Structural complexity in monodisperse systems of isotropic particles

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Abstract

It has recently been shown that identical, isotropic particles can form complex crystals and quasicrystals. In order to understand the relation between the particle interaction and the structure, which it stabilizes, the phase behavior of a class of two-scale potentials is studied. In two dimensions, the phase diagram features many phases previously observed in experiment and simulation. The three-dimensional system includes the sigma phase with 30 particles per unit cell, not grown in simulations before, and an amorphous state, which we found impossible to crystallize in molecular dynamics. We suggest that the appearance of structural complexity in monodisperse systems is related to competing nearest neighbor distances and discuss implications of our result for the self-assembly of macromolecules.

1 Introduction

When kept long enough at low temperatures, most systems develop long-range order. The easiest crystallization is expected for monodisperse systems, because only topological, but no additional chemical ordering is necessary. If the particles are isotropic, then a first reasoning suggests a preference to form simple, close-packed crystals, since this allows all of them to have the same, high first coordination numbers. A look at the periodic table reveals that indeed the ground states of most metals are bcc, fcc, or hcp [1]. Similar simple crystals are found in mesoscopic or macroscopic systems like for example globular proteins [2], monodispersed colloids [3], and bubble rafts on liquid surfaces [4].

In some of the systems above, quantum mechanics does not play an important role. Hence, it should in principle be possible to understand crystallization by using classical

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pair interactions. For monodisperse systems there is only one type of interaction given by the shape of the potential function. Many common potentials are smooth and have a single minimum only. Simulations with these potentials usually lead to simple crystals. An example is the Lennard-Jones (LJ) potential.

Nevertheless, the situation is not always that easy. Over the last years, more complex structures have been observed in experiments and simulations. A large part of work in this direction started after the discovery of quasicrystals in metallic alloys and was carried out with the aim to understand their formation. Another type of complex order are periodic crystals with large unit cells, so-called complex crystals. Whereas the lattice constants of a simple crystal are comparable to the range of the particle interactions, the unit cell of a complex crystal is stabilized indirectly, e.g. by geometric constraints.

On the theoretical side, the obvious procedure to promote structural complexity is to use potentials with a more complicated radial dependence. It has been shown with double-minima potentials [5], oscillating potentials [6], and a repulsive barrier [7] that the energy of an icosahedral phase can be lower than the energy of a class of trial structures including close-packed phases. Surprisingly, even in the LJ system, a quasicrystal is unstable only by a small energy difference [8].

These early works relied on general arguments and did not try to observe real crystals in simulations. Dzugutov was the first to actually grow a stable one-component dodecagonal quasicrystal from the melt [9], although it was later found to be only metastable [10]. He used a LJ potential with an additional bump to disfavor the formation of simple crystals. Although no further work on other three-dimensional systems has been reported, there are many investigations focusing on two-dimensional systems, where computation and visualization is easier. The first such study applied a variation of the Dzugutov potential and found a planar dodecagonal quasicrystal [11]. Furthermore, it was pointed out that a decagonal quasicrystal appears with a square-well [12] and a ramp potential [13].

Experiments show that nature is quite ingenious in her way to assemble identical particles. First of all, a few complex ground states of elemental metals are known to exist. A notable example is α-manganese, which has cubic symmetry with 58 atoms per unit cell. Thermodynamically stable high-temperature phases are β-boron with 105 atoms and β-uranium with 30 atoms per unit cell [11]. The latter is isostructural to σ-CrFe and known as the sigma phase. Furthermore, commensurately modulated phases are common at high pressures [14].

Recently, different kinds of macromolecules have been observed to self-assemble into complex phases: (i) Under appropriate experimental conditions, tree-like molecules (dendrons) forming spherical micelles arrange to a dodecagonal quasicrystal [15]. (ii) T-shaped molecules can be designed in such a way that they organize into liquid crystalline honeycombs [16]. (iii) ABC-star polymers form cylindrical columns according to square-triangle quasicrystals, a two-dimensional version of the sigma phase [17], and other Archimedean tilings.

How can structural complexity be understood from bottom-up? It is instructive to study the ground state for small portions of the system — more or less spherical clusters — as a function of the particle number \( N \). The structure of small clusters (\( N < 200 \) in three
dimensions, \( N < 30 \) in two dimensions) is often different from the bulk crystal \[18\]. The reason is the competition between local lowest energy configurations and the necessity of continuation in space. For example in a monodisperse LJ system, icosahedral coordination occurs in small clusters \[19\], although the hcp phase is the lowest energy bulk crystal \[20\]. On the other hand, if small clusters already have simple structure, then the bulk phase will also be simple. A local order, which is incompatible with periodicity, is a necessary condition for structural complexity in the bulk.

