A Columnar Liquid Quasicrystal – Honeycomb with Triangular, Square and Trapezoidal Cells

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Quasicrystals are intriguing structures, having long-range positional correlations but no periodicity, typically with rotational symmetries that are "forbidden" in normal crystals. While a variety of quasicrystals with different symmetries have been discovered in metal alloys, for reasons we don't yet fully understand, in soft matter all nano- and mesoscale quasicrystals discovered so far are always based on the random tiling of squares and triangles [1-3]. Here we present the discovery of a two-dimensional columnar liquid quasicrystal, with a honeycomb structure consisting of triangular, square and, for the first time, trapezoidal cells.[4] Optimal local packing of such three different kinds of cells leads to dodecagonal clusters (Fig. 1, left). To maximize the presence of such dodecagonal clusters, the system abandons periodicity but adopts a quasiperiodic structure following strict packing rules. (Fig.1, right). This paves the way to "program" a variety of 2D and 3D complex and functional structures by designing nanoobjects with specific geometrical shapes and their packing rules.

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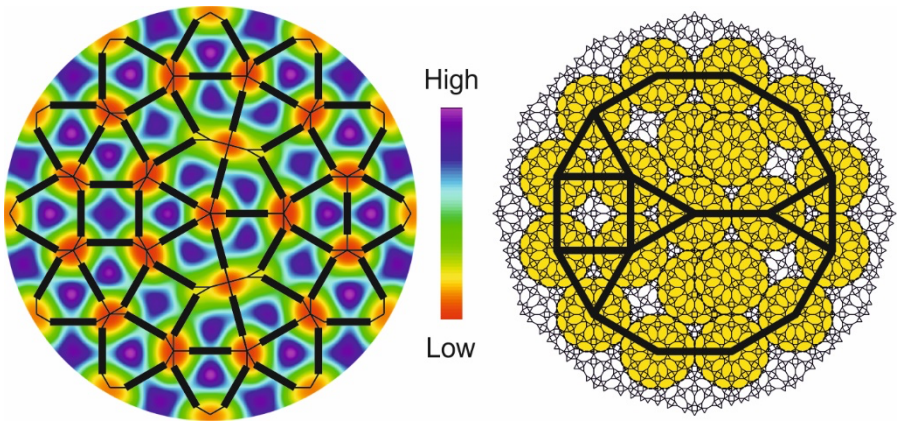

Fig. 1. Left: Electron density map, from triangular, square and trapezoidal cells to a local dodecagonal cluster. Right: Strictly quasiperiodic tiling of dedecagonal clusters.

Diverse Quasicrystals in Liquid Crystal Polymers: a Self-Consistent Field Study

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Recently, an increasing number of soft quasicrystals (QCs) have been discovered. However, theoretical study of soft QCs is still a big challenge. The reasons can be attributed to three aspects: suitable soft matter systems, realistic physical models, accurate and efficient algorithms. In this talk, we give a theoretical study of soft QCs for liquid crystal polymer systems, which has been extensively studied both in experiments and theories and can self-assembled into abundant crystals and possibly form QCs. Then we employ the self-consistent field theory (SCFT) to establish a realistic model for this system. SCFT is one of the most widely used mean-field models to study the equilibrium states of inhomogeneous soft matters, which can describe the microscopic information of polymerchain, such as the topology of macromolecule, interaction between different chemical monomers, and volume fraction chains. From a mathematical viewpoint, the SCFT is a high-dimensional nonlinear variational problem with multiple solutions and multi-parameters. Here we develop a series of advanced numerical methods and parallel techniques to solve the SCF model. Meanwhile, we give three self-similar dodecagonal tilings as well as their inflation rules in mathematics. Based on SCFT, we find that these QCs indeed exist in liquid crystal polymer systems. Furthermore, we also analyze the thermodynamic stability of these QCs. These results could provide a guideline to discover new QCs in soft matters.

Estimation of continuum/discrete models for QC formation

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Quasicrystals (QCs) are ordered structures lacking periodic translational symmetry. Despite intensive studies on the structural characterization of QCs, the kinetics and dynamics of QC formation are still elusive. To get insight into their generic mechanism, phenomenological models of QC formation are useful. There are two approaches: continuum nonlinear partial differential equations (PDEs) and discrete particle models. From a continuum approach, it was shown that at least two length scales are necessary for the formation of QCs [1]. The discrete models, using particles with multiple interaction length scales and anisotropic interactions, have also been used to clarify QC formation [2]. From the phenomenological models that were found, we may analyze the pictures required for the pattern, such as interactions between particles. When encountering a new pattern, we do not know the interactions leading to the pattern and, therefore, need to find a governing equation and parameters. However, finding the governing equation has been relying on a sophisticated guess and trial and error.
In this study, we discuss our recent efforts to estimate the best PDE or particle model for the objective pattern we want to reproduce [3,4]. First, we propose a method to estimate the best dynamical PDE from one snapshot of an objective pattern under the stationary state without ground truth [3]. We apply the method to the patterns, such as 2D dodecagonal QCs and Frank-Kasper structures. We also generate 3D dodecagonal QCs from a PDE model (Fig.1). Second, we propose an optimization method for the inverse structural design of anisotropic patchy particles (Fig.2). We use the relative entropy approach and find that five-fold symmetry is necessary for the 2D dodecagonal QCs. We will also discuss how to control the dynamical process of QC formation.

