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Crystallization in Block Copolymer Melts with a Dominant Phase

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Abstract

In this paper we derive a new model for diblock copolymer melts with a dominant phase that is simple enough to be amenable not only to numerics but also to analysis, yet sophisticated enough to reproduce the hexagonally packed cylinder patterns observed in experiments.

Starting from a sharp-interface continuum model, a nonlocal energy functional involving a Wasserstein cost, we derive the new model using Gamma-convergence in a limit where the volume fraction of one phase tends to zero. The limit energy is defined on atomic measures; in three dimensions the atoms represent small spherical blobs of the minority phase, in two dimensions they represent thin cylinders of the minority phase.

We then study minimisers of the limit energy. Numerical minimisation is performed in two dimensions by recasting the problem as a computational geometry problem involving power diagrams. The numerical results suggest that the small particles of the minority phase tend to arrange themselves on a triangular lattice as the number of particles goes to infinity. This is proved in the companion paper [BPT] and agrees with patterns observed in experiments. This is a rare example of a nonlocal energy-driven pattern formation problem in two dimensions where it can be proved that the optimal pattern is periodic, and the first time it has been proved that minimisers of a diblock copolymer energy are periodic.
1 Introduction

Block copolymers are a famous example of a pattern-forming system and even appear in the popular science literature [Bal09]. A diblock copolymer molecule consists of a polymer chain of type A bonded covalently to another polymer chain of type B. Due to a repulsive force between the A and B chains, in diblock copolymer melts the phases separate at the microscale to produce a wide variety of patterns including lamellae, cylinders, gyroids, and spheres. See Figure 1.

Figure 1: Some examples of three-dimensional patterns arising in models of block-copolymer melts. These figures have been obtained in [CPW09] by numerical minimisation of the Ohta-Kawasaki energy functional, a functional that is closely related to the models of this paper.

This spontaneous pattern formation occurs because the A and B blocks repel each other and so try to arrange themselves to be as far away from each other as possible under the constraint that each A block is bonded covalently to a B block. Apart from being beautiful examples of a pattern forming system, block copolymers have the potential to be used as microscale structuring agents to develop new materials with prescribed macroscale properties [BF99].

In this paper we derive a new, idealised model for diblock copolymers. The model is applicable in the parameter regime where one phase has a large volume fraction and where the repulsive force between the A- and the B- blocks is large. The starting point in the derivation is the following sharp-interface continuum model.

The starting point: a sharp-interface continuum model. Let $\Omega$ be the domain occupied by the diblock copolymer melt, which we take to be an open, connected and bounded subset of $\mathbb{R}^d$, $d \geq 2$. Let $u \in BV(\Omega; \{0,1\})$ be a phase indicator, where the support of $u$ represents the region occupied by the A-blocks, and the support of $1-u$ represents the region occupied by the B-blocks. Let $m \in (0,1)$ be the mass fraction of A:

$$m = \frac{1}{|\Omega|} \int_{\Omega} u(x) \, dx.$$ 

This represents the average volume of the A-blocks compared to the B-blocks. We assume that $u = 0$ on $\partial \Omega$, implying that the boundary prefers to be in contact with the B phase. Let $p \in [1, \infty)$. We assign the following energy to $u$:

$$E_{p,m}(u) = m^{\frac{1-d}{d}} \int_{\Omega} |\nabla u| + W_p \left( \frac{1-u}{1-m}, \frac{u}{m} \right)$$ 

where $W_p$ is the $p$-Wasserstein transport cost, which is defined as follows:

$$W_p(\mu,\nu) = \inf \left\{ \int_\Omega |x - T(x)|^p \, d\mu : T : \Omega \to \Omega, T_\# \mu = \nu \right\}$$
for measures $\mu$, $\nu$ such that $\mu(\Omega) = \nu(\Omega) = |\Omega|$ and $\mu$ is absolutely continuous with respect to the Lebesgue measure. Note that $W_p$ is the $p$-th power of the $p$-Wasserstein metric. See, e.g., [Vil03].

An energy of the form (1.1) was derived in [PV10], starting from a kinetic model. The covalent bond between the A- and B-blocks was modelled as a spring, where $p = 2$ corresponds to a linear spring model. The repulsive force between the A- and B-blocks was modelled with a general repulsive potential. Taking an appropriate $\Gamma$-limit of the kinetic model leads to (1.1). The first term of $E$ in (1.1) comes from the repulsive potential and prefers phase separation (since it penalises the perimeter of the support of $u$), while the second term models the covalent bonds and prefers phase mixing. The competition between the two terms determines the pattern.

We will consider the limit $m \to 0$, i.e., the limit in which phase A has vanishing volume fraction. The energy (1.1) is scaled in such a way that we see $O(1)$ particles of A in the limit. Note that (1.1) is non-dimensionalised, in the sense that the physical parameters do not appear explicitly, such as the Flory-Huggins interaction parameter $\chi$ (the repulsion strength between the A- and B-blocks) and the index of polymerization $N$. The scaling regime we consider, however, corresponds to sending $\chi N$ to infinity at the same time as sending the volume fraction of A to zero; see [CPW09, CP11] for a discussion of this limit for the related Ohta-Kawasaki functional.

