Order in atomistic systems and the Read Shockley law

Florian Theil & Anvar Atayev (Warwick, UK) jointly with Alessandro Giuliani (Roma Tre),

Rome, February 2023

Outline

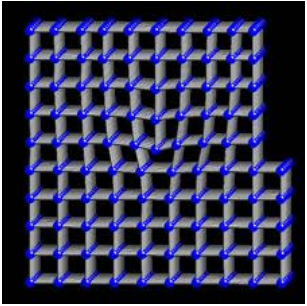
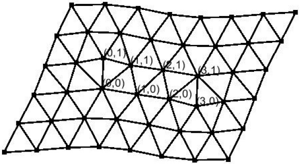
Introduction

- Models from Materials Sciences typically involve several scales
- Many phenomena and many models
- Phenomena are universal

Dislocations

Dislocations are

- point-like defects if $d = 2$,
- loop-like defects if $d = 3$

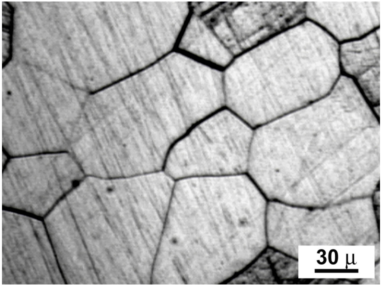




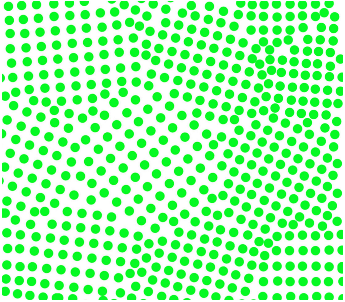
- Dislocations are characterized by the **Burgers vector**, the defect of closed paths.
- Dislocations are topological defects, they cannot be created or destroyed by moving a finite number of particles within an infinite configuration.

Importance of dislocations

Dislocations are the microscopic explanation of *plastic behaviour* (not relevant for this talk)

Grain boundaries in polycrystals can be interpreted as dislocations (relevant for this talk).





Motivation for the Ariza-Oritz model

- Natural representation of dislocations, grains and temperature
- Mathematical structure simple enough to allow rigorous analysis
- Could lead to quantitative explanation of scars (below).

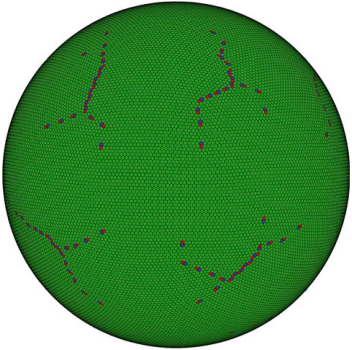


Fig. 6.1 (Bordachev-Hardin-Saff, p 296) Scar configuration

The Ariza-Ortiz model

Reference configuration: Triangular ($d = 2$) or fcc ($d = 3$) lattice

$$\mathcal{L} = \{n_1 b_1 + \ldots + n_d b_d \ : \ n \in \mathbb{Z}^d\}$$

where b_i are the basis vectors.

Nearest neighbors: $x \sim y$ if $x, y \in \mathcal{L}$ and $|x - y| = 1$,

Displacement: $u(x) \in \mathbb{R}^d, \ x \in \mathcal{L}$,

Slip: $\sigma(x, y), \ x \sim y$,

Energy:

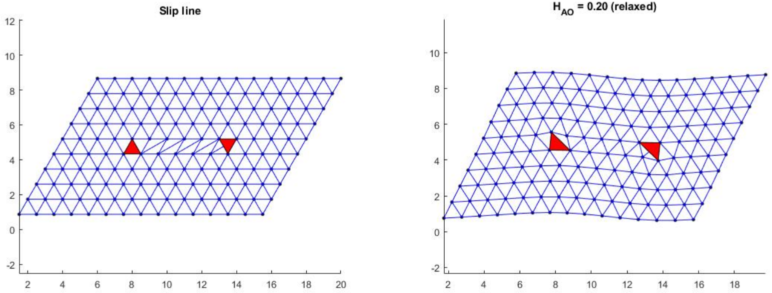
$$H_{\mathrm{AO}}(u, \sigma) = \frac{1}{2} \sum_{x \sim y} [(u(y) - u(x) - \sigma(x, y)) \cdot (y - x)]^2.$$

Invariance wrt linearized rotation: $H_{\mathrm{AO}}(u + \varphi, \sigma) = H_{\mathrm{AO}}(u, \sigma)$ if $\varphi(x) = Sx$ and $S \in \mathbb{R}^{d \times d}_{\mathrm{skew}}$, ie. $S^* = -S$.