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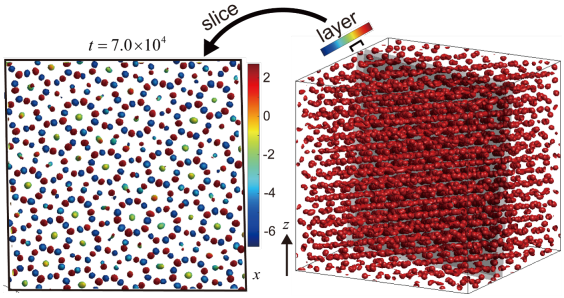

Fig.1: The dodecagonal QC obtained by the phase-field-crystal PDE model.

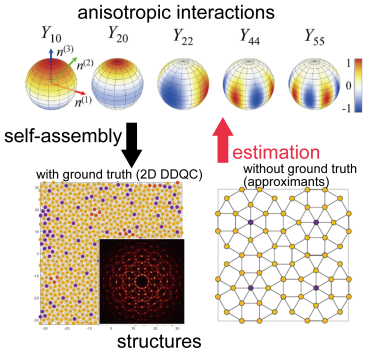

Fig.2: Estimation of the interactions between patchy particles.

Periodic and Quasiperiodic Tilings with Complexity in Microphase-Separated Pentablock Polymers

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Block polymers are known to self-assemble into microphase-separated structures in condensed state. Bulk structures of four-component pentablock polymers of the AS_1IS_2P(A:poly(4-vinylbenzyldimethylamine, S:polystyrene, I:polyisoprene, P:poly(2-vinylpyridine)) type are investigated in this work. Three copolymer samples were prepared based on anionic polymerizations *in vacuo*, with keeping the volume fractions of four component almost constant [1]. Only the variable molecular parameter, $\gamma = f_{S1}/f_{S2}$, is the ratio of two polystyrene blocks. Two series of binary blends from two out of three parent samples, AS_1IS_2P-*4* (γ = 0.93), AS_1IS_2P-*5* (γ = 0.56), AS_1IS_2P-*6* (γ =1.94), were prepared. The sample films were obtained by solvent casting from dilute polymer solutions, followed by heating for two weeks at 150℃ and finally annealing. Morphological observation was carried out by transmission electron microscopy (TEM, JEOL-JEM1400) coupled with small-angle X-ray scattering (SAXS, station BL-40XU at SPring-8 facility, Japan).

Figure 1a) shows a TEM image obtained from 46_9010 blend, which partly includes two kinds of 8/3 tilings (red and orange), 3.3.3.4.4 (purple) and 3.3.4.3.4 (blue) tilings. Fourier-transformed data from this TEM image is shown in Figure 1b), where twelve diffraction spots are clearly recognized though the spots are not exactly at equal distance from the image center, indicating the real image is slightly deformed. The number ratio of triangle/square is 544/235 ≒ 2.31_4, this value being close enough to $4/\sqrt{3}$ ≒ 2.30_9, and it is satisfying the necessary condition for triangle/square tiling with dodecagonal symmetry [2]. In addition, it has been found this basic condition commonly holds covering fairly wide γ range of $0.80 \leq \gamma \leq 1.0$, indicating this molecular system can exhibit aperiodic tiling pattern as a stable structure quite easily [3]. Moreover, it was also clarified that the strength of phason strain is different among the patterns depending on the *g* value of the system.

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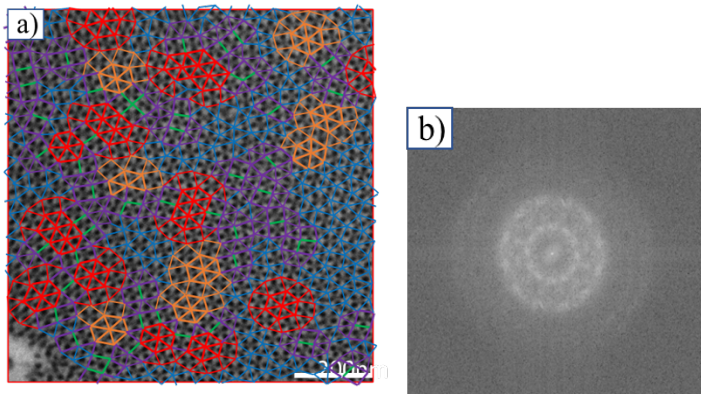

Fig.1: a) A TEM image representing a quasicrystalline tiling with dodecagonal symmetry. The two 8/3 tilings and the related patterns are drawn in red and orange and 3.3.3.4.4 tiling is in purple, while 3.3.4.3.4 tiling is in blue. b) FFT pattern obtained from the TEM in a).