It is convenient to rewrite the energy in the following way: Define $v := \frac{n}{m}$, $n := \frac{1}{m}$, and $F_{p,n}(v) := E_{p,1/n}(v/n)$ so that

\[
F_{p,n}(v) = \begin{cases} 
\frac{n^{1/d}}{\Omega} \int |\nabla v| + W_p \left( \frac{n - v}{n - 1}, v \right) & \text{if } v \in K_n, \\
+\infty & \text{otherwise},
\end{cases} \tag{1.2}
\]

where

\[
K_n := \left\{ v \in BV(\Omega; \{0, n\}) : \frac{1}{|\Omega|} \int_{\Omega} v(x) \, dx = 1, \quad v = 0 \text{ on } \partial \Omega \right\}. \tag{1.3}
\]

This energy is the starting point for our analysis.

**The new model.** By taking the $\Gamma$-limit of $F_{p,n}$ as $n \to \infty$ we obtain the following model. Recall that sending $n \to \infty$ corresponds to sending the volume fraction of phase A to zero, in which case phase A can be represented by a measure of the form

\[
\nu = \sum_{i=1}^{M} m_i \delta_{x_i} \quad \text{with} \quad \sum_{i=1}^{M} m_i = |\Omega|.
\]

In three dimensions the points $x_i \in \Omega$ represent small spherical blobs of phase A in a sea of phase B, and the weights $m_i > 0$ represent the relative size of the blobs. In two dimensions the points $x_i$ represent thin cylinders of phase A in a cross-section orthogonal to the cylinders. In Theorem 2.4 we show that $F_{p,n}$ Gamma-converges to an energy of the form

\[
F_p(\nu) = \lambda \sum_i m_i^{d-1} + W_p(1, \nu) \tag{1.4}
\]

where $\lambda > 0$ and the 1 in $W_p(1, \nu)$ denotes the Lebesgue measure on $\Omega$. Note that the number $M$ in the definition of $\nu$ is not prescribed and is an unknown of the problem. The first term
of $F_p$ represents the repulsion between the A- and B-blocks and is minimised when $M = 1$, which corresponds to complete phase separation where there is just one particle of phase A. The second term of $F_p$ represents the covalent bonds between the A- and B-blocks and can be made arbitrarily small by taking $M \to \infty$, corresponding to complete phase mixing, i.e., infinitely many particles of A equidistributed in B. The competition between the two terms and the parameter $\lambda$ determines the nature of the minimisers.

Minimisers of the limit energy. After deriving Euler-Lagrange equations for the limit energy $F_p$ in Section 3 we limit our attention to $p = 2$ and two space dimensions.

Numerical Minimisation. In Section 4 we minimise $F_2$ numerically. This is challenging since (a) $F_2$ has infinitely many local minimisers, and (b) it is difficult to evaluate numerically; evaluating the Wasserstein distance is equivalent to solving an infinite-dimensional linear programming problem. The second difficulty is addressed by using a deep connection between the Wasserstein cost and power diagrams. This connection, made in [M11], seems to be little known in the theoretical optimal transportation community. It allows the minimisation of $F_2$ to be reformulated as a computational geometry problem.

Figure 2 shows a number of minimisers $\nu$ of $F_2$ that were obtained using this method, in collaboration with Steven Roper [BR]. The points represent the support of $\nu$ and the polygons represent the corresponding transport regions (the regions transported onto the support of $\nu$ by the optimal transport map $T$ for $W_2(1, \nu)$). We see that, as $\lambda \to 0$, the support of $\nu$ tends to a triangular lattice and the transport regions tend to a hexagonal tiling. This agrees with the hexagonally packed cylinder patterns observed experimentally (see e.g. [BF99]).

Rigorous characterisation of the pattern. Figure 2 and many other figures like it, strongly suggest that the triangular lattice is optimal in some way, and that minimisers tend to approximate this optimal lattice, ‘as far as the boundary allows’. This statement of crystallisation we have formulated in an exact way, and proved with Florian Theil. A non-rigorous version is given in Section 5 and the full version and the proof are given in the companion paper [BPT].

Related work. The energy (1.1) is related to the Ohta-Kawasaki energy, which is a nonlocal Cahn-Hilliard energy, in which the nonlocality is a negative Sobolev norm rather than a Wasserstein distance. This energy has been very well studied, both in one and in higher dimensions (see e.g. [CPW09]).

Alternative models of diblock copolymers with a dominant phase are derived in [RW07, CP10, CP11, Mur10, Nie11, GC09, CS, GMS11, GMS12]. These are derived starting from the Ohta-Kawasaki energy. For the limiting models, however, exact crystallisation results of the form [BPT] do not exist. In fact, this is the first time it has been proved that multi-dimensional minimisers of a diblock copolymer energy are periodic. Until now the closest results were the weak periodicity results of [ACO09] and [Spa09]. Note, however, that the diblock copolymer models analysed in these papers are different from and more sophisticated than the limit model we study here.

There is tantalizing evidence that minimisers of $F_2$ in three dimensions also agree with experiments, where it is observed that the minority phase forms small spheres centred on a body-centred cubic lattice (see Section 6). Verifying this conjecture numerically will be the subject of a future paper.
This paper (along with the companion paper [BPT]) gives a rare example of an energy-driven pattern formation problem in two dimensions where it can be proved that the optimal pattern is periodic. Some previous results for problems arising in materials science include [Rad81], [The06] and [AYFS12]. Proofs in three dimensions are even rarer [HHM+10]. Also, while the hexagonal pattern appears in a wide range of situations, again there are few rigorous results [FT72, Gru99, FT01, MB02].

The energy (1.4) and the results in this paper have applications beyond diblock copolymers. Energies of the form of our limit energy (1.4) arise in optimal location problems [LWS54, BS09, BJM11], quantization and image processing [Ger79, M11] and are related to many other problems in computational geometry [DFG99].

**Outline of the paper.** In Section 2 the discrete limit energy (1.4) is derived from the continuum energy (1.2) using Gamma-convergence. Euler-Lagrange equations for the limit
energy are derived in Section 3. Up to this point all the results hold in $\mathbb{R}^d$, $d \geq 2$, and with general $p$-Wasserstein cost. In the rest of the paper we restrict our attention to two dimensions and $p = 2$. In Section 4 we compute minimisers of the limit energy numerically. Section 5 reports results from the companion paper [BPT], where minimisers are characterised analytically. Finally, in Section 6 we make a conjecture about minimisers in three dimensions.

2 The Small Volume Fraction Limit Model

In this section we find the $\Gamma$-limit of $F_{p,n}$ as $n \to \infty$, i.e., as the volume fraction of phase A tends to zero. By doing this we obtain a simpler model that is more amenable to numerics and analysis.

Theorem 2.1 (Compactness). Let $\{v_n\} \subset K_n$ be a sequence with bounded energy:

$$\sup_{n>0} F_{p,n}(v_n) \leq C < \infty.$$ 

Then $v_n dx \rightharpoonup^s \nu$, where

$$\nu = \sum_i m_i \delta_{x_i}, \quad m_i \geq 0$$

is an at most countable sum of dirac masses located at points $x_i \in \Omega$. Moreover

$$\sum_i m_i = |\Omega|, \quad \sum_i m_i^{d-1} < \infty.$$ 

Proof. This follows almost immediately from the Second Concentrated Compactness Lemma of P. L. Lions [Lio85]. From the given sequence $v_n$, define the rescaled sequence $w_n := n^{-\frac{d}{2}} v_n$. Since $v_n$ has bounded energy, the sequence $\nabla w_n$ is bounded in $\mathcal{M}$, the space of bounded Radon measures. Also

$$\int_{\Omega} w_n = n^{-\frac{d}{2}} \int_{\Omega} v_n = n^{-\frac{d}{2}} |\Omega| \to 0,$$

which implies that $w_n \to 0$ in $L^1(\Omega)$. Note that

$$w_n^{1,*} = w_n^{\frac{d}{d-1}} = v_n.$$ 

Since $\int_{\Omega} v_n dx = |\Omega|$, the sequence $w_n^{1,*} dx \equiv v_n dx$ is bounded and so $w_n^{1,*} dx \rightharpoonup \nu$ for some $\nu \in \mathcal{M}$. Therefore $w_n$ satisfies the assumptions of the Second Concentrated Compactness Lemma, which implies that the limit measure $\nu$ is of the form given in the assertion. □

Remark. For the case $d = 2$ there is an elementary proof that does not rely on the industrial-strength compactness lemma used above. In two dimensions the diameter of a connected set can be bounded by its perimeter, $2 \text{Diam}(S) \leq \text{Per}(S)$. The energy bound on $v_n$ implies that the perimeter of the support of $v_n$ tends to zero. Therefore the diameter of each connected component of the support of $v_n$ tends to zero, which implies that the limit measure $\nu$ is a sum of dirac masses.

Let $K$ be the following set of Radon measures on $\mathbb{R}^d$:

$$K = \left\{ \nu = \sum_{i=1}^{\infty} m_i \delta_{x_i} : m_i \geq 0, \ x_i \in \Omega, \ x_i \neq x_j \text{ if } i \neq j, \ \sum_{i=1}^{\infty} m_i = |\Omega|, \ \sum_{i=1}^{\infty} m_i^{\frac{d-1}{d}} < \infty \right\}.$$
Theorem 2.4 (Γ-convergence: The small volume fraction limit). Let $\nu$ be a Radon measure on $\mathbb{R}^d$. Define

$$F_p(\nu) := \begin{cases} \int d\alpha(d) \frac{1}{d} \sum_i \frac{m_i}{d^{1/d}} + W_p(1, \nu) & \text{if } \nu \in K, \\ +\infty & \text{otherwise}, \end{cases}$$

where $\alpha(d)$ is the volume of the unit ball in $\mathbb{R}^d$. With respect to the topology of weak convergence of measures, $F_{p,n}$ Gamma-converges to $F_p$ as $n \to \infty$, i.e.,

(i) Let $v_n \in K_n$ satisfy $v_n dx \rightharpoonup \nu$ for some $\nu \in K$. Then

$$F_p(\nu) \leq \liminf_{n \to \infty} F_{p,n}(v_n).$$

(ii) Given $\nu \in K$, there exists a sequence $v_n$ in $K_n$ such that $v_n dx \rightharpoonup \nu$ and

$$\lim_{n \to \infty} F_{p,n}(v_n) = F_p(\nu).$$

Proof. First we prove (ii). By approximation (see e.g. [Bra02, Remark 1.29]) we can assume that $\nu$ is a finite sum of dirac masses:

$$\nu = \sum_{i=1}^{\infty} m_i \delta_{x_i} \in K.$$ We can also assume that none of the points $x_i$ belong to the boundary of $\Omega$. Define $r_i$ by

$$r_i = \frac{m_i}{n \alpha(d)}$$

so that the ball $B(x_i, r_i)$ has volume $m_i/n$. Let $v_n$ be the function taking values in $\{0, n\}$ with support $\bigcup_i B(x_i, r_i)$. Note that, for $n$ sufficiently large, the balls $B(x_i, r_i)$ are disjoint and are contained in $\Omega$. Therefore $v_n \in K_n$. It is easy to check that

$$v_n dx \rightharpoonup \nu, \quad \frac{n - v_n}{n - 1} \rightharpoonup 1. \quad (2.5)$$

Since the $p$-Wasserstein distance metrizes weak convergence of measures (see [Vil03, Theorem 7.12]), it follows that

$$W_p\left(\frac{n - v_n}{n - 1}, v_n\right) \to W_p(1, \nu). \quad (2.6)$$

Recall that $d\alpha(d)$ is the surface area of the unit ball in $\mathbb{R}^d$. Therefore for all $n$

$$n^{-\frac{1}{d}} \int_\Omega |\nabla v_n| = d\alpha(d) \frac{1}{d} \sum_i \frac{m_i}{d^{1/d}}. \quad (2.7)$$

Combining (2.6) and (2.7) yields (ii).