Point particle configurations

$$\mathcal{C} = \{x + u(x) \ : \ x \in \mathcal{L}\}$$

Example: Dislocation dipole



Left: Unrelaxed dislocation dipole. Right: Relaxed dipole.
$\sigma(x, x') = (1, 0)$ if (x, x') is a non-horizontal nearest neighbor pair between the dislocations and 0 else,

Random dislocation configurations

- Recall gauge invariance

$$H_{\mathrm{AO}}(u+v, \sigma + \mathrm{d}v) = H_{\mathrm{AO}}(u, \sigma) \text{ for all } v : \mathcal{L} \to \mathcal{L}.$$

- Slips σ and σ' are gauge equivalent if $\sigma - \sigma' = \mathrm{d}v$ for some v.
- $\mathcal{S}$ are representatives of non-equivalent slip fields.
- Boltzmann-Gibbs distribution

$$\mathbb{P}_\beta(u, \sigma) = \frac{1}{Z(\beta)} \exp(-\beta\,(H_{\mathrm{AO}}(u, \sigma) + w(\mathrm{d}\sigma)))$$

- Partition sum

$$Z(\beta) = \sum_{\sigma \in \mathcal{S}} \exp(-\beta\, w(\mathrm{d}\sigma)) \int \exp(-\beta\, H_{\mathrm{AO}}(u, \sigma))\,\mathrm{d}u.$$

- Exterior derivative

$$\mathrm{d}\sigma(x, y, z) = \sigma(x, y) + \sigma(y, z) + \sigma(z, x).$$

Long-range order and orientational order

Mermin-Wagner Theorem: Long-range order in 3 dimensions, orientational order in two dimensions.

Orientational order is weaker than LRO.

- Long-range order means that *positions* are ordered. Observables that can measure LRO:

$$c_\beta(v_0; x, y) = \mathbb{E}_\beta(\cos([u(y) - u(x)] \cdot v_0)).$$

- Orienational order means that angles are ordered. Observables that can measure OO:

$$c_\beta(v_0, h; x, y) = \mathbb{E}_\beta(\cos([u(x+h) - u(x) - u(y+h) + u(y)] \cdot v_0)).$$

Existence of order at low temperatures

Theorem

There are positive constants C, β_0 *such that*

$$c_\beta(x, y; v_0) \geq e^{-C/\beta}\Big(1 + O\big(\tfrac{\log|x-y|}{|x-y|}\big)\Big), \qquad |x-y| \gg 1$$

if $v_0 \in \mathcal{L}^*$ *and* $\beta > \beta_0$.

The corresponding result in two dimensions is *much* harder and only conjectured.

Previous work

- Fröhlich and Spencer (CMP 1982) obtained similar results for the rotator models in three dimensions.
- In the two dimensional case (Fröhlich-Spencer 1981) only orientational order is present. It is the first rigorous mathematical treatment of the Kosterlitz-Thouless transition (Nobel prize 2016).

The key difference between earlier results by Fröhlich and Spencer and the current results is the invariance with respect to linearized rotations.

Decompose energy into elastic and dislocation energy

Recall

$$H_{\mathrm{AO}}(u,\sigma) = \frac{1}{2}\langle \mathrm{d}u - \sigma, B(\mathrm{d}u - \sigma)\rangle.$$

Let $q \in \Omega_2^*$ be the Burgers field such that $\mathrm{d}q = 0$ and

$$\sigma_{\boldsymbol{q}} = \mathrm{argmin}\{H(0,\sigma) \ : \ \mathrm{d}\sigma = q\}, \quad u_{\boldsymbol{q}} = \mathrm{argmin}_{\boldsymbol{u}} H(u, \sigma_{\boldsymbol{q}}),$$

then

$$H_{\mathrm{AO}}(u,\sigma) = H_{\mathrm{AO}}(u - u_{\boldsymbol{q}}, 0) + H_{\mathrm{AO}}(0, \sigma_{\boldsymbol{q}}).$$

