Local Defects in the Thomas-Fermi-von Weiszäcker Theory of Crystals

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Introduction

A crystal is a material with a simple and repetitive nuclear arrangement. In reality, crystals are not perfect, it is common to find imperfections in the nuclear arrangement. The introduction of a local defect disturbs the nuclear arrangement throughout the crystal. Understanding defects is important to gain a deeper insight into the properties of crystals.

My interest is in understanding the re-arrangement of nuclei that is caused by the introduction of a defect into an otherwise perfect crystal. We use the Thomas-Fermi-von Weiszäcker model to associate an energy to each nuclear arrangement. This leads to a variational problem for finding the minimising displacement.

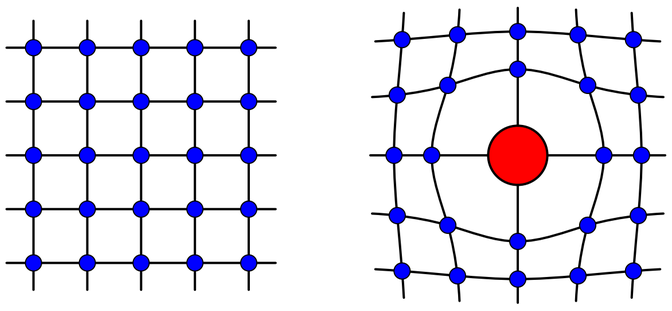


Figure : A 2D sketch of a perfect lattice and a lattice which has been re-arranged due to the presence of a local defect.

The Thomas-Fermi-von Weiszäcker Model

To describe the system, we use $u, \phi, m : \mathbb{R}^3 \to \mathbb{R}$, where

- u - the **root electron density**, $u \geq 0$.
- m - the **nuclear distribution**, $m \geq 0$.
- ϕ - the **Coulomb potential** generated by u and m.

Using these, the **Thomas-Fermi-von Weiszäcker energy** of this system is defined by

$$E^{TFW}(u, \phi, m) = \int_{\mathbb{R}^3} |\nabla u|^2 + \int_{\mathbb{R}^3} u^{10/3} + \frac{1}{2} \int_{\mathbb{R}^3} \phi(m - u^2).$$

The first two terms describe the kinetic energy and the last term describes the Coulomb energy of the system due to the charged particles.

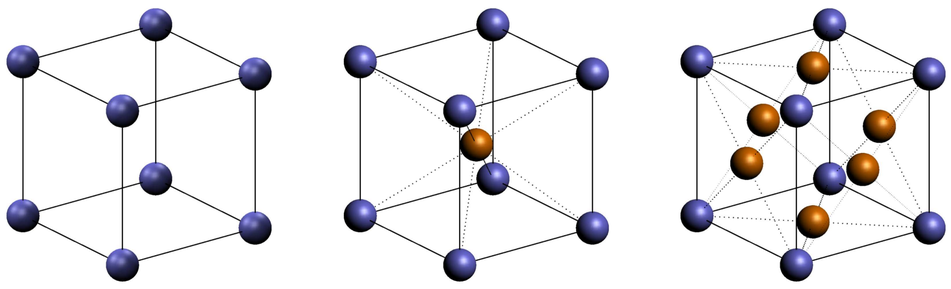
We consider an infinite system, so given a nuclear distribution m, by minimising the energy per unit volume, we obtain a **ground-state** (u, ϕ), which solves

$$-\Delta u + \frac{5}{3} u^{7/3} - \phi u = 0,$$
$$-\Delta \phi = 4\pi(m - u^2).$$

The **existence and uniqueness** of a solution to this system is guaranteed under broad assumptions on m and is shown in [1].

The Periodic System

Let $\Lambda \subset \mathbb{R}^3$ be a Bravais lattice, so $\Lambda = \mathbb{Z}a_1 + \mathbb{Z}a_2 + \mathbb{Z}a_3$, where $a_1, a_2, a_3 \in \mathbb{R}^3$ are linearly independent vectors and $\min_{i=1,2,3} |a_i| = 1$. Below are three examples of Bravais lattices.



Primitive cubic | Body-centered cubic | Face-centered cubic

To define the nuclear distribution, let $0 < \delta < 1/2$ and choose $\eta \in C_c^\infty(B_\delta(0))$ such that η is non-negative, radial and satisfies $\int_{\mathbb{R}^3} \eta(x)\, dx = 1$. This function is used to describe an individual nucleus. Using this, the **periodic nuclear distribution** is defined by

$$m_{per}(x) = \sum_{l \in \Lambda} \eta(x - l).$$

The **periodic ground-state** (u_{per}, ϕ_{per}) is the unique, Λ-periodic solution to

$$-\Delta u_{per} + \frac{5}{3} u_{per}^{7/3} - \phi_{per} u_{per} = 0,$$
$$-\Delta \phi_{per} = 4\pi(m_{per} - u_{per}^2).$$

References

[1] Isabelle Catto, Claude Le Bris, and Pierre-Louis Lions. *The mathematical theory of thermodynamic limits: Thomas-Fermi type models*. Oxford Mathematical Monographs. The Clarendon Press Oxford University Press, New York, 1998. ISBN 0-19-850161-7.

[2] V. Ehrlacher, C. Ortner, and A. V. Shapeev. Analysis of boundary conditions for crystal defect atomistic simulations. *ArXiv e-prints*, 1306.5334, 2013. URL http://arxiv.org/abs/1306.5334v2.

Acknowledgements

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The Defective System

A **local defect** is described by $\rho_{def}^{nuc} \in C_c^\infty(\mathbb{R}^3)$ and could represent an impurity, interstitial or vacancy.

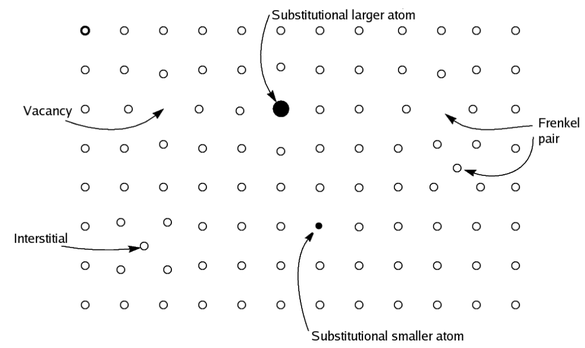

Figure : Examples of local defects in a crystal. Image by Kai Nordlund.

We now define the space of admissible lattice displacements

$$\mathcal{W}^{1,2}(\Lambda) = \left\{ U_\Lambda : \Lambda \to \mathbb{R}^3 \;\middle|\; \left(\sum_{l \in \Lambda} \sum_{i=1}^{3} \frac{|U_\Lambda(l + a_i) - U_\Lambda(l)|^2}{|a_i|^2} \right) < \infty, \lim_{|l| \to \infty} U_\Lambda(l) = 0 \right\}.$$

Given a lattice displacement $U_\Lambda \in \mathcal{W}^{1,2}(\Lambda)$, define a new nuclear distribution by

$$m_{U,def}(x) = \sum_{l \in \Lambda} \eta(x - l - U_\Lambda(l)) + \rho_{def}^{nuc}(x),$$

where we suppose that $m_{U,def} \geq 0$. The corresponding ground-state $(u_{U,def}, \phi_{U,def})$ is the unique distributional solution to

$$-\Delta u_{U,def} + \frac{5}{3} u_{U,def}^{7/3} - \phi_{U,def} u_{U,def} = 0,$$
$$-\Delta \phi_{U,def} = 4\pi(m_{U,def} - u_{U,def}^2).$$

The Energy Difference

We consider the two **energy differences**

$$\mathcal{E}(U_\Lambda) = E^{TFW}(u_U, \phi_U; m_U) - E^{TFW}(u_{per}, \phi_{per}; m_{per}),$$
$$\mathcal{E}^{def}(U_\Lambda) = E^{TFW}(u_{U,def}, \phi_{U,def}; m_{U,def}) - E^{TFW}(u_{per}, \phi_{per}; m_{per}).$$

Provided $\mathcal{E}^{def}(U_\Lambda)$ is well-defined for each $U_\Lambda \in \mathcal{W}^{1,2}(\Lambda)$, define

$$\mathcal{I}^{def} = \inf\{ \mathcal{E}^{def}(U_\Lambda) \mid U_\Lambda \in \mathcal{W}^{1,2}(\Lambda) \}.$$

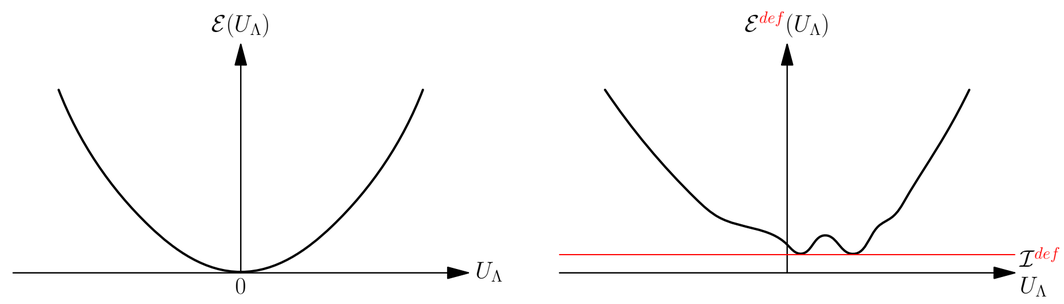

Figure : A sketch of the energy difference without a defect, and the difference with a defect.

The main tool for studying both energy minimisation problems is the following result.

Exponentially-weighted Estimates

Suppose $R_1, R_2 \in C^k(\mathbb{R}^3) \cap W^{k,\infty}(\mathbb{R}^3)$ for some $k \in \mathbb{N}$. Suppose further that $\inf u_1 > 0, \inf u_2 > 0$, $u_1, u_2, \phi_1, \phi_2 \in C^{k+2}(\mathbb{R}^3) \cap W^{k+2,\infty}(\mathbb{R}^3)$ and that $(u_1 - u_2, \phi_1 - \phi_2)$ solve the following system

$$-\Delta(u_1 - u_2) = \frac{5}{3}\left(u_2^{7/3} - u_1^{7/3}\right) + \phi_1 u_1 - \phi_2 u_2 + R_1,$$
$$-\Delta(\phi_1 - \phi_2) = 4\pi\left(u_2^2 - u_1^2\right) + R_2.$$

Then there exists $C_k, \widetilde{\gamma}_k > 0$ such that for all $0 \leq \gamma \leq \widetilde{\gamma}_k$ and $\widetilde{x} \in \mathbb{R}^3$

$$\sum_{|\alpha| \leq k+2} \int_{\mathbb{R}^3} \left(|\partial^\alpha (u_1 - u_2)(x)|^2 + |\partial^\alpha (\phi_1 - \phi_2)(x)|^2 \right) e^{-2\gamma|x - \widetilde{x}|} dx$$
$$\leq C_k \sum_{|\beta| \leq k} \int_{\mathbb{R}^3} \left(|\partial^\beta R_1(x)|^2 + |\partial^\beta R_2(x)|^2 \right) e^{-2\gamma|x - \widetilde{x}|} dx.$$

If in addition, $G_1, G_2 \in H^k(\mathbb{R}^3)$, choosing $\gamma = 0$ gives

$$\|u_1 - u_2\|_{H^{k+2}(\mathbb{R}^3)} + \|\phi_1 - \phi_2\|_{H^{k+2}(\mathbb{R}^3)} \leq C_k' \left(\|G_1\|_{H^k(\mathbb{R}^3)} + \|G_2\|_{H^k(\mathbb{R}^3)} \right).$$

In short, a small perturbation of m causes an exponentially decaying response in u, ϕ.

Applications

This exponential estimate is vital in investigating the properties of $\mathcal{E}^{def}$, such as its regularity as a functional. With Taylor's theorem in mind, we can express $\mathcal{E}^{def}$ in terms of it's derivatives, so we have for $U_\Lambda \in \mathcal{W}^{1,2}(\Lambda)$

$$\mathcal{E}^{def}(U_\Lambda) = \langle \delta\mathcal{E}^{def}(0), U_\Lambda \rangle + \int_0^1 (1 - t) \langle \delta^2 \mathcal{E}^{def}(tU_\Lambda) U_\Lambda, U_\Lambda \rangle \, dt.$$

We can study $\mathcal{E}^{def}$ by investigating the right-hand side of the above equation.

Conclusion

Using the results that we have shown, we aim to show that the energy minimisation problem with a defect is well-defined. Further to this, we wish to understand the decay properties of a minimising displacement.