big(T_R\bar{u}, \mu_\#\big)\right\|_{\dot{\mathscr{W}}_R(\Lambda)' \times \mathbb{R}} \leq CR^{-\min\{1,d/2\}}. \tag{5.27}$$

Step 3. Stability. We have from (5.22) that

$$\delta_u \mathcal{F}^{\Lambda_R}(T_R\bar{u}, \mu_\#) = -\delta_u^2 \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#). \tag{5.28}$$

Using Lemma 3.1 and the facts that $v = 0$ and $T_R\bar{u} = 0$ outside B_R, we have that there exists a constant $\gamma_{\rm s}$, such that

$$\left|\left\langle \big(\delta_u^2 \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#) - \delta_u^2 \mathcal{G}(T_R\bar{u}, \mu_\#)\big)v, v\right\rangle\right| \leq Ce^{-\gamma_{\rm s} R_{\rm b}} R^d \|Dv\|^2_{\ell^2_\gamma}. \tag{5.29}$$

The proof of this estimate is straightforward and we refer to [14, Proof of (4.10)] for an analogous one. Together with (3.12) and (5.21) this leads to

$$\begin{aligned}
&\big\langle -\delta_u \mathcal{F}^{\Lambda_R}(T_R\bar{u},\mu_\#)v, v\big\rangle \;=\; \big\langle \delta^2\mathcal{G}^{\Lambda_R}(T_R\bar{u},\mu_\#)v, v\big\rangle \\
=\;& \big\langle \delta^2\mathcal{G}(\bar{u},\mu_\#)v, v\big\rangle + \big\langle \big(\delta^2\mathcal{G}(T_R\bar{u},\mu_\#) - \delta^2\mathcal{G}(\bar{u},\mu_\#)\big)v, v\big\rangle \\
&+\big\langle \big(\delta^2\mathcal{G}^{\Lambda_R}(T_R\bar{u},\mu_\#) - \delta^2\mathcal{G}(T_R\bar{u},\mu_\#)\big)v, v\big\rangle \\
\geq\;& \big(\bar{c} - C(R^{-d/2} + e^{-\gamma_{\rm s}R_{\rm b}}R^d)\big)\|Dv\|_{\ell^2_\gamma}^2 \;\geq\; \frac{\bar{c}}{2}\|Dv\|_{\ell^2_\gamma}^2 \qquad \forall\, v \in \dot{\mathscr{W}}_R(\Lambda) \qquad (5.30)
\end{aligned}$$

for sufficiently large R and $c_{\rm b}$. Therefore, $-\delta_u\mathcal{F}^{\Lambda_R}(T_R\bar{u},\mu_\#)$ is positive definite.

Similar to (5.12), we have that there exists a constant $a_0 > 0$ such that

$$N_{{\rm e},R}^{-1}\delta_\tau \mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#) \geq a_0. \qquad (5.31)$$

It remains to estimate the off-diagonal terms of $\mathcal{J}_R(T_R\bar{u},\mu_\#)$. Note that

$$\frac{\partial N^{\Lambda_R}(y,\tau)}{\partial y(\ell)} = 2\sum_{s=1}^{N_R} f'(\lambda_s - \tau)\left\langle \psi_s \left| \frac{\partial \mathcal{H}(y^{\Lambda_R})}{\partial y(\ell)} \right| \psi_s \right\rangle,$$

which together with

$$\frac{-\partial F_\ell^{\Lambda_R}(y,\tau)}{\partial \tau} = 2\sum_{s=1}^{N_R} f'(\lambda_s - \tau)\,\left\langle \psi_s \left| \frac{\partial \mathcal{H}(y^{\Lambda_R})}{\partial y(\ell)} \right| \psi_s \right\rangle$$

implies

$$-\delta_\tau \mathcal{F}^{\Lambda_R}(T_R\bar{u},\mu_\#) = \delta_u \mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#). \qquad (5.32)$$

We then observe that there exists a constant $b_0 > 0$ such hat

$$\big\langle \delta_u\mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#), v\big\rangle \leq b_0\|Dv\|_{\ell^2_\gamma} \qquad \forall\, v \in \dot{\mathscr{W}}_R(\Lambda). \qquad (5.33)$$