2 Phase diagram for the two-dimensional system

There are two mechanisms to introduce structural complexity: either by destabilizing simple phases or by stabilizing a complex phase. An example for the destabilization mechanism is the Dzugutov potential. We adopt the stabilization mechanism, because it has the advantage that the choice of the target structure can be controlled more directly.

The particles are assumed to interact with an isotropic two-scale potential. A simple ansatz is the Lennard-Jones-Gauss (LJG) potential

\[
V(r) = \frac{1}{r^{12}} - \frac{2}{r^{6}} - \epsilon \exp \left( - \frac{(r - r_0)^2}{2\sigma^2} \right),
\]

which has for small \( r_0 \) the shape of a shoulder, and otherwise represents a double-well with first minimum at \( r \approx 1 \) with depth \( V(1) \approx 1 \) and second minimum around \( r_0 \) with \( V(r_0) \approx \epsilon \). The parameter \( \sigma \) specifies the width of the second minimum. The shoulder form has been used extensively to observe liquid-state anomalies \[21\] and for understanding liquid-liquid transitions \[22\]. Surprisingly, almost nothing has been known until recently \[23, 24\] about the solid-state behavior of \( V \).

In two dimensions, the local lowest energy configurations are regular polygons. As shown in Fig. 1(a), there are two possibilities: polygons with or without central atom. An \( n \)-gon without central atom is stabilized by having the second minimum at

\[
r_0 = 2 \cos(\pi/n).
\]

The \( m \)-gon with central atom is favorable for

\[
r_0^{-1} = 2 \sin(\pi/m).
\]

The values \( n = 3 \) and \( m = 6 \) lead to hexagonal local order (Hex), the value \( n = 4 \) to squares (Sqa), and \( n = 6 \) to honeycombs (Hon). Furthermore, pentagonal \( (n = 5, \text{Pen}) \), decagonal \( (m = 10, \text{Dec}) \), and dodecagonal \( (m = 12, \text{Dod}) \) local order is possible. We find that \( m \)-gons are not stable for other values of \( m \). For \( n > 6 \) the vacancy is too big. The sequence of local orders as a function of \( r_0 \) is expected to look like in Fig. 1(b).

Next, we calculate the \( T = 0, p = 0 \) phase diagram in the \( r_0-\epsilon-\sigma^2 \) parameter space via annealing simulations and structural relaxation. For details, we refer to \[24\], where the same procedure has been applied. The result is depicted in Fig. 2. A wide second
minimum ($\sigma^2 = 0.042$) stabilizes mostly simple phases. There are two hexagonal lattices (Hex, Hex2), which are connected continuously along small $\epsilon$-values. A rapid increase of the lattice constant is observed at the dashed line. Additionally, the square lattice (Sqa) and a phase built from deformed pentagons and triangles (Pen2) are found.

Further structures appear for $\sigma^2 = 0.02$: a complicated phase with decagons (Xi), a related one with flattened honeycombs (Xi2), a phase with pentagons and hexagons (Pen), the two-dimensional sigma phase (Sig), and alternating rhombs (Rho). In the case of $\sigma^2 = 0.01$, parallel rhombs (Rho2) are stable. We remark that the phase diagram differs slightly from the one published in [24] due to a higher precision of the relaxation: Sig2 and Sig3 are now unstable, whereas Xi2 and Pen2 appear as new phases. In total, nine ground states have been discovered, among them five complex crystals (Tab. 1).

The sequence of phases in Fig. 2 follows the local order analysis in Fig. 1. Hence, the phase diagram can be understood as the result of stabilizing regular polygons. We assume that the behavior is universal in the sense that the phase diagram looks similar for most two-scale interaction potentials.

It is interesting to study the ground state energy per particle, $E$, as a function of the potential parameters. In Fig. 3 the rescaled energy $E'(r_0, \epsilon) = E/(\epsilon + 1)$ is plotted. The

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**Figure 1:** (a) The local lowest energy configurations in two-dimensional monodisperse systems are polygons with or without a central atom. (b) Expected phase behavior of two-scale potentials. $r_0$ is the position of the second minimum.

**Table 1:** The complex crystals observed in the LJG system. The nearest-neighbor distance is equal 1.
Figure 2: Phase diagram of the two-dimensional LJG system for three values of $\sigma^2$. For each crystal the decoration of a unit cell is shown.
rescaling enforces convergence in the limit $\epsilon \to \infty$. For a given phase the energy has a minimum near $r_0$ defined by (2) and (3). Sometