Locality of the Thomas-Fermi-von Weizsäcker Equations

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Introduction

A crystal is a material with a simple, periodic nuclear arrangement. In reality, **crystals are imperfect**. One broad class of imperfections are called **local defects**, such as vacancies, impurities and interstitial atoms and arise naturally in crystals.

My interest is in understanding the rearrangement of nuclei due to the presence of a local defect in an otherwise perfect crystal. We use the **Thomas-Fermi-von Weizsäcker (TFW)** model to associate an energy to each nuclear arrangement. This leads to a **variational problem** for finding the minimising displacement. The challenge of the TFW model is mainly due to the **long-range Coulomb interaction** of the nuclei and electrons.

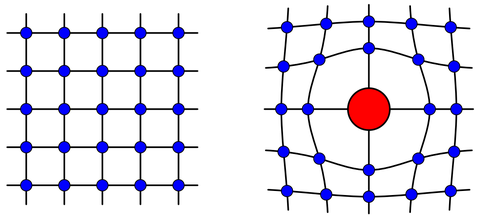

Figure : A 2D sketch of a perfect lattice and a lattice which has been rearranged due to the presence of a local defect.

Our main results involve showing **pointwise stability estimates** for a broad class of nuclear distributions. It follows that the TFW model possesses both **locality and neutrality** properties, that local defects are neutral in the TFW model. In addition, using a **renormalisation** procedure, we show that the energy minimisation problem is well-defined.

The Thomas-Fermi-von Weizsäcker Model

To describe the **three-dimensional** system, we define $u, \phi, m : \mathbb{R}^3 \to \mathbb{R}$

- u - the **root electron density**, $u \geq 0$.
- m - the **nuclear distribution**, $m \geq 0$.
- ϕ - the **Coulomb potential** generated by u and m, solving $-\Delta\phi = 4\pi(m - u^2)$.

Using these, the **Thomas-Fermi-von Weizsäcker energy** of the 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 third 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 a **thermodynamic limit** argument, we obtain a **ground-state** (u, ϕ) solving

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

and in addition that $\inf u > 0$. The **existence and uniqueness** of a solution to this system is guaranteed under broad assumptions on m and is shown in [1].

Uniform Regularity Estimates

Let $\omega : \mathbb{R} \to \mathbb{R}_{\geq 0}$ satisfy $\lim_{R\to\infty} \omega(R) = +\infty$, then define the **class of nuclear distributions**

$$\mathcal{M}(M, \omega) = \left\{ m : \mathbb{R}^3 \to \mathbb{R}_{\geq 0} \;\middle|\; \|m\|_{L^\infty(\mathbb{R}^3)} \leq M,\ \forall R > 0 \ \inf_{x\in\mathbb{R}^3} \int_{B_R(x)} m(z)\, \mathrm{d}z \geq \omega(R)R \right\}.$$

Adapting the **existence** argument of [1] yields

Lemma

For $m \in \mathcal{M}(M, \omega)$, the ground-state (u, ϕ) satisfies

$$\|u\|_{W^{3,\infty}(\mathbb{R}^3)} \leq C(1 + M^{13/4}), \quad \|\phi\|_{W^{1,\infty}(\mathbb{R}^3)} \leq C(1 + M^{3/2}), \quad \inf_{x\in\mathbb{R}^3} u(x) \geq c_{M,\omega} > 0.$$

Pointwise Stability Estimates

Adapting the **uniqueness** argument of [1] leads to the **stability** result

Theorem

Let $m_1, m_2 \in \mathcal{M}(M, \omega)$, then the corresponding ground states $(u_1, \phi_1), (u_2, \phi_2)$ satisfy

$$|(u_1 - u_2)(y)| + |(\phi_1 - \phi_2)(y)| \leq C\left(\int_{\mathbb{R}^3} |(m_1 - m_2)(x)|^2 e^{-2\gamma|x-y|}\, \mathrm{d}x\right)^{1/2}$$

This has several immediate consequences

Corollary

Let $m_1, m_2 \in \mathcal{M}(M, \omega)$.

- (Local estimates) Suppose $m_1 - m_2$ has support in $B_R(0)$. Then
$$|(u_1 - u_2)(y)| + |(\phi_1 - \phi_2)(y)| \leq C_R\, e^{-\gamma|y|}.$$
- (Decay estimates) Suppose that
$$|(m_1 - m_2)(x)| \leq C(1 + |x|)^{-r},$$
for some $r > 0$, then
$$|(u_1 - u_2)(y)| + |(\phi_1 - \phi_2)(y)| \leq C_r(1 + |y|)^{-r}.$$
- (Global estimates) Suppose $m_1 - m_2 \in L^2(\mathbb{R}^3)$, then
$$\|u_1 - u_2\|_{H^4(\mathbb{R}^3)} + \|\phi_1 - \phi_2\|_{H^2(\mathbb{R}^3)} \leq C\|m_1 - m_2\|_{L^2(\mathbb{R}^3)}.$$

Lemma - Neutrality of Local Defects

Let $m_1, m_2 \in \mathcal{M}(M, \omega)$ and suppose that $m_1 - m_2$ has support in $B_{R'}(0)$, then

$$\left| \int_{B_R(0)} (m_1 - u_1^2 - m_2 + u_2^2) \right| \leq Ce^{-\gamma R}.$$

It follows that local defects are neutral in TFW and the excess charge decays exponentially away from the defect.

The Defective System

The **perfect crystal** is given by $\Lambda = \mathbb{Z}^3$ and $\eta \in C_c^\infty(\mathbb{R}^3), \eta \geq 0$, a function which represents an individual nucleus in the arrangement. A **local defect** is described by $\rho_{def}^{nuc} \in C_c^\infty(\mathbb{R}^3)$

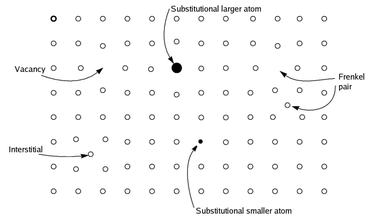

Figure : Examples of local defects in a crystal. Image by Kai Nordlund.

We now define the space of **lattice displacements**

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

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

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

The Minimisation Problem

We consider the two **energy difference functionals**

$$\mathcal{E}(V_\Lambda) = E^{TFW}(u_V, \phi_V; m_V) - E^{TFW}(u_{per}, \phi_{per}; m_{per}),$$
$$\mathcal{E}^{def}(V_\Lambda) = E^{TFW}(u_{V,def}, \phi_{V,def}; m_{V,def}) - E^{TFW}(u_{per}, \phi_{per}; m_{per}).$$

If $\mathcal{E}^{def}(V_\Lambda)$ is well-defined for each $V_\Lambda \in \mathcal{W}^{1,2}(\Lambda)$ and is bounded below, we may define

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

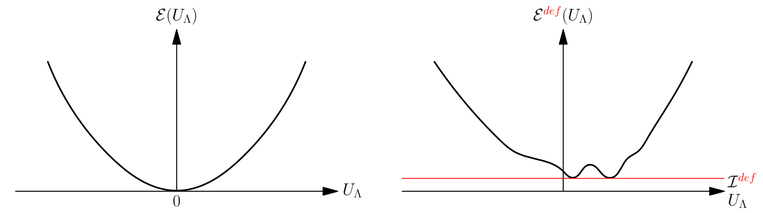

Figure : A sketch of the energy difference without a defect, and the difference with a defect.

The challenge is to show that the functionals $\mathcal{E}, \mathcal{E}^{def}$ are well-defined on $\mathcal{W}^{1,2}(\Lambda)$, as they are the difference of **infinite energies!** If we can show this, by [2], we then obtain **decay results for minimising displacements** of $\mathcal{I}^{def}$.

Renormalisation

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 for $V_\Lambda \in \mathcal{W}^{1,2}(\Lambda)$

$$\mathcal{E}^{def}(V_\Lambda) = \left[\mathcal{E}^{def}(V_\Lambda) - \mathcal{E}^{def}(0) - \langle \delta\mathcal{E}^{def}(0), V_\Lambda\rangle\right] + \langle \delta\mathcal{E}^{def}(0), V_\Lambda\rangle.$$

The bracketed term corresponds to the Hessian of the functional, whereas the final term corresponds to the forcing of acting on the displaced nuclear configuration.

There are two techniques for controlling the right-hand side to show $\mathcal{E}^{def}$ **is well-defined**.

- Decompose the energy functionals into **site energies** by partitioning space into regions corresponding to an individual nucleus.
- Use a **change of variables** argument, apply a **deformation** mapping the reference configuration to the displaced configuration, allowing us to compare the two systems using **predictor variables**.

Outlook

- Dislocations.
- Numerical Simulations.
- More advanced electronic structure models - Hartree-Fock, Kohn-Sham.

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.

Acknowledgements

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