Hence $\mathbb{P}_\beta$ is a product distribution:

$$\mathbb{P}_\beta(u,\sigma) = \frac{\exp(-\beta\, H(u - u_{\boldsymbol{q}}, 0))}{Z_{\mathrm{el}}(\beta)} \times \frac{\exp(-\beta\,(H(0,\sigma_{\boldsymbol{q}}) + w(\mathrm{d}\sigma)))}{Z_{\mathrm{disl}}(\beta)}.$$

Elastic fluctuations (spin waves)

Recall

$$c = \mathbb{E}_\beta(\exp(i\langle u, g\rangle))$$

for some $g \in \Omega_0$.
Choose $\mathrm{d}^* h = g$, then

$$\begin{aligned}\mathbb{E}_\beta(\exp(i\langle u, g\rangle)) &= \mathbb{E}_\beta(\exp(i\langle u, \mathrm{d}^* h\rangle)) = \mathbb{E}_\beta(\exp(i\langle \mathrm{d}u, h\rangle)) \\ &= \mathbb{E}_\beta(\exp(i\langle u - u_q, g\rangle)) \times \mathbb{E}_\beta(\exp(-i\langle \sigma_q, h\rangle)\end{aligned}$$

Fourier coefficient of a continuous and a discrete Gaussian measure.
Recall:

$$\int \exp(-\langle x, Ax\rangle) \cos(\langle k, x\rangle)\, \mathrm{d}x = \left(\frac{\pi}{|A|}\right)^{\frac{1}{2}} \exp(-\pi^2\langle k, A^{-1}k\rangle).$$

In our setting: A^{-1} is the Green's function. In three dimensions $A^{-1}(x, y) = O(|x - y|^{-1})$.

Dislocation fluctuations (vortex waves)

Cut a a long story short

The field σ_q satisfies

$$\begin{aligned} \mathrm{d}^* B\sigma_q &= 0, \\ \mathrm{d}\sigma_q &= q \end{aligned}$$

Continuum analogue:

$$\begin{aligned} \nabla \cdot (\sigma + \sigma^T) &= 0, \\ \mathrm{curl}\,\sigma &= q \end{aligned}$$

- Hodge decomposition: $\sigma = \mathrm{d}u + \mathrm{d}^* V, \quad (\sigma = \nabla u + \mathrm{curl}\ V)$.
- $V = \mathrm{d}\Delta^{-1} q$
- $H_{\mathrm{AO}}(0, \sigma_q) = \frac{1}{2}\langle Gq, BGq \rangle$ with $G = (1 - \mathrm{d}A^{-1}\mathrm{d}^* B)\mathrm{d}^*\Delta^{-1}$.

Need that

$$A^{-1}\mathrm{d}^* B^2 \mathrm{d}A^{-1}(x, x') = o(1), \quad |x - x'| \gg 1,$$

this holds if $A^{-1} = O(|x|^{-1})$

Cluster expansion

We are interested in $\frac{Z_\beta(h)}{Z_\beta(0)}$ with

$$Z_\beta(h) = \sum_{\mathrm{d}_2 q = 0} \exp(i\langle \sigma_q, h\rangle) \exp(-\beta(w(q) + H_{\mathrm{AO}}(0, \sigma_q))) = \sum_{\mathrm{d}_2 q = 0} K(q, h).$$

The dislocation configuration q can be decomposed into disjoint loops:

$$K(q, h) = \prod_{j=1}^{n} K(q_j, h).$$

Thus

$$Z_\beta(h) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{q_1, \dots, q_n} \prod_{j=1}^{n} K(q_j, h).$$

Now estimate the individual terms!

