Session II - Monday, August 31 - afternoon

PL2

CABINET OF CURIOSITIES: SELF-ASSEMBLY OF UNUSUAL CRYSTAL STRUCTURES

M. Engel[1], P. F. Damasceno[2], C. L. Phillips[3], J. Dshemuchadse[1], S. C. Glotzer[4]

[1]University of Michigan, Department of Chemical Engineering, MI 48105, USA
[2]University of Michigan, Applied Physics Programme, MI 48105, USA
[3]Argonne National Laboratory, Argonne, IL 60439, USA
[4]University of Michigan, Department of Materials Science and Engineering, MI 48105, USA

Atoms like to order. And although ordering often results in simple lattices, surprises are frequently encountered when searching long enough in parameter space. The discovery of the first quasicrystals was one such surprise, the growth of intermetallic crystal structures with thousands of atoms per unit cell another one. In many instances we do not understand why nature resorts to complexity, but we may certainly be intrigued by its observation.

In this presentation I will show several examples of unusual periodic and aperiodic crystal structures that we recently self-assembled from a disordered melt on the computer. Some of the crystals have atomic analogues. Many are hitherto unknown. None of them could have easily been predicted from the characteristics of the model alone. Our findings provide insight into the relationship of local geometry and crystallographic symmetry and the origin of stability of aperiodic order.

S2-L1

DEFORMATION OF TSAI CLUSTER EXTRACTED FROM HIGH-TEMPERATURE 1/1 PHASES - DIFFRACTION DATA REFINEMENT ASSISTED BY MODELLING

M. Mihalkovič[1,2,3], D. Liu[2,3], T. Yamada[4] and M. de Boissieu[2,3]

[1]Institute of Physics, Slovak Academy of Sciences, 84511 Bratislava, Slovakia
[2]Univ. Grenoble Alpes, SIMaP, F-38000 Grenoble, France [3]CNRS, SIMaP, F-38000 Grenoble, France
[4]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-9870, Japan
mihalkovic@savba.sk

Binary so called Tsai phases Cd6RE or Sc6Zn manifest intriguing competition between icosahedral symmetry of the outer shells of the constituting Tsai cluster, cubic symmetry of the crystalline lattice decorated by the clusters, and finally tetrahedral symmetry of the Cd4/Zn4 tetrahedral arrangement of the innermost cluster shell. Using physical model of fully relaxed icosahedral Tsai cluster whose shells deform to accommodate the tetrahedron at the cluster center, we revisit high-temperature datasets of Cd6Yb, Cd6Tb and ScZn6. Twelve possible orientational states of the tetrahedron lead to twelve orientations of the deformed adjacent shells of twenty-atom dodecahedron and 30-atom icosidodecahedron cluster shells, leading to several doubly and triply splitted Wyckoff sites. The refinement solutions improve reliability R-factors and remove (anisotropic) "static" spatial disorder contribution to thermal factors. Finally, using fitted empirical potentials, the refined deformed cluster shells can be used to fit mediated Cd4-Cd4 (Zn4-Zn4) interactions, that can be subsequently used for modelling low-temperature phase transitions observed in these phases.

S2-L2

CONTROLLING THE SELF-ASSEMBLY OF CLUSTER QUASICRYSTALS IN SYSTEMS CONSISTING OF ONE OR TWO TYPES OF SOFT ISOTROPIC PARTICLES

Ron Lifshitz

Raymond and Beverly Sackler School of Physics & Astronomy, Tel Aviv University,
*Tel Aviv 69978 Israel,*
ronlif@tau.ac.il

First discovered in liquid crystals made of amphiphilic dendritic macromolecules [1], self-assembled soft quasicrystals – predominantly with 12-fold symmetry – have since appeared in a wide variety of physical and chemical systems including ABC-star polymers [2], sphere-forming block copolymers [3,4], systems of nanoparticles [5], and in mesoporous silica [6]. In addition to having promising applications, especially in the optical domain, these materials give us the opportunity to study quasicrystals in ways that were impossible before. The main reason for this is the fact that their building blocks – rather than being individual atoms – are composed of large synthesized particles such as macromolecules, nanoparticles, and colloids. At these dimensions it may be possible to track the dynamics of individual particles, manipulate their positions, or even artificially place them at pre-assigned locations. Most important for our current discussion is the fact that it might be possible to design the interaction between particles. If so, an obvious question to ask, given a particular target structure, is how one should design this interaction to obtain the given structure.

In this talk I shall explain how to do just that, assuming that the particles interact via *ultrasoft* isotropic pair potentials that allow the particles to overlap. Such ultrasoft potentials are known to give rise to the formation of so-called *cluster crystals* [7], where the structure is composed of clusters of overlapping particles rather than the individual particles themselves. Moreover, these ultrasoft potentials can be Fourier transformed, which enables us to use a design scheme, recently proposed together with Barkan and Diamant [8,9], based on earlier ideas from the physics of Faraday waves [10]. The essential ingredient in our design scheme is the use of two length scales in the isotropic pair potentials. Along with an effective many-body interaction arising from entropy, these two length scales can then be used to control the assembled structure. This scheme was recently tested using molecular dynamics simulations, together with Barkan and Engel [11], on a system consisting of a single type of soft particles, allowing us numerically to obtain novel cluster crystals, including decagonal and dodecagonal cluster quasicrystals, as shown in Figure 1. More recently, together with Barkan and Mayzel [12], our design scheme was generalized for treating binary systems, consisting of two types of soft isotropic particles. Images of our newly self-assembled binary cluster quasicrystals will be shown here for the first time.