Now we turn our attention to (i). Let $v_n dx \rightharpoonup \nu$, where $\nu = \sum_{i=1}^{\infty} m_i \delta_{x_i} \in K$. Fix $M \in \mathbb{N}$. By Lemma 5.3 in [CP10] we can modify the sequence $v_n$ to obtain a sequence $\tilde{v}_n$ such that

$$\tilde{v}_n = \sum_{i=1}^{M} v^n_i$$

where $v^n_i \in BV(\Omega; \{0, n\})$ have disjoint supports, $\text{dist}(\text{supp } v^n_i, \text{supp } v^n_j) > 0$ for all $i \neq j$, and satisfy

$$\text{w-liminf}_{n \to \infty} v^n_i \geq m_i \delta_{x_i}, \quad i \in \{1, \ldots, M\} \quad (2.8)$$

in the sense of distributions, and

$$\int_\Omega |\nabla v_n| \geq \int_\Omega |\nabla \tilde{v}_n|. \quad (2.9)$$
This modification is necessary so that we can apply the Isoperimetric Inequality (with optimal constant) as follows:

\[
\int_{\Omega} |\nabla \tilde{v}_n| = n^{-\frac{1}{d}} \sum_{i=1}^{M} \int_{\mathbb{R}^d} |\nabla v^n_i| \geq n^{-\frac{1}{d}} \sum_{i=1}^{M} da(d)^{\frac{1}{d}} \left( \int_{\mathbb{R}^d} \left| v^n_i \right|^{\frac{d}{d-1}} dx \right)^{\frac{d-1}{d}},
\]

(2.10)

where the last equality holds since \( v_i^n \) takes values in \( \{0, n\} \). Equations (2.9) and (2.10) imply that

\[
F_{p,n}(v_n) \geq d\alpha(d)^{\frac{1}{d}} \sum_{i=1}^{M} \left( \int_{\mathbb{R}^d} v^n_i dx \right)^{\frac{d-1}{d}} + W_p \left( \frac{n - v_n}{n - 1}, v_n \right).
\]

Therefore by using (2.8) and the fact that the Wasserstein distance metrizes weak convergence of measures we obtain

\[
\lim_{n \to \infty} F_{p,n}(v_n) \geq d\alpha(d)^{\frac{1}{d}} \sum_{i=1}^{M} m_i^{\frac{d-1}{d}} + W_p(1, \nu).
\]

This holds for all \( M \in \mathbb{N} \). Therefore it also holds for \( M = \infty \) and we obtain the desired result. \( \square \)

### 3 Euler-Lagrange Equations

In the rest of the paper we study the limit energy \( F_p \). We start by deriving two Euler-Lagrange equations.

**Proposition 3.1** (Euler-Lagrange equation obtained by varying \( x_i \)). Let \( \nu = \sum_i m_i \delta_{x_i} \in K \) be a minimiser of \( F_p \). Let \( V_i \subseteq \Omega \) be the set of points transported to \( x_i \) by the optimal transport map \( T \) for \( W_p(1, \nu) \), i.e., \( V_i = T^{-1}(x_i) \). Then for each \( i \)

\[
0 = \int_{V_i} (x_i - x)|x_i - x|^{p-2} dx.
\]

For the case \( p = 2 \) this says that each mass \( x_i \) is located at the centre of mass of its transport region \( V_i \).

**Proof.** We vary the positions of the dirac masses, but not their weights, using an inner variation along the same lines as [JKO98]. Suppose that \( \nu = \sum_i m_i \delta_{x_i} \) is a minimiser of \( F_p \). We consider variations of the form \( \nu_\tau = \Phi_\tau \# \nu \), where \( \{\Phi_\tau\}_{\tau \geq 0} \) is a 1-parameter family of smooth invertible maps from \( \mathbb{R} \) to \( \mathbb{R} \) such that \( \Phi_0(x) = x \). To be precise, we define \( \Phi_\tau \) through the following ODE. Let \( \xi \in C_0^\infty(\mathbb{R}; \mathbb{R}) \). Define \( \Phi_\tau(y) = \Phi(\tau, y) \) by

\[
\frac{d}{d\tau} \Phi(\tau, y) = \xi(\Phi(\tau, y)) \quad \tau \geq 0,
\]

\[
\Phi(0, y) = y.
\]