Low energy structures: Grains (Ariza-Ortiz perspective)

Definition

(u, σ) supports a 'perfect grain' $\mathcal{G} \subset \mathcal{L}$ with orientation $S \in \mathbb{R}^{3\times 3}_{\mathrm{skew}}$

$$u(x) - u(y) - \sigma(x,y) = \begin{cases} S(x-y) & \text{if } \{x,y\} \subset \mathcal{G}, \\ 0 & \text{if } \{x,y\} \subset \mathcal{G}^c, \end{cases}$$

$$\sigma(x,y) = 0 \text{ if } x \sim y \text{ and } \{x,y\} \subset \mathcal{G}^c.$$

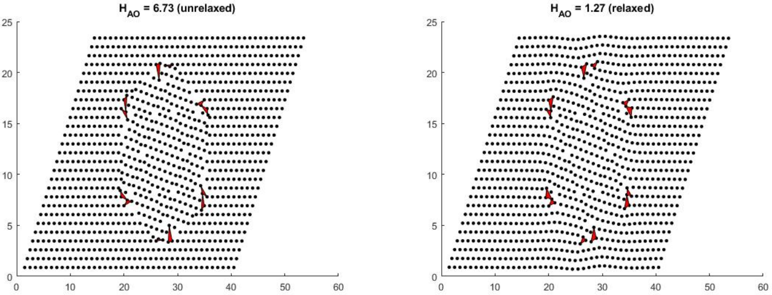
Energy cost of a grain is **not** automatically proportional to **volume** of grain thanks to the invariance under linearized rotations.

Theorem (Upper bound)

$$\min\{H(u,\sigma) \ : \ (u,\sigma) \textit{ support perfect grain } \mathcal{G} \textit{ with orientation } S\} = O(|\partial\mathcal{G}|).$$

The minimum energy is bounded by the size of the grain **boundary**.

Visualization



Left: Displacement u with $S = \frac{1}{5}\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$.

Right: Relaxed displacement field u_σ which minimizes $H_{\mathrm{AO}}(\cdot, \sigma)$ subject to Neumann boundary conditions.

Colored triangles indicate the support of $\mathrm{d}\sigma$.

The Read-Shockley law

The energy density (per unit length/aera) γ of a low-angle boundaries depends on the degree of misorientation θ between the neighbouring grains. Read-Shockley law

$$\gamma_{\mathrm{RS}}(\theta) = (c_0 - c_1 \log \theta)\, \theta,$$

where c_0 is proportional to the core-energy of a single dislocation and $c_1 \sim (1-\nu)G$ (ν is the Poisson ratio, G is the shear modulus).

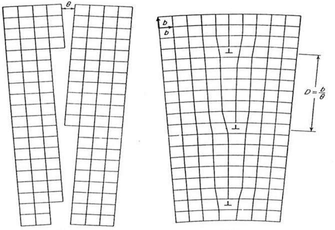
Note: $\gamma_{\mathrm{RS}}(\cdot)$ is strictly concave on [0,1].

Significance: Dislocation structures exhibit concentrations

$$2\gamma_{\mathrm{RS}}(\theta/2) - \gamma_{\mathrm{RS}}(\theta) = \log 2\, c_1\, \theta > 0$$

Low angle grain boundaries

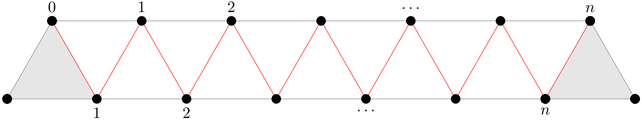
Grain boundaries can be seen as walls of edge dislocations with the same Burgers vector.



Dislocation dipoles

$$q^n_{\mathrm{dip}} \quad = \quad (\mathbf{1}_{f_0} - \mathbf{1}_{f_n})\, b_1 \tag{1}$$

with $b_1 = \binom{1}{0}$, $b_3 = -\frac{1}{2}\binom{1}{\sqrt{3}}$ and $f_n = (0, b_1, -b_3) + nb_1$.



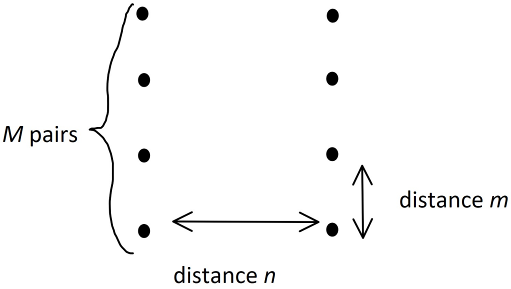
Shaded triangles, corresponding to faces f_0 and f_n, indicate the support of q^n_{dip}. In red: the support of a slip field σ^n_{dip} such that $\mathrm{d}\sigma^n_{\mathrm{dip}} = q^n_{\mathrm{dip}}$.