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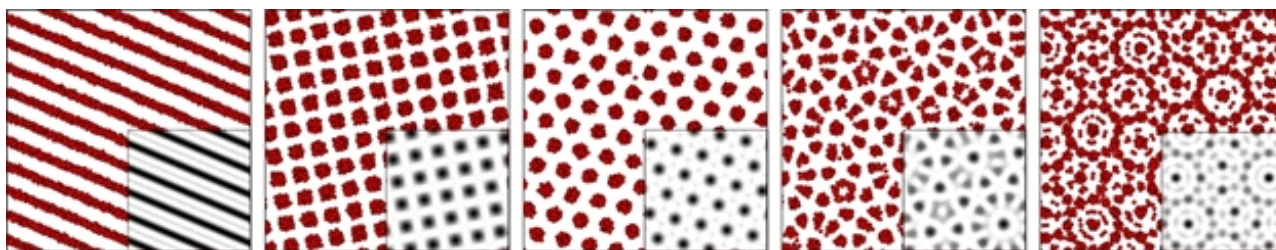
Figure 1. Five cluster crystals that were assembled spontaneously in computer simulations using the design scheme of Ref. [9] for the intermolecular interaction. Molecules are represented by red particles in the main figures, while the grey-scale figures in the corners display the corresponding structures, as predicted by mean-field theory. From left to right: stripes, 4-fold and 6-fold periodic crystals, and 10-fold and 12-fold quasicrystals. Reprinted from Ref. [11].

S2-L3

ATOMIC SCALE SIMULATION OF THE STRUCTURE AND DIFFUSE SCATTERING OF THE ZnSc QUASICRYSTAL AND 1/1 APPROXIMANT

D. Liu[1-2], M. Mihalkovic[3], T. Yamada[4], M. de Boissieu[1-2]

[1]Univ. Grenoble Alpes, SIMaP, F-38000 Grenoble, France
[2]CNRS, , SIMaP, F-38000 Grenoble, France
[3] Institute of Physics, Slovak Academy of Sciences, 84511 Bratislava, Slovakia
[4] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-9870, Japan
Marc.de-boissieu@simap.grenoble-inp.fr

The binary CdYb icosahedral quasicrystal, referred to as Tsai type quasicrystal, is one of the rare quasicrystalline system for which a detailed understanding of the atomic structure [1] and some of their physical properties has been achieved [2]. The structure is described as a packing of three clusters: a large triacontahedron (LTR), a double Friauf polyhedron (DFP) and a prolate rhombohedron [1]. The central part of the cluster is a tetrahedron that induces a strong distortion of the surrounding shells, and breaks their icosahedral symmetry. Studies of the 1/1 Zn-Sc approximant and the i-Zn-Mg-Sc quasicrystal, combining quasielastic neutron scattering and atomic scale simulations have shown that at high temperature the tetrahedron behaves as a single Cd_4 'molecule' and reorient dynamically with a time scale of the order 1 ps, giving an exceptional dynamical flexibility to this system [3-4]. In the 1/1 cubic approximant this dynamics take place up to the transition temperature where the system undergoes a transition to a monoclinic phase and an ordering of the terahedra, with pretransitional diffuse scattering [5].

Understanding the mechanisms that stabilise long range quasiperiodic order remains one of the main challenge in the field. In particular the balance between the energetic and entropic part, in particular the one related to phason fluctuations (see [6]) is far from being understood. Phason fluctuations are known to give rise to a characteristic signature in term of diffuse scattering, which has been observed in all icosahedral quasicrystal, although with a varying intensity and shape anisotropy [6]. To tackle this problem we have undertaken an atomic scale simulation, using oscillating potentials and large approximant (5/3) for the quasicrystal and large supercell (4x4x4) for the 1/1 approximant. The 5/3 approximant is described as a canonical cell tiling. Molecular dynamics at different temperature has been carried out and the simulated Bragg and diffuse scattering has been followed carefully. Clear differences between th periodic approximant and the quasicrystal have been observed and will be discussed.

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S2-L4

QUASIPERIODIC CANONICAL-CELL TILING WITH CUBIC SYMMETRY

Nobuhisa Fujita

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
nobuhisa@tagen.tohoku.ac.jp

In canonical-cell tiling models of icosahedral quasicrystals and their approximants, the atomic structure is described as a packing of icosahedral clusters that are centered on the vertices of a tiling composed of four basic polyhedra called the canonical cells [1]. This so-called canonical-cell geometry has indeed been observed in many approximants to icosahedral quasicrystals categorized as either P-type or F-type. Hence, it is highly likely that the geometry applies also to icosahedral quasicrystals, for which the corresponding tiling should be quasiperiodic. To date, however, it has never been proved that the canonical cells can tile the space in a quasiperiodic manner such that icosahedral symmetry is globally retained. In this work, an inflation rule for the canonical cells is worked out, and the existence of a quasiperiodic canonical-cell tiling is confirmed for the first time. In the inflation process, each of the canonical cells is expanded by a factor of tau^3 (tau: golden mean), and it is then divided into cells of the original sizes. It is shown that there are several different ways to divide expanded cells of the same shape, still the division rules are uniquely determined according to their local environments. The atomic surface of this quasiperiodic canonical-cell tiling is revealed through mapping the vertices of a large patch into the internal space. It then turns out that, although the supporting module is icosahedral, the atomic surface exhibits cubic symmetry.

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