Anomalous assembly of ill-fitting elements

1. **Geometric frustration and compatibility conditions for two dimensional director fields**
   Authors: Idan Niv and Efi Efrati
   arXiv:1706.08187

2. **Geometrical frustration yields fibre formation in self-assembly**
   Authors: Martin Lenz and Thomas A. Witten
   Nature Physics (2017), DOI: 10.1038/NPHYS4184

Recommended with a Commentary by Gregory M. Grason, University of Massachusetts, Amherst

The effects of geometric frustration are most commonly studied in thermodynamically large systems, like anti-ferromagnetic spin lattices, bulk models of glassy amorphous spheres, or blue phases of chiral liquid crystals [1, 2]. In such boundary-free systems, geometric frustration is known to give rise to rich spectrum of highly degenerate and heterogeneous ground states. These bulk ground states are often punctuated by extensive networks of topological defects that mediate the conflict between preferred local interactions and non-local geometric constraints. Two recent studies highlight a distinct, and less widely known, effect of geometric frustration in self-assembling systems. In these models, frustration arises from the "ill-fitting" shape of self-assembly constituents which is incompatible with uniform, strain-free cohesive assembly in the bulk.

The first study, by Niv and Efrati (NE), considers a model of 2D nematic assemblies, motivated by observations of a multitude of complex and heterogeneous states of order in 'bent core' liquid crystals. As shown schematically in Fig. 1, the packing of these "banana-shaped" molecules in the 2D plane is expected to favor configurations where the director, $\mathbf{n}$, aligned to long axis of molecule has uniform *local bend*, favored by the curved axes of the molecule, and simultaneously *zero splay*, which is favorable for uniform density of rod-like objects. The generalization of this model to 3D has been explored to explain the spontaneous emergence of chiral and polar order in the so-called 'twist-bend' phase of bent cores [3]. As a stepping stone to this more complex 3D scenario, NE aim to formulate the generic geometrical constraints of this ordering on 2D manifolds and their consequences for thermodynamics. While examples of frustration of nematic order on 2D surfaces have been studied for decades [4], almost all of these have focused on the case of closed or boundary free manifolds as well the more restricted case of nematogens that favor vanishing of both splay *and* bend.

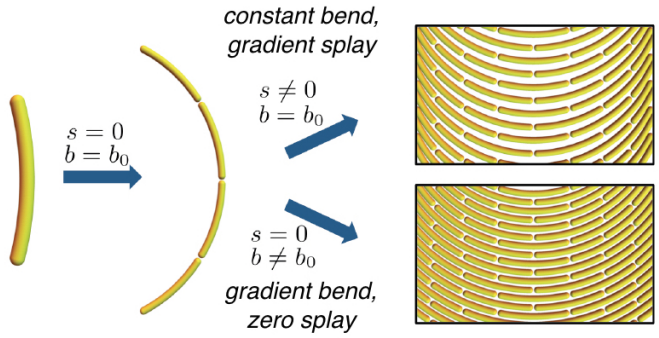

Figure 1: A schematic of frustration in planar bent core (i.e., "banana-shaped") liquid crystals (adapted from NE).

The scope of their study is twofold: First, to derive the generic geometric constraints arising from the incompatible surface geometry and preferred local director $\mathbf{n}$; and second, to demonstrate the thermodynamic consequences of frustration between preferred local texture and manifold shape on the size-dependence of a finite domain of the 2D nematic. They formulate these constraints in terms of two scalar fields, *splay*, $s = \nabla \cdot \mathbf{n}$; and *bend*, $b = |(\mathbf{n} \cdot \nabla)\mathbf{n}|$, and ask the question, what are allowed values for s and b given a 2D manifold of some shape?

Based on the geometry of integral coordinates generated by $\mathbf{n}$ and $\mathbf{n}_\perp$, the unit field perpendicular to $\mathbf{n}$, NE derive what they call the 'pre-compatibility condition',

$$K = -b^2 - s^2 - \mathbf{n} \cdot \nabla s + \mathbf{n}_\perp \cdot \nabla b,$$

where K is the Gaussian curvature. This elegant expression unifies the geometric constraints for a diverse class of problems, some well known like the requirement for some combination of non-zero splay and bend texture for $K \neq 0$, and some less well known, such as the fact that uniform (strain free) combinations of splay and bend are only possible on constant *negative* curvature surfaces (i.e. $b^2 + s^2 = -K$). Most significant, NE show how this formula leads to a natural definition of "geometric charge" associated with the incompatibility of a preferred local texture with splay and bend, s_0 and b_0, respectively, and the curvature. When the quantity $(s_0^2 + b_0^2 + K)$ is non-zero there must be gradients of either s or b away from their preferred values (along $\mathbf{n}$ or $\mathbf{n}_\perp$, respectively). NE demonstrate the effect of this geometric charge for a patch of planar ($K = 0$) 2D nematic with a preferred bend, $b_0 \neq 0$, and unfavorable splay, $s_0 = 0$, and show the ground state always negotiates this frustration through gradients patterns of splay and bend, like the curvature focusing texture in Fig.1, bottom right. The deviation of splay and bend from their preferred values generically grows with domain size as $\sim b_0 L$, acquiring a free energy cost that grows as $\sim b_0^2 L^4$, that is, faster than the area. Hence, they demonstrate frustration, as quantified by the the geometric charge $(s_0^2 + b_0^2 + K)$ in 2D nematics leads to a *super-extensive* cost of domain growth of the type has been argued to provide an equilibrium limitation to assembly, restraining the cohesive tendency towards infinite domain size [5]. This behavior is anomalous relative to canonical, or unfrustrated, assemblies in the sense that thermodynamics becomes sensitive to domain size, and under some conditions becomes self-limiting, at length scales that are arbitrarily much larger than that constituent molecules. That is, chemical potential to for adding another molecule "knows" the global size of the assembly at length scales far in excess of the interaction range.

The size-sensitivity of frustrated 2D nematics appears to be connected to the emergent size-selection in another class of geometrically frustrated assemblies, studied in a paper by

Lenz and Witten (LW). Their model considers the cohesive assembly of soft 2D 'building blocks' with stress-free shapes that are incompatible with (gap-free) planar tiling: regular pentagons and octagons, as well as irregular hexagons (see Fig.2). They perform simulations where particle clusters form via sequential additional with subunits gaining a cohesive energy $-\sigma$ when two edges are in perfect contact, while the change in length and orientation of block edges needed to maintain cohesive contact leads to an elastic energy cost of deformation proportional to elastic modulus, k. They argue that in the stiff-block limit of $\sigma/k \to 0$ "tree-like" or fractal clusters are favorable, possessing an extensive number of unbonded edges, while in the opposite floppy-block limit of $\sigma/k \to \infty$, 2D "bulk" assemblies are stable as the assembly pays only a nominal elastic cost to deform blocks into a shape compatible with planar tiling. Beyond these intuitive limits, Lenz and Witten show also, via simulations of sequentially growing clusters, that at an intermediate range of σ/k, the frustrated soft particles form *fibers*, quasi-1D assemblies that take on a well-defined and finite widths that grow unlimited longitudinally. Surprisingly, this intermediate, self-limiting fiber regime seems to be generic for the range of incompatible particle shapes considered. Accounting for the differences in elastic strain needed to "compatibilize" blocks, the shift in the range of σ/k where fibers occur can be rationalized.

On the face of it, the size-selectivity in these two distinct models would appear to result from the identical mechanism, i.e. the scale dependence of elastic costs of frustrated assemblies. However, there are some key differences that highlight current gaps in the still primitive understanding of the emergent behavior of geometrically frustrated assemblies. First, in the nematic model of NE, as well as in almost all other known models of geometrically frustrated assembly, one can identify something that plays the role of geometric charge that acts as a source for stress generation and which can often be interpreted as a mismatch between the ideal Riemannian curvature of the particle packing and that of their embedding space. While in the discrete ill-fitting particle model of LW, it is possible to associate an ideal Gaussian curvature for the 2D tiling of pentagonal or octagonal particles (uniformly positive or negative, respectively), the irregular hexagons, which also form the same self-limiting fibers, cannot be so obviously be mapped onto an compatible tiling on a non-Euclidean surface, or at least, not one that provides a useful notion of "geometric charge" associated with elastic deformations in their planar assembly.

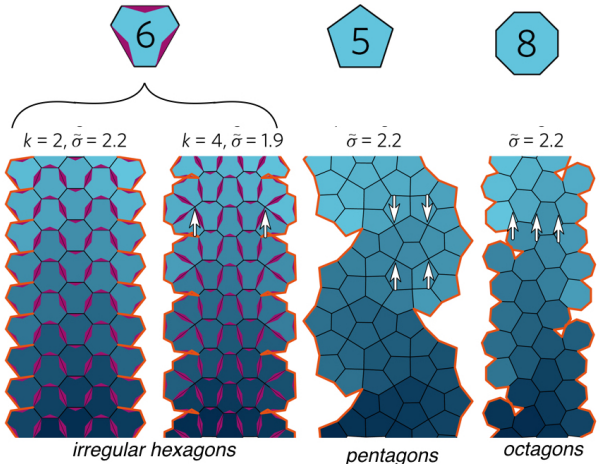

Figure 2: Periodic repeated of finite width fibers formed in simulations of flexible, and incompatible 2D particles (adapted from LW), with topological defects (4-coordinated vertices).

This apparent absence of "geometric charge" from at least some of the block shapes studied by LW highlights a further distinction. In the model of NE, the elastic cost of shape

misfit can accumulate to indefinitely large scales (i.e., as compared to bent-core molecules), hence the result that deviations from preferred texture grow as a power law L. This cumulative, or power law, stress growth arises fairly generically under conditions where the degree of frustration can be taken to be arbitrarily small, so that topological defects that would "neutralize" the frustration do not appear. In the results of LW, even for the case of "geometrically-charged" pentagonal or octagonal blocks, it is clear that such neutralizing defects abound, more or less, limiting the ability of inter-particle stresses to accumulate on length scales larger than the inter-defect separation. Therefore, for the discrete model studied by LW and unlike the "geometrically charged" model of NE, the elastic cost of frustration is fairly local, likely extending over a finite range of $\sim 1-3$ blocks from the free edge to the core of the assembly. As such, it is perhaps not surprising that the finite width of fibers in the LW model does not exceed the few ($\lesssim 8$) block size. The finite range of elastic penetration may be further connected to the observation that finite-width fibers of LW are definitively shown to be only metastable, kinetically accessible only under conditions where bulk 2D assemblies are the thermodynamic ground state, whereas equilibrium conditions for self-limiting domain size (arbitrarily larger than the block size) are known to exist when frustration-induced stress grow as a power law [5], as in the case of the bent-core nematic model of NE.

Clearly, it remains to be understood whether the behaviors predicted in these two models are qualitatively similar fixed points belonging to the same "universality class" of geometrically frustrated assembly, or instead fundamentally distinct phenomena. This gap in our knowledge points to the need for new models, and more important, new experiments, that can bridge between scale-free, power law and local (exponentially screened) stress growth in frustrated assemblies. Notwithstanding the incomplete theoretical understanding of geometrically frustrated assemblies, the unique possibility to use single block types to target many-particle structures of well-defined and finite size raises some intriguing possibilities for "bottom up" approaches to materials design.

References

[1] J.-F. Sadoc and R. Mosseri, *Geometrical Frustration*, (Cambridge Univ. Press, 2006).

[2] G. Tarjus, S. A. Kivelson, Z. Nussinov and P. Voit, J. Phys,: Condens. Matter **17**, R1143 (2005).

[3] Z. Parsouzi, S. M. Shamid, V. Borshch, P. K. Challa, A. R. Baldwin, M. G. Tamba, C. Welch, G. H. Mehl, J. T. Gleeson, A. Jakli, O. D. Lavrentovich, D. W. Allender, J. V. Selinger and S. Sprunt, Phys. Rev. X **6**, 021041 (2016).

[4] M. J. Bowick and L. Giomi, Adv. Phys. **58**, 449 (2009).

[5] G. M. Grason, J. Chem. Phys. **145**, 110901 (2016).