(3.2)
Since in our case the measure $\nu$ has such a simple form, the push-forward $\nu_\tau = \Phi_\tau#\nu$ reduces to $\nu_\tau = \sum_i m_i \delta_{\Phi_\tau(x_i)}$. Formally, the Euler-Lagrange equation is

$$\frac{d}{d\tau} F_p(\nu_\tau)|_{\tau=0} = 0. \quad (3.3)$$

Since we are not varying the weights $m_i$ of the Dirac masses, the left-hand side of this equation reduces to $\partial_\tau W_p(1, \nu_\tau)|_{\tau=0}$. Computing this derivative rigorously requires some care. The same calculation as in [JKO98, p. 11] shows that equation (3.3) leads to the following Euler-Lagrange equation:

$$0 = \int_{\Omega \times \Omega} \xi(y) \cdot (y - x)|y - x|^{p-2} d\gamma \quad \text{for all } \xi \in C_0^\infty \quad (3.4)$$

where $\gamma$ is an optimal transport plan for the pair $(1, \nu)$, i.e.,

$$W_p(1, \nu) = \int_{\Omega \times \Omega} |y - x|^p d\gamma(x, y). \quad (3.5)$$

Now we rewrite equation (3.4) in the form of the proposition statement. If $T$ is an optimal transport map, so that $\nu = T#1$ and $\gamma = (\text{id} \times T)#1$, then equation (3.4) can be written as

$$0 = \int_{\Omega} \xi(T(x)) \cdot (T(x) - x)|T(x) - x|^{p-2} dx \quad \text{for all } \xi \in C_0^\infty. \quad (3.6)$$

Note that $T$ maps $\Omega$ onto $\text{spt}(\nu) = \bigcup_i \{x_i\}$. Let $V_i$ denote the set of points mapped to $x_i$ by $T$, i.e., $V_i = T^{-1}(x_i)$. Then equation (3.6) reduces to

$$0 = \sum_i \int_{V_i} \xi(x_i) \cdot (x_i - x)|x_i - x|^{p-2} dx \quad \text{for all } \xi \in C_0^\infty. \quad (3.7)$$

Since this holds for all $\xi \in C_0^\infty$ we arrive at the Euler-Lagrange equation

$$0 = \int_{V_i} (x_i - x)|x_i - x|^{p-2} dx. \quad (3.8)$$

□

**Proposition 3.9** (Euler-Lagrange equation obtained by varying $m_i$). Let $\nu = \sum_{i=1}^M m_i \delta_{x_i} \in K$ be a minimiser of $F_p$ consisting of a finite number of dirac masses. Let $(\phi_*, \psi_*)$ be an optimal Kantorovich potential pair for the problem of transporting $1$ to $\nu$, i.e.,

$$W_p(1, \nu) = \int_{\Omega} \phi_*(x) dx + \sum_i m_i \psi_*(x_i)$$

and $\phi(x) + \psi(x_i) \leq |x - x_i|^p$ for almost all $x \in \Omega$ and all $i$. Then

$$\alpha(d)^{\frac{1}{2}} (d - 1) m_i^{-\frac{1}{d}} + \psi_*(x_i) = \text{constant}$$

where the constant is independent of $i$.

The constant appearing in the proposition is the Lagrange multiplier for the constraint $\sum_i m_i = |\Omega|$.
Proof. This time we keep the positions of the dirac masses fixed and vary their weights in the following way. Define
\[ m_i^\eta = m_i + \eta n_i, \quad n_i \in \mathbb{R}, \quad \sum_i n_i = 0. \] (3.10)

Given \( n_i \), for \( \eta \) sufficiently small we have \( m_i^\eta > 0 \) for all \( i \) and so \( \nu^\eta := \sum_i m_i^\eta \delta_{x_i} \in K \). Let \((\phi^\eta_*, \psi^\eta_*)\) be an optimal Kantorovich potential pair for the problem of transporting \( 1 \) to \( \nu^\eta \), i.e.,
\[ W_p(1, \nu^\eta) = \int_\Omega \phi^\eta_* dx + \sum_i m_i^\eta \psi^\eta_*(x_i) \] (3.11)
and \( \phi^\eta_*(x) + \psi^\eta_*(x_i) \leq |x - x_i|^p \) for almost all \( x \in \Omega \) and all \( i \). By adding and subtracting a constant to \( \psi^\eta_* \) and \( \phi^\eta_* \) we can assume that \( \psi^\eta_*(x_1) = 0 \), and similarly \( \psi_*(x_1) = 0 \); by Lemma 3.17 below, then \( \psi^\eta_*(x_i) \to \psi(x_i) \) for all \( i \).

Since \((\phi^\eta_*, \psi^\eta_*)\) is admissible, we can estimate
\[ W_p(1, \nu) \geq \int_\Omega \phi^\eta_* dx + \sum_i m_i \psi^\eta_*(x_i). \] (3.12)

Therefore by equations (3.10)–(3.12),
\[ W_p(1, \nu^\eta) - W_p(1, \nu) \leq \eta \sum_i n_i \psi^\eta_*(x_i). \] (3.13)

Therefore, since \( \nu \) is a minimiser of \( F_p \),
\[ 0 \leq \frac{1}{\eta} [F_p(\nu^\eta) - F_p(\nu)] \leq \sum_i \left[ d\alpha(d)^\frac{1}{2} \left( (m_i^\eta)^{\frac{d-1}{2}} - (m_i)^{\frac{d-1}{2}} \right) \eta + n_i \psi^\eta_*(x_i) \right]. \] (3.14)

Taking the limit of the right-hand side as \( \eta \to 0 \) gives
\[ 0 \leq \sum_i \left[ d\alpha(d)^\frac{1}{2} (d - 1) m_i^{-\frac{1}{2}} + \psi_*(x_i) \right] n_i \] (3.15)
for all \( n_i \) satisfying (3.10). Therefore
\[ d\alpha(d)^\frac{1}{2} (d - 1) m_i^{-\frac{1}{2}} + \psi_*(x_i) = \text{constant} \] (3.16)
as required. \[\square\]

Lemma 3.17. Let \( \nu = \sum_{i=1}^M m_i \delta_{x_i} \) and \( \nu^\eta = \sum_{i=1}^M m_i^\eta \delta_{x_i} \) satisfy \( m_i^\eta \to m_i \) as \( \eta \to 0 \). Let \((\phi_*, \psi_*)\) and \((\phi^\eta_*, \psi^\eta_*)\) be corresponding Kantorovich potentials, and assume that \( \psi_*(x_1) = \psi^\eta_*(x_1) = 0 \). Then \( \psi^\eta_*(x_i) \to \psi_*(x_i) \) for all \( i \).

Proof. This result is a small extension of [BS09 Lemma 3.4], who proved the result for \( p > 1 \). Here we extend it to all \( p \geq 1 \). The only new requirement is a proof that optimal potentials are unique for \( p \geq 1 \), up to addition of constants, and we now show this. Fix \( \nu = \sum_{i=1}^M m_i \delta_{x_i} \); note that the Kantorovich pair \((\phi_*, \psi_*)\) satisfies
\[ \phi_*(x) = \min_i \{|x - x_i|^p - \psi_*(x_i)| \}, \quad \text{for } x \in \Omega, \]
so that

\[ W_p(1, \nu) = \sup_{\{\psi(x_i)\}_i} \int_\Omega \min_i (|x - x_i|^p - \psi(x_i)) \, dx + \sum_i m_i \psi(x_i) \]

\[ = \sup_{a = \{a_i\}_{i=1}^M} \inf_{\{\Omega_i\}_{i=1}^M} \text{partition of } \Omega \sum_i \int_{\Omega_i} (|x - x_i|^p - a_i) \, dx + \sum_i m_i a_i. \]

The function \( f \) is affine along lines of the form \( a + b(1, \ldots, 1) \), for \( b \in \mathbb{R} \), and strictly concave in all other directions. This follows from remarking that if \( \{\Omega_i\}_i \) is an optimal partition of \( \Omega \) for \( a = \{a_i\}_i \), then for a perturbed \( a + \tilde{a} \) we have

\[ f(a + \tilde{a}) - f(a) = \]

\[ \inf_{\{\tilde{\Omega}_i\}_{i=1}^M} \sum_i \int_{\tilde{\Omega}_i} (|x - x_i|^p - a_i - \tilde{a}_i) \, dx - \sum_i \int_{\Omega_i} (|x - x_i|^p - a_i) \, dx + \sum_i m_i \tilde{a}_i \]

\[ \leq \sum_i \int_{\Omega_i} (|x - x_i|^p - a_i - \tilde{a}_i) \, dx - \sum_i \int_{\Omega_i} (|x - x_i|^p - a_i) \, dx + \sum_i m_i \tilde{a}_i \]

\[ = \sum_i \tilde{a}_i (m_i - |\Omega_i|), \]

and the inequality is strict whenever \( \{\Omega_i\}_i \) is not an optimal partition for \( a + \tilde{a} \), which is whenever the \( \tilde{a}_i \) are not all equal. This strict inequality implies the strict concaveness of \( f \) in non-constant directions, and therefore the \( a_i \) (and the \( \psi^*(x_i) \)) are uniquely determined up to constants.

\[ \square \]

**Remark.** It can also be shown that stationary points satisfy the Euler-Lagrange equation given in Proposition 3.9, not only minimisers, by using that \( \phi_{\nu}^* \rightarrow \phi^* \) uniformly. This follows from the fact that \( \phi_{\nu}^* \) is \( |x - y|^p \)-concave (c.f. [BS09, Lemma 3.4]). Then it can be shown that \( F_p(\nu^\eta) \) is differentiable with respect to \( \eta \) and so we do not need to use the fact that \( \nu \) is a minimiser, just that it is a stationary point. The Euler-Lagrange equation given in Proposition 3.1 also holds for stationary points.

### 4 Numerical Optimisation in 2D

In the remainder of the paper we study minimisers of the limit energy derived in Theorem 2.4. We limit our attention to two dimensions, \( d = 2 \), and to \( p = 2 \). By rescaling we can assume that \( \Omega \subset \mathbb{R}^2 \) has area 1 and that the energy has the form

\[ F(\nu) = \lambda \sum_{i=1}^M \sqrt{m_i} + W_2(1, \nu) \]  

(4.1)

for some constant \( \lambda > 0 \), where \( \nu = \sum_{i=1}^M m_i \delta_{x_i} \) with \( m_i > 0 \), \( \sum_{i=1}^M m_i = 1 \), \( x_i \in \Omega \), \( x_i \neq x_j \) if \( i \neq j \). The parameter \( \lambda \), which comes from the rescaling, can also be thought of as modelling the repulsive strength between the A- and B-blocks. This parameter was suppressed in the original energy (1.2).
Note that $M$ is not fixed \textit{a priori}. The first term of $F$ is minimised when $M = 1$, i.e., when $\nu$ consists of just one dirac mass (placed anywhere). The minimum value of the second term of $F$ converges to 0 as $M \to \infty$ (since the Lebesgue measure can be approximated arbitrarily well by dirac masses). The parameter $\lambda$ and the competition between the two terms determines the value of $M$ for minimisers and the minimising patterns. For example, when $\lambda$ is large the first term of $F$ dominates and $M = 1$ and the minimiser is $\nu = \delta_{x_1}$, where $x_1$ is the centre of mass of $\Omega$. As $\lambda$ decreases, $M$ increases. The scaling of the energy suggests that $M \sim \lambda^{-2/3}$.

### 4.1 Minimisers when $\lambda = 0$ and $M$ is fixed: Centroidal Voronoi Tessellations.

To get an intuition for the problem we first consider the simpler problem where $\lambda = 0$ and $M$ is prescribed. In this case the energy reduces to

$$F(\nu) = W_2(1, \nu)$$

where $\nu = \sum_{i=1}^{M} m_i \delta_{x_i}$ for some $M \in \mathbb{N}$ fixed. (Note that $M$ must be fixed since otherwise $F$ has no minimum.) This energy is well-studied in both the theoretical optimal transportation literature and the computational geometry literature (e.g. [DFG99]) and has applications in optimal location problems (e.g., urban planning [LWS54, BS09, BJM11]), quantization (e.g., image compression and signal processing [Ger79, M11]) and data clustering (e.g., k-means clustering [IKI94, DFG99]). We briefly recall how the problem of minimising $F$ can be converted into an optimal partitioning problem.

Let $T_M$ be the set of partitions of $\Omega$ into $M$ sets:

$$T_M = \left\{ \{U_i\}_{i=1}^{M} \subseteq \Omega : \bigcup_{i=1}^{M} U_i = \Omega, U_i \cap U_j = \emptyset, i \neq j \right\}. \quad (4.2)$$

Then $F$ can be written as

$$F(\nu) = \min_{T_M} \left\{ \sum_{i=1}^{M} \int_{U_i} |x - x_i|^2 \, dx : |U_i| = m_i \forall i \right\}. \quad (4.3)$$

Here $U_i = T^{-1}(\{x_i\})$ where $T$ is the optimal transportation map. Therefore

$$\min_{\nu} F(\nu) = \min_{\{x_i, m_i\}_{i=1}^{M}} \min_{T_M} \left\{ \sum_{i=1}^{M} \int_{U_i} |x - x_i|^2 \, dx : |U_i| = m_i \forall i \right\} \quad (4.4)$$

$$= \min_{\{x_i\}_{i=1}^{M}, \{m_i\}_{i=1}^{M}} \sum_{i=1}^{M} \int_{U_i} |x - x_i|^2 \, dx.$$

In other words, instead of minimising $F$ over points $\{x_i\}_{i=1}^{M}$ and weights $\{m_i\}_{i=1}^{M}$, we can minimise

$$G(\{x_i, U_i\}_{i=1}^{M}) = \sum_{i=1}^{M} \int_{U_i} |x - x_i|^2 \, dx \quad (4.5)$$
over points \( \{ x_i \}_{i=1}^M \) and partitions \( \{ U_i \}_{i=1}^M \) of \( \Omega \). It is known that \( G \) is minimised when the partition \( \{ U_i \}_{i=1}^M \) is the Voronoi tessellation \( \{ V_i \}_{i=1}^M \) generated by the points \( \{ x_i \}_{i=1}^M \) and simultaneously each \( x_i \) is the centre of mass of its own Voronoi cell:

\[
V_i = \{ x \in \Omega : |x - x_i| < |x - x_j| \forall j \neq i \},
\]

\[
x_i = \frac{1}{|V_i|} \int_{V_i} x \, dx.
\]

Condition (4.7) is just the Euler-Lagrange equation for \( G \) obtained by varying the points \( x_i \). If condition (4.6) is not satisfied it is easy to see that \( G \) can be decreased by replacing the partition \( \{ U_i \}_{i=1}^M \) with the Voronoi tessellation \( \{ V_i \}_{i=1}^M \) generated by the points \( x_i \). These special types of Voronoi tessellations \( \{ x_i, V_i \} \) satisfying (4.6) and (4.7) are known as Centroidal Voronoi Tessellations (CVTs). See [DFG99] for a nice survey of CVTs.

Minimisers of the original energy (4.1) with \( \lambda > 0 \) turn out to be very close to CVTs, as illustrated in Figure 4. Therefore CVTs (which are easy to compute using Lloyd’s algorithm) can be used to generate good approximate minimisers. Developing a convergent minimisation algorithm, however, requires a different approach, which we discuss in the following section.

### 4.2 Minimisers when \( \lambda > 0 \): Centroidal Power Diagrams.

Minimising the energy (4.1) numerically is challenging, not only because it has infinitely many local minimisers, but also because it is challenging even to evaluate \( F(\nu) \) for a given \( \nu \); from the Kantorovich formulation of Wasserstein cost \( W_2(1, \nu) \), in terms of measures on \( \Omega \times \Omega \) with marginals 1 and \( \nu \), we see that evaluating \( W_2(1, \nu) \) directly is equivalent to solving an infinite-dimensional linear programming problem. For the case \( \lambda = 0 \) studied in the previous section this could be avoided. We show that it can also be avoided for \( \lambda > 0 \) by rewriting the energy in new coordinates.

Let \( \{ x_i, w_i \}_{i=1}^M \) be a set of weighted points, \( x_i \in \Omega, w_i \in \mathbb{R} \). To this we can associate a type of generalised Voronoi diagram called a power diagram \( \{ P_i \}_{i=1}^M \), which is a polygonal
Figure 4: Minimisers of $F$ (defined in equation (4.1)) are close to being Centroidal Voronoi Tessellations (CVTs). Left: A CVT of three points (empty circles indicate the generators of the Voronoi cells, dashed lines indicate the boundaries of the Voronoi cells) and a minimiser $\nu$ of $F$ for $\lambda = 0.1$ (solid circles indicate the support $\{x_i\}$ of $\nu$, solid lines indicate the boundaries of the transport regions). Right: A CVT of five points and a minimiser of $F$ for $\lambda = 0.026$.

partition of $\Omega$ defined as follows:

$$P_i = \{x \in \Omega : |x - x_i|^2 - w_i < |x - x_j|^2 - w_j \forall j \neq i\}.$$ 

Note that if all the weights $w_i$ are equal, then the power diagram is just a standard Voronoi tessellation. For a comprehensive treatment of generalised Voronoi diagrams see [OBSC00].