Exterior calculus notation:

$$\begin{aligned} \mathrm{d}u(x,y) &= u(x) - u(y), \\ \mathrm{d}\sigma(x,y,z) &= \sigma(x,y) + \sigma(y,z) + \sigma(z,x). \end{aligned}$$

Dislocation wall

$$q_{\mathrm{grain}}^{M,n,m}(f) = \sum_{j=1}^{M} q_{\mathrm{dip}}^{n}(f - jm(b_2 - b_3)).$$



Number of dislocation pairs: M

Distance between dislocation cores with same (different) signs: m (n).

The Read-Shockley law IV

Theorem

$$E_{\mathrm{dip}}(n) = \min\left\{H_{AO}(u,\sigma)\ :\ \mathrm{d}\sigma = q^n_{\mathrm{dip}}\right\} = \frac{\log n}{2\pi\sqrt{3}} + O(1), \quad n \gg 1,$$

$$\begin{aligned} E_{\mathrm{grain}}(n,m) &= \lim_{M\to\infty} \frac{1}{\sqrt{3}mM} \min\left\{H_{\mathrm{AO}}(u,\sigma)\ :\ \mathrm{d}\sigma = q^{M,n,m}_{\mathrm{grain}}\right\} \\ &= \frac{\log m}{6\pi m} + O(1/m), \quad m \gg 1. \end{aligned}$$

Energy of dipole grows **logarithmically** with distance. Energy of wall is **proportional** to length of wall and **independent** of distance.

Read-Shockley law: $\gamma(\theta) = (c_0 - c_1 \log\theta)\theta + o(\theta), \quad 0 < \theta = \frac{1}{m} \ll 1,$
γ_s is the grain boundary energy density θ is the orientation difference.

Capacitor law

Compare with version of energy **not** invariant under linearized rotations.

$$\mathcal{E}[q] = \frac{1}{2} \min_{(u,\sigma)} \left\{ |\mathrm{d}u - \sigma|^2 \ : \ \mathrm{d}\sigma = q \right\} = \frac{1}{2} \min_{v} \left\{ |v|^2 \ : \ \mathrm{d}v = q \right\},$$

Theorem

$$\begin{aligned} \mathcal{E}[q^n_{\mathrm{dip}}] &= \frac{\sqrt{3}}{2\pi} \log n + O(1), \qquad n \gg 1, \\ \lim_{M\to\infty} \frac{1}{M} \mathcal{E}[q^{M,n,m}_{\mathrm{grain}}] &= \frac{n}{2m} + O(1), \qquad n \gg 1. \end{aligned}$$

- Recall from Physics: Energy of two capacitor plates is **proportional** to the distance.
- Invariance under linearized rotations affects scaling of energy minima significantly.

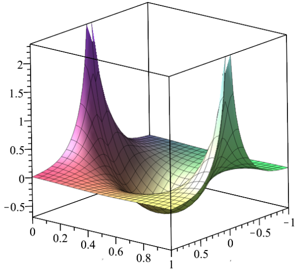
Towards a rigorous proof of the Read-Shockley law

Recall RS-law: $\gamma(\theta) = -c\theta \log \theta + O(\theta)$, $0 < \theta \ll 1$.
Can use continuum setting: $\omega = \{x_1, x_2, \dots x_N\} \subset \mathbb{R} \times \mathbb{T}$:

$$E(\omega) = -\frac{\log \theta}{\theta} + \frac{\theta}{N}\left(N \log N + \sum_{i<j} F(x_i - x_j)\right),$$

where

$$F_{\mathrm{cont}}(x) = \frac{x_1 \sinh(x_1)}{\cosh(x_1) - \cos(x_2)} - \log(\cosh(x_1) - cos(x_1)) - \log 2$$



Conclusions and Outlook

Reference: Giuliani-T JEMS 24 (2022), 3505–3555.

- First rigorous, quantitative result on equilibrium dislocation configurations
- Results due to a complete decoupling between dislocations and elastic field

Outlook

- Two dimensions (orientational order, hexatic phases)
- Non-Euclidean version, e.g. on spheres etc.
- Modelling of scar behaviour.