To see this, we have

$$\begin{aligned}
&\big\langle \delta_u\mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#), v\big\rangle \\
&\qquad = \big\langle \delta_u\mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#) - \delta_u\mathcal{N}(T_R\bar{u},\mu_\#), v\big\rangle + \big\langle \delta_u\mathcal{N}(T_R\bar{u},\mu_\#), v\big\rangle,
\end{aligned}$$

where the first term is estimated analogously to (5.24)

$$\big|\big\langle \delta_u\mathcal{N}^{\Lambda_R}(T_R\bar{u},\mu_\#) - \delta_u\mathcal{N}(T_R\bar{u},\mu_\#), v\big\rangle\big| \leq Ce^{-\gamma_{\rm c}R_{\rm b}}R^{d-1/2}\|Dv\|_{\ell^2_\gamma}$$

and the second term can be estimated by using similar arguments as those in [13] and [21, Lemma 2.1]

$$\begin{aligned}
\big\langle \delta_u\mathcal{N}(T_R\bar{u},\mu_\#), v\big\rangle \;&=\; \sum_{\ell\in\Lambda}\big\langle \delta_u\mathcal{N}_\ell(\mathbf{0},\mu_\#), Dv(\ell)\big\rangle - \sum_{\ell\in\Lambda^{\rm hom}}\big\langle \delta_u\mathcal{N}_\#(\mathbf{0},\mu_\#), Dv(\ell)\big\rangle \\
&\quad + \sum_{\ell\in\Lambda}\big\langle \delta_u^2\mathcal{N}_\ell(\theta_\ell T_R\bar{u},\mu_\#)Du(\ell), Dv(\ell)\big\rangle \\
&\leq\; C\|Dv\|_{\ell^2_\gamma}
\end{aligned}$$

with $\theta_\ell \in (0,1)$ depending on ℓ and the constant C depending on $T_R\bar{u}$.

To show the stability, we want to solve

$$\mathcal{J}_R\big(T_R\bar{u}, \mu_\#\big)(v,\kappa) = (w,\xi)$$

for any $(w,\xi) \in \dot{\mathscr{W}}_R(\Lambda)' \times \mathbb{R}$. We first obtain from (5.31) and (5.33) that

$$|\kappa| \le a_0^{-1}\Big|\xi - N_{\mathrm{e},R}^{-1} b_0 \|Dv\|_{\ell^2_\gamma}\Big| \le C|\xi|. \tag{5.34}$$

To obtain v, we solve

$$\delta_u^2 \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#)v = w + \kappa \delta_u \mathcal{G}^{\Lambda_R}(T_R\bar{u}, \mu_\#).$$

By using (5.30), (5.32) and (5.33), we obtain that

$$\|Dv\|_{\ell^2_\gamma} \le C\big(\|w\|_{\dot{\mathscr{W}}_R(\Lambda)'} + b_0|\xi|\big) \le C\big(\|w\|_{\dot{\mathscr{W}}_R(\Lambda)'} + |\xi|\big).$$

This together with (5.34) implies that

$$\mathcal{J}_R\big(T_R\bar{u}, \mu_\#\big) : \dot{\mathscr{W}}_R(\Lambda) \times \mathbb{R} \to \dot{\mathscr{W}}_R(\Lambda)' \times \mathbb{R} \ \text{ is an isomorphism.} \tag{5.35}$$

Step 4. Application of Inverse Function Theorem. With the consistency (5.27) and the stability (5.35), we can apply the inverse function theorem [32, Lemma B.1] on the function $\mathcal{T}_R$ around the point $\big(T_R\bar{u}, \mu_\#\big)$, to obtain the existence of $\bar{u}_R$ and the estimate (3.13). □

5.4 Proof of Theorem 3.3

Proof of Theorem 3.3. Since $\|D\bar{u}_{R_j}\|_{\ell^2_\gamma}$ is bounded, we have from Theorem 3.1 that

$$|\bar{\mu}_{R_j} - \mu_\#| \le C R^{-\min\{1,d/2\}}. \tag{5.36}$$

Again using $\sup_j \|D\bar{u}_{R_j}\|_{\ell^2_\gamma} < \infty$, we have from the Banach-Alaoglu theorem (note that $\dot{\mathscr{W}}^{1,2}$ becomes a Hilbert space after factoring out a constant shift) that there exists a subsequence (not relabelled) and $\bar{u} \in \mathrm{Adm}(R)$ such that

$$\bar{u}_{R_j} \overset{w}{\rightharpoonup} \bar{u} \qquad \text{in } \dot{\mathscr{W}}^{1,2}(\Lambda) \quad \text{as } j \to \infty.$$

Since $v \mapsto D_\rho v(\ell)$ is a linear functional on $\dot{\mathscr{W}}^{1,2}(\Lambda)$ for any $\ell \in \Lambda$ and $\rho \in \Lambda - \ell$, we have (3.14).