Power diagrams can be used to give an explicit formula for the Wasserstein transport cost that is easy to evaluate; it can be shown that

$$W_2 \left(1, \sum_i |P_i| \delta_{x_i}\right) = \sum_i \int_{P_i} |x - x_i|^2 dx,$$

i.e., the power cells $P_i$ are the transport regions for the points $x_i$. This follows from Brenier’s Theorem [Bre91] (see [M11]) and was also proved in [AIA98], although not stated in the language of Wasserstein costs. This motivates us to change coordinates and rewrite the energy (4.1) as

$$E(\{x_i, w_i\}) := F \left(\sum_i |P_i| \delta_{x_i}\right) = \sum_i \left\{\lambda \sqrt{|P_i|} + \int_{P_i} |x - x_i|^2 dx\right\}. \quad (4.8)$$

Suppose that $\{x_i, w_i\}$ is a minimiser of $E$. Then by Proposition 3.1 each $x_i$ is at the centre of mass of its power cell $P_i$ (since $P_i$ is also its transport region). Therefore minimisers of $E$ are Centroidal Power Diagrams. This, along with a version of Proposition 3.9 in $\{x_i, w_i\}$-coordinates, is used in the forthcoming paper [BR] to develop a generalised Lloyd’s algorithm for minimising a class of energies that includes $E$.

Figure 2 shows minimisers of $E$ for decreasing values of $\lambda$ computed using this algorithm. Observe that as $\lambda \to 0$ the power diagrams tend towards a hexagonal tiling of $\Omega$, and the generators $x_i$ tend to a triangular lattice. In the following section we see that this limiting behaviour can be proved rigorously.
5 Exact Characterisation of Minimisers in 2D

Let $\nu_\lambda$ be a minimiser of $F$ (defined in equation (4.1)). The numerical results in the previous section suggest that, as $\lambda \to 0$, the support $\{x_i\}_{i=1}^M$ of $\nu_\lambda$ tends to a triangular lattice, and the associated transport regions $V_i$ tend to a regular hexagonal tiling of $\Omega$. A precise statement of this is proved in the companion paper [BPT]. Here we just give a rough statement. Let $\Omega \subset \mathbb{R}^2$ have area 1. We rescale $\Omega$ to obtain a domain $\Omega_\lambda$ that blows up as $\lambda \to 0$: 

$$\Omega_\lambda := \left( \frac{2c_6}{\lambda} \right)^{\frac{1}{3}} \Omega$$

where $c_6 := \frac{5\sqrt{3}}{54}$ is the cost of transporting the Lebesgue measure restricted to a unit area regular hexagon onto a dirac mass located as its centre. Under this rescaling the energy $F$ becomes, up to a factor $\lambda^{4/3}(2c_6)^{-4/3}$, the following:

$$\tilde{F}(\nu) = 2c_6 \sum_{i=1}^M \sqrt{m_i} + W_2(1, \nu)$$

where $\nu = \sum_{i=1}^M m_i \delta_{x_i}$ is a measure on the rescaled domain $\Omega_\lambda$. Then [BPT] Theorems 1–4 can be stated roughly as follows:

- Let $\Omega$ be a polygonal domain with at most six sides. For $\lambda > 0$, the energy $\tilde{F}$ is bounded from below by the energy of a measure supported on a triangular lattice (to be more precise, the energy of a measure supported at the centres of $|\Omega_\lambda|$ unit-area regular hexagons).

- This lower bound can be achieved in the limit $\lambda \to 0$. (This statement holds for any Lipschitz domain $\Omega$.) It can also be achieved for $\lambda > 0$ if $\Omega$ is a periodic domain of the right aspect ratio (meaning that it exactly fits an integer number of unit-area regular hexagons).

- If the energy of $\nu = \sum_{i=1}^M m_i \delta_{x_i}$ is close to the lower bound, then $\{x_i\}$ is close to being a triangular lattice.

6 Conjecture About Minimisers in 3D

When the minority phase has a very low volume fraction, it is observed experimentally that it forms small spheres embedded in a sea of the majority phase. These spheres are centred on a BCC (body-centred cubic) lattice (see e.g. [BF99]). In this paper we have focussed on minimisers of the energy (1.1) in 2D. We conjecture however that minimisers in 3D are indeed BCC lattices. There is tantalizing evidence for this. We demonstrated numerically that in 2D minimisers of our energy are close to being centroidal Voronoi tessellations (CVTs), meaning that the transport regions for the support $\{x_i\}$ of the optimal measure $\nu$ are close to being a CVT. We expect the same to be true in 3D. It is not known what the optimal CVTs are in 3D, but there is strong numerical evidence to suggest that they are generated by the BCC lattice [DW05].

Therefore we conjecture the following in 3D: Let $\nu_\lambda$ be a minimiser of $F_2$ (defined in Theorem 2.4). As $\lambda \to 0$, the support $\{x_i\}_{i=1}^M$ of $\nu_\lambda$ tends to a BCC lattice. Proving this seems out of reach, but it will be studied numerically in a forthcoming paper.
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References