Now it is only necessary to show that $\delta\mathcal{G}(\bar{u}) = 0$. Let $v \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ have compact support B_{R_v}. Then, for j sufficiently large, $v|_{\Lambda_{R_j}}$ is an admissible test function for (3.11). Thus, using (2.13) we obtain

$$0 = \big\langle \delta_u \mathcal{G}^{\Lambda_{R_j}}(\bar{u}_{R_j}, \bar{\mu}_{R_j}), v\big\rangle = \sum_{\ell \in \Omega_v} \mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u}_{R_j}, \bar{\mu}_{R_j}) \cdot v(\ell),$$

where $\Omega_v := \big\{\ell \in \Lambda,\ v(\ell) \neq 0\big\}$. To complete the proof we only need to show that

$$\mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u}_{R_j}, \bar{\mu}_{R_j}) \to \mathcal{F}_\ell(\bar{u}, \mu_\#) \qquad \text{for all } \ell \in \Omega_v, \text{ as } j \to \infty. \tag{5.37}$$

To see this, we have

$$\begin{aligned} & \big|\mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u}_{R_j},\bar{\mu}_{R_j}) - \mathcal{F}_\ell(\bar{u},\mu_\#)\big| \\ = \;& \big|\mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u}_{R_j},\bar{\mu}_{R_j}) - \mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u},\bar{\mu}_{R_j})\big| + \big|\mathcal{F}_\ell^{\Lambda_{R_j}}(\bar{u},\bar{\mu}_{R_j}) - \mathcal{F}_\ell(\bar{u},\bar{\mu}_{R_j})\big| \\ & + \big|\mathcal{F}_\ell(\bar{u},\bar{\mu}_{R_j}) - \mathcal{F}_\ell(\bar{u},\mu_\#)\big| \\ =: \;& T_{1,j} + T_{2,j} + T_{3,j}. \end{aligned}$$

Note that (3.14) implies

$$\limsup_{j\to\infty} \|D\bar{u} - D\bar{u}_{R_j}\|_{\ell^2_\gamma(\Lambda\cap B_{2R_v})} = 0,$$

which together with the fact

$$\mathcal{F}_\ell^\Omega(u,\tau) = \sum_{\rho\in\ell-\Omega} \mathcal{G}^\Omega_{\ell-\rho,\rho}\big(Du(\ell-\rho),\tau\big) - \sum_{\rho\in\Omega-\ell} \mathcal{G}^\Omega_{\ell,\rho}\big(Du(\ell),\tau\big) \qquad \text{with } \Omega = \Lambda_{R_j} \tag{5.38}$$

and Lemma 2.1 leads to

$$\limsup_{j\to\infty} |T_{1,j}| \le Ce^{-\eta_1 R_v}. \tag{5.39}$$

Using (3.3) and (5.38) with $\Omega = \Lambda$, we can estimate $T_{2,j}$ by

$$|T_{2,j}| \le Ce^{-\eta_1 R_j}. \tag{5.40}$$

Finally, we have from (5.36) that

$$|T_{3,j}| \le C|\bar{\mu}_{R_j} - \mu_\#| \le CR_j^{-\min\{1,d/2\}}. \tag{5.41}$$

Taking into accounts (5.39), (5.40), (5.41) and the fact that R_v can be chosen arbitrarily large (independent of j), we obtain (5.37) and complete the proof. □

Appendix A Periodic boundary conditions

Periodic boundary condition (i.e. the *supercell model*) is the most popular choice for simulating crystalline defects. To implement periodic boundary conditions, let $\Omega_R \subset \mathbb{R}^d$ be connected such that $B_R \subset \Omega_R$, for $\mathsf{B} = (b_1, \cdots, b_d) \in \mathbb{R}^{d\times d}$ non-singular, $b_i \in \Lambda^{\rm hom}$, $\bigcup_{\alpha\in\mathbb{Z}^d}\{\mathsf{B}\alpha + \Omega_R\} = \mathbb{R}^d$, and the shifted domains $\mathsf{B}\alpha + \Omega_R$ are disjoint. The computational cell is defined by

$$\Lambda_R^\# := \Omega_R \cap \Lambda.$$

We consider a *torus* tight binding model, defined as follows; an alternative periodic model is desribed in Remark A.1. Let $N_R := \#(\Lambda_R^\#)$. Then for $y : \Lambda_R^\# \to \mathbb{R}^d$, the Hamiltonian matrix $\mathcal{H}^\#(y) \in \mathbb{R}^{N_R\times N_R}$ has the matrix elements

$$\Big(\mathcal{H}^\#(y)\Big)_{\ell k} = \begin{cases} h_{\rm ons}\Big(\displaystyle\sum_{\substack{j\in\Lambda_R^\#\setminus\ell \\ \alpha\in\mathbb{Z}^d}} \varrho(r_{\ell(j+\mathsf{B}\alpha)})\Big) + \displaystyle\sum_{\alpha\in\mathbb{Z}^d\setminus\mathbf{0}} h_{\rm hop}(r_{\ell(\ell+\mathsf{B}\alpha)}) & \text{if } \ell = k; \\ \displaystyle\sum_{\alpha\in\mathbb{Z}^d} h_{\rm hop}(r_{\ell(k+\mathsf{B}\alpha)}) & \text{if } \ell \ne k, \end{cases} \tag{A.1}$$

where ϱ, $h_{\rm ons}$ and $h_{\rm hop}$ are given by (2.2), and $r_{\ell(j+B\alpha)} = |B\alpha + y(j) - y(\ell)|$. We can then compute the eigenpairs of $\mathcal{H}^{\#}(y)$ and define the corresponding (local) analytic QoIs and (local) density of states analogously as in § 2. We will denote these objects by the same symbolds as in § 2.

Repeating the proofs in § 5.1 verbatim, we obtain locality result of local analytic QoIs:

$$\left| \frac{\partial^j O_\ell(y,\tau)}{\partial [y(m_1)]_{i_1} \cdots \partial [y(m_j)]_{i_j}} \right| \leq C_j e^{-\gamma_j \sum_{t=1}^{j} r^{\#}_{\ell m_t}}, \tag{A.2}$$

which is identical to Lemma B.1, but the distance $r_{\ell k}$ is replaced with the *torus distance*

$$r^{\#}_{\ell k} := \min_{\alpha \in \mathbb{Z}^d} \big| y(\ell) - y(k) + \mathsf{B}\alpha \big|.$$

Analogously to § 3.2, we can again define the pointwise thermodynamic limit of the local density of states and of local analytic QoIs, and observe that they inherit again the locality (A.2).

Turning to the formulation of force equilibration, the set of admissible displacements is now given by

$$\begin{aligned} \mathrm{Adm}^{\#}(R) := \big\{ u : \Lambda_R^{\#} \to \mathbb{R}^d \;\big|\; & |y(\ell) - y(k) + \mathsf{B}\alpha| \geq \mathfrak{m} |\ell - k + \mathsf{B}\alpha| \\ & \text{for any } \ell, k \in \Lambda_R^{\#} \text{ and } \alpha \in \mathbb{Z}^d, \text{ for some } \mathfrak{m} > 0 \big\}. \end{aligned}$$

The Helmholtz free energy for $u \in \mathrm{Adm}^{\#}(R)$ is given by

$$\mathcal{E}^{\#}_R(u) = \mathcal{E}^{\#}_R\big(u, \mu(u)\big) := \sum_{\ell \in \Lambda_R^{\#}} \mathcal{E}_\ell^{\Lambda_R^{\#}}\big(Du(\ell), \mu\big),$$

where the chemical potential $\mu = \mu(u)$ is chosen such that

$$N_{{\rm e},R} = \mathcal{N}^{\#}_R(u, \mu) := \sum_{\ell \in \Lambda_R^{\#}} \mathcal{N}_\ell^{\Lambda_R^{\#}}\big(Du(\ell), \mu\big) \tag{A.3}$$

with $N_{{\rm e},R}$ a prescribed number of electrons contained in Ω_R. Here, $\mathcal{E}_\ell^{\Lambda_R^{\#}}$ and $\mathcal{N}_\ell^{\Lambda_R^{\#}}$ are local analytic QoIs for the above torus model.

We can now derive the limit of chemical potential with periodic boundary conditions, which is an analogous result to Theorem 3.1, but with an improved convergence rate due to the fact that boundary effects no longer occur.

Theorem A.1. *Let Λ satisfy* **(R)**, $\Lambda_R^{\#} := \Lambda \cap B_R \uparrow \Lambda$ *and* $N_R := \#(\Lambda_R^{\#})$. *For each R let $u_R^{\#} : \Lambda_R^{\#} \to \mathbb{R}^d$ with $y_R^{\#}(\ell) := \ell + u_R^{\#}(\ell)$ a configuration with parameter $\mathfrak{m}$ independent of R.*

Let $N_{{\rm e},R} \in \mathbb{R}$ be a prescribed number of electrons in the subsystem Λ_R, chosen such that $|N_R - N_{{\rm e},R}|$ is bounded as $R \to \infty$. Then, the chemical potential $\mu_R^{\#}$ solving (A.3) *is well-defined and satisfies*

$$\big|\mu_R^{\#} - \mu_{\#}\big| \leq C_1^{\#} R^{-d} \|Du_R^{\#}\|_{\ell^1_\gamma} \leq C_2^{\#} R^{-d/2} \|Du_R^{\#}\|_{\ell^2_\gamma} \tag{A.4}$$

with some constants $C_1^{\#}$ and $C_2^{\#}$.

Proof. The proof is analogous to that of Theorem 3.1. The main difference lies in that there is no surface term in T_3 and T_4. More specifically, (5.9) is replaced by

$$|T_3| \le C \sum_{\ell \in \Lambda_R^\#,\ |\ell| \ge R_{\rm def}} e^{-\gamma_0(|\ell| - R_{\rm def})} \le C. \qquad \square$$

We now consider the thermodynamic limit of the equilibrium problem with periodic boundary conditions corresponding to (2.9):

$$(\bar u_R^\#, \bar\mu_R^\#) \in \arg\min \Big\{ \mathcal{E}_R^\#(u_R, \tau) \ :\ \mathcal{N}_R^\#(u_R, \tau) = N_{{\rm e},R},\ u_R \in {\rm Adm}^\#(R) \Big\}. \tag{A.5}$$

The following two results establish that the thermodynamic limit of (A.5) as $R \to \infty$ is again (3.10), i.e., the same as with clamped boundary conditions. The proofs are analogous to those of Theorems 3.2 and 3.3, with the exception of the proof of stability of the approximation. For the latter we refer to [21, Thm. 7.7] for an analogous result that is readily adapted. Hence, we do not give details but only mention again that the convergence rate is improved here as well.

Theorem A.2. *Assume that $|N_R - N_{{\rm e},R}|$ is bounded as $R \to \infty$. If $\bar u \in {\rm Adm}(\Lambda)$ is a strongly stable solution of* (3.10) *in the sense that* (3.12) *holds with some constant $\bar c > 0$, then, for R sufficiently large there exists a solution $(\bar u_R^\#, \bar\mu_R^\#)$ of* (A.5) *satisfying*

$$\big\| D\bar u - D\bar u_R^\# \big\|_{\ell^2_\gamma(\Lambda_R)} + \big| \bar\mu_R^\# - \mu_\# \big| \le C R^{-d/2}. \tag{A.6}$$

Theorem A.3. *Let $R_j \uparrow \infty$ and $(\bar u_{R_j}^\#, \bar\mu_{R_j}^\#)$ be solutions to* (A.5). *If $|N_{R_j} - N_{{\rm e},R_j}|$ is bounded and $\sup_{j>0} \|D\bar u_{R_j}\|_{\ell^2_\gamma(\Lambda_R)} < \infty$, then there exists a subsequence (not relabelled) and $\bar u \in {\rm Adm}(\Lambda)$ such that*

$$\bar\mu_{R_j}^\# \to \mu_\# \quad \text{and} \quad D_\rho \bar u_{R_j}^\#(\ell) \to D_\rho \bar u(\ell) \quad \forall\ \ell \in \Lambda,\ \rho \in \Lambda - \ell. \tag{A.7}$$

Moreover, each such accumulation point $\bar u$ solves (3.10).

Remark A.1. *An alternative approach is to approximate the local defect by repeating the computational cell periodically, which yields an infinite lattice of defects,*

$$\Lambda_R^{\rm per} := \bigcup_{\alpha \in \mathbb{Z}^d} \{ {\sf B}\alpha + \Omega_R \}.$$

The associated set of admissible displacements is

$$\begin{aligned} {\rm Adm}^{\rm per}(R) := \big\{ u : \Lambda_R^{\rm per} \to \mathbb{R}^d \ \big|\ & x + u \in \mathscr{A}(\Lambda_R^{\rm per}), \\ & u(\ell + b_i) = u(\ell) \text{ for } \ell \in \Lambda_R^{\rm per},\ i = 1, \cdots, d \big\}. \end{aligned}$$

The Helmholtz free energy for $u \in {\rm Adm}^{\rm per}(R)$ is given by

$$\mathcal{E}_R^{\rm per}(u) = \mathcal{E}_R^{\rm per}\big(u, \mu(u)\big) := \sum_{\ell \in \Lambda_R} \mathcal{E}_\ell^{\Lambda_R^{\rm per}}\big(Du(\ell), \mu\big),$$

where the chemical potential $\mu = \mu(u)$ is chosen such that

$$N_{\mathrm{e},R} = \mathcal{N}_R^{\mathrm{per}}(u,\mu) := \sum_{\ell \in \Lambda_R} \mathcal{N}_\ell^{\Lambda_R^{\mathrm{per}}}\big(Du(\ell),\mu\big) \tag{A.8}$$

with $N_{\mathrm{e},R}$ the number of electrons contained in the periodic cell Ω_R. Note that the local analytic QoIs $\mathcal{E}_\ell^{\Lambda_R^{\mathrm{per}}}$ and $\mathcal{N}_\ell^{\Lambda_R^{\mathrm{per}}}$ are defined by the thermodynamic limits in the infinite lattice of defects Λ_R^{per}. In practise, the quantities $\mathcal{E}_R^{\mathrm{per}}(u,\mu)$ and $N_{\mathrm{e},R}(u,\mu)$ are computed via Bloch's theorem (Brilluoin zone integration).

Then the thermodynamic limit of the equilibrium problem within this setting is given by:

$$(\bar{u}_R^{\mathrm{per}}, \bar{\mu}_R^{\mathrm{per}}) \in \arg\min \Big\{ \mathcal{E}_R^{\mathrm{per}}(u_R,\tau) \ : \ \mathcal{N}_R^{\mathrm{per}}(u_R,\tau) = N_{\mathrm{e},R},\ u_R \in \mathrm{Adm}^{\mathrm{per}}(R) \Big\}. \tag{A.9}$$

We conclude that similar results as Theorem A.1, A.2 and A.3 are true within this framework (see the preprint [12] for more details).

Appendix B Dislocations

We consider a model for straight dislocation lines obtained by projecting a 3D crystal. For a 3D lattice $B\mathbb{Z}^3$ with dislocation direction parallel to e_3 and Burgers vector $\mathsf{b} = (\mathsf{b}_1, \mathsf{b}_2, \mathsf{b}_3) = (\mathsf{b}_1, 0, \mathsf{b}_3)$, we consider displacements $W : B\mathbb{Z}^3 \to \mathbb{R}^3$ that are periodic in the direction of the dislocation direction e_3. Thus, we choose a projected reference lattice $\Lambda := A\mathbb{Z}^2 = \{(\ell_1,\ell_2) \mid \ell = (\ell_1,\ell_2,\ell_3) \in B\mathbb{Z}^3\}$, which is again a Bravais lattice. We can define a macroscopically applied deformation $P \in \mathbb{R}^{2\times 3}$ by $P(\ell_1,\ell_2) = (\ell_1,\ell_2,\ell_3)$.

Let $\hat{x} \in \mathbb{R}^2$ be the position of the dislocation core and $\Gamma := \{x \in \mathbb{R}^2 \mid x_2 = \hat{x}_2,\ x_1 \geq \hat{x}_1\}$ be the "branch cut", with $\hat{x}$ chosen such that $\Gamma \cap \Lambda = \emptyset$. Following [21], we define the far-field predictor u_0 by

$$u_0(x) := u^{\mathrm{lin}}(\xi^{-1}(x)), \tag{B.1}$$

where $u^{\mathrm{lin}} \in C^\infty(\mathbb{R}^2 \setminus \Gamma; \mathbb{R}^d)$ is the continuum linear elasticity solution (see [21] for the details) and

$$\xi(x) = x - \mathsf{b}_{12}\frac{1}{2\pi}\eta\left(\frac{|x-\hat{x}|}{\hat{r}}\right)\arg(x-\hat{x}), \tag{B.2}$$

with $\arg(x)$ denoting the angle in $(0,2\pi)$ between x and $\mathsf{b}_{12} = (\mathsf{b}_1,\mathsf{b}_2) = (\mathsf{b}_1,0)$, and $\eta \in C^\infty(\mathbb{R})$ with $\eta = 0$ in $(-\infty,0]$, $\eta = 1$ in $[1,\infty)$ removes the singularity.

The configuration y is now decomposed into

$$y(\ell) = y_0(\ell) + u(\ell) \qquad \forall\ \ell \in \Lambda,$$

where the predictor $y_0 = Px + u_0$ is constructed in such a way that y_0 jumps across Γ and encodes the presence of the dislocation. One can treat anti-plane models of pure screw dislocations by admitting displacements of the form $u_0 = (0,0,u_{0,3})$ and

$u = (0, 0, u_3)$. Similarly, one can treat the in-plane models of pure edge dislocations by admitting displacements of the form $u_0 = (u_{0,1}, u_{0,2}, 0)$ and $u = (u_1, u_2, 0)$ [21].

There is an ambiguity in the definition of y_0 in that we could have equally placed the jump into the left half-plane $\{x_1 \le \hat{x}_1\}$. The role of ξ in the definition of u_0 is that applying a plastic slip across the plane $\{x_2 = \hat{x}_2\}$ via the definition

$$y^S(x) := \begin{cases} y(\ell), & \ell_2 > \hat{x}_2, \\ y(\ell - \mathsf{b}_{12}) - \mathsf{b}_3 e_3, & \ell_2 < \hat{x}_2 \end{cases}$$

achieves exactly this transfer: it leaves the (3D) configuration invariant, while generating a new predictor $y_0^S \in C^\infty(\Omega_\Gamma)$ where $\Omega_\Gamma = \{x_1 > \hat{x}_1 + \hat{r} + \mathsf{b}_1\}$. Since the map $y \mapsto y^S$ represents a relabelling of the atom indices and an integer shift in the out-of-plane direction, we can apply the isometry and permutation invariance of O_ℓ (see Remark 3.1) to obtain

$$O_\ell(y) = O_{S^*\ell}(y^S), \tag{B.3}$$

where S is the ℓ^2-orthogonal operator with inverse $S^* = S^{-1}$ defined by

$$Su(\ell) := \begin{cases} u(\ell), & \ell_2 > \hat{x}_2, \\ u(\ell - \mathsf{b}_{12}), & \ell_2 < \hat{x}_2 \end{cases} \quad \text{and} \quad S^*u(\ell) := \begin{cases} u(\ell), & \ell_2 > \hat{x}_2, \\ u(\ell + \mathsf{b}_{12}), & \ell_2 < \hat{x}_2. \end{cases}$$

We can translate (B.3) to a statement about u_0 and V_ℓ. Let $S_0 w(x) = w(x), x_2 > \hat{x}_2$ and $S_0 w(x) = w(x - \mathsf{b}_{12}) - \mathsf{b}, x_2 < \hat{x}_2$, then we obtain that $y_0^S = Px + S_0 u_0$ and $S_0 u_0 \in C^\infty(\Omega_\Gamma)$ and $S_0(u_0 + u) = S_0 u_0 + Su$. The permutation invariance (B.3) can now be rewritten as an invariance of $\mathcal{O}_\ell (\equiv \mathcal{O}_\#, \ \forall\ \ell \in \Lambda$ since $\Lambda = A\mathbb{Z}^2)$ under the slip S_0:

$$\mathcal{O}_\#\big(D(u_0 + u)(\ell)\big) = \mathcal{O}_\#\big(\mathsf{e}(\ell) + \mathsf{D}u(\ell)\big) \qquad \forall\ u \in \mathrm{Adm}(\Lambda),\ \ell \in \Lambda \tag{B.4}$$

where

$$\mathsf{e}(\ell) := (\mathsf{e}_\rho(\ell))_{\rho \in \Lambda - \ell} \quad \text{with} \quad \mathsf{e}_\rho(\ell) := \begin{cases} S^* D_\rho S_0 u_0(\ell), & \ell \in \Omega_\Gamma, \\ D_\rho u_0(\ell), & \text{otherwise}, \end{cases} \tag{B.5}$$

and

$$\mathsf{D}u(\ell) := (\mathsf{D}_\rho u(\ell))_{\rho \in \Lambda - \ell} \quad \text{with} \quad \mathsf{D}_\rho u(\ell) := \begin{cases} S^* D_\rho S u(\ell), & \ell \in \Omega_\Gamma, \\ D_\rho u(\ell), & \text{otherwise}. \end{cases} \tag{B.6}$$

The following lemma gives the decay estimate of e (see [13] and [21, Lemma 3.1]).

Lemma B.1. *If the predictor u_0 is defined by* (B.1) *and $\mathsf{e}(\ell)$ is given by* (B.5)*, then there exists a constant C such that*

$$|\mathsf{e}_\sigma(\ell)| \le C|\sigma| \cdot |\ell|^{-1}. \tag{B.7}$$

Similar to (3.9), we can define grand potential difference functional for dislocation

$$\begin{aligned} \mathcal{G}^{\mathrm{d}}(u) &:= \sum_{\ell \in \Lambda} \Big(\mathcal{G}_\#\big(Du_0(\ell) + Du(\ell), \mu_\#\big) - \mathcal{G}_\#\big(Du_0(\ell), \mu_\#\big) \Big) \\ &= \sum_{\ell \in \Lambda} \Big(\mathcal{G}_\#\big(\mathsf{e}(\ell) + \mathsf{D}u(\ell), \mu_\#\big) - \mathcal{G}_\#\big(\mathsf{e}(\ell), \mu_\#\big) \Big), \end{aligned} \tag{B.8}$$

where (B.4) is used. The following two lemmas are analogous to Lemma 3.2 and 5.1 in the case of dislocations. We refer to [13] (see also [21]) for a rigorous proof.

Lemma B.2. *If u_0 is given by* (B.1)*, then $\mathcal{G}^{\rm d}$ is well-defined on* $\mathrm{Adm}(\Lambda)$ *and ν times Fréchet differentiable.*

Lemma B.3. *If $\bar{u} \in \mathrm{Adm}(\Lambda)$ is a strongly stable solution to* (3.10) *with $\mathcal{G} \equiv \mathcal{G}^{\rm d}$ in the sense that* (3.12) *with some constant $\bar{c} > 0$, then there exists a constant $C > 0$ such that*

$$|\mathsf{D}\bar{u}(\ell)|_\gamma \le C(1+|\ell|)^{-2}\log(2+|\ell|) \qquad \forall \ell \in \Lambda. \tag{B.9}$$

We can derive the limit of chemical potential similar to Theorem 3.1.

Theorem B.1. *Let $\Lambda = A\mathbb{Z}^2$, $\Lambda_R := \Lambda \cap B_R \uparrow \Lambda$ and $N_R := \#\Lambda_R$. For each R let $u_R : \Lambda_R \to \mathbb{R}^d$ with $y_R(\ell) := \ell + u_0(\ell) + u_R(\ell)$ a* configuration *with parameter $\mathfrak{m}$ independent of R.*

Let $N_{{\rm e},R} \in \mathbb{R}$ be a prescribed number of electrons in the subsystem Λ_R, chosen such that $|N_R - N_{{\rm e},R}|$ is bounded as $R \to \infty$. Then, the chemical potential μ_R solving $N(y_R, \mu_R) = N_{{\rm e},R}$ is well-defined and satisfies

$$\left|\mu_R - \mu_\#\right| \le CR^{-1}. \tag{B.10}$$

Proof. The proof is similar to that of Theorem 3.1 in § 5.2. It is only necessary to rewrite (5.8) by

$$\begin{aligned}
& N(y_R,\mu_R) - N(y_R,\mu_\#) \\
= \;& N_{{\rm e},R} - N_{\#,R} + \sum_{\ell\in\Lambda_R} \mathcal{N}_\#(\mathbf{0},\mu_\#) - \sum_{\ell\in\Lambda_R} \mathcal{N}_\ell^{\Lambda_R}\big(Du_0(\ell)+Du(\ell),\mu_\#\big) \\
= \;& \big(N_{{\rm e},R} - N_{\#,R}\big) + \sum_{\ell\in\Lambda_R}\Big(\mathcal{N}_\#\big(\mathbf{0},\mu_\#\big) - \mathcal{N}_\ell^{\Lambda_R}(\mathbf{0},\mu_\#)\Big) \\
& \quad + \sum_{\ell\in\Lambda_R}\Big(\mathcal{N}_\ell^{\Lambda_R}(\mathbf{0},\mu_\#) - \mathcal{N}_\ell^{\Lambda_R}\big(\mathsf{e}(\ell)+\mathsf{D}u(\ell),\mu_\#\big)\Big) \\
=: \;& T_1^{\rm d} + T_2^{\rm d} + T_3^{\rm d},
\end{aligned} \tag{B.11}$$

where $T_1^{\rm d}$ is uniformly bounded, $T_2^{\rm d}$ is estimated by $|T_2^{\rm d}| \le CR$ (analogous to (5.9) with $d = 2$), and $T_3^{\rm d}$ is estimated by using Lemma 2.1, B.1 and B.3

$$|T_3^{\rm d}| \le C\sum_{\ell\in\Lambda_R} |\mathsf{e}_\ell + \mathsf{D}u(\ell)|_\gamma \le CR. \tag{B.12}$$

This together with (5.12) completes the proof. □

To justify the thermodynamic limits of dislocations, we define a sequence of finite-domain equilibrium problem for dislocations: Find $(\bar{u}_R, \bar{\mu}_R) \in \mathrm{Adm}(R) \times \mathbb{R}$ such that

$$(\bar{u}_R,\bar{\mu}_R) \in \arg\min\Big\{\mathcal{E}^{\Lambda_R}(u_0+u_R,\tau) \;:\; \mathcal{N}^{\Lambda_R}(u_0+u_R,\tau) = N_{{\rm e},R},\; u_R \in \mathrm{Adm}(R)\Big\}. \tag{B.13}$$

Using the same arguments as those in § 5.3 and § 5.4, we have the following results for dislocations, which are analogous to Theorem 3.2 and 3.3. We refer to the preprint [12] for more details of the proof.

Theorem B.2. *Let $\Lambda = A\mathbb{Z}^2$ and $|N_R - N_{\mathrm{e},R}|$ be bounded as $R \to \infty$. If $\bar{u} \in \mathrm{Adm}(\Lambda)$ is a strongly stable solution of* (3.10) *with $\mathcal{G} \equiv \mathcal{G}^{\mathrm{d}}$ in the sense that* (3.12) *with some constant $\bar{c} > 0$, then there are constants $R_0^{\mathrm{d}}, c_{\mathrm{b}}^{\mathrm{d}} > 0$ such that, for $R > R_0^{\mathrm{d}}$ and $R_{\mathrm{b}} > c_{\mathrm{b}}^{\mathrm{d}} \log R$, there exists a solution $(\bar{u}_R, \bar{\mu}_R)$ of* (B.13) *satisfying*

$$\left\|\mathsf{D}\bar{u} - \mathsf{D}\bar{u}_R\right\|_{\ell^2_\gamma(\Lambda_R)} + \left|\bar{\mu}_R - \mu_\#\right| \leq CR^{-1} \log R. \tag{B.14}$$

Theorem B.3. *Let $\Lambda = A\mathbb{Z}^2$, $R_j \uparrow \infty$ and $(\bar{u}_{R_j}, \bar{\mu}_{R_j})$ be solutions to* (B.13)*, If $|N_{R_j} - N_{\mathrm{e},R_j}|$ is bounded and $\sup_{j>0} \|\mathsf{D}\bar{u}_{R_j}\|_{\ell^2_\gamma(\Lambda_R)} < \infty$, then there exists a subsequence (not relabelled) and $\bar{u} \in \mathrm{Adm}(\Lambda)$ such that*

$$\bar{\mu}_{R_j} \to \mu_\# \quad \text{and} \quad \mathsf{D}_\rho \bar{u}_{R_j}(\ell) \to \mathsf{D}_\rho \bar{u}(\ell) \quad \forall\ \ell \in \Lambda,\ \rho \in \Lambda - \ell \tag{B.15}$$

Moreover, each such accumulation point $\bar{u}$ solves (3.10) *with $\mathcal{G} \equiv \mathcal{G}^{\mathrm{d}}$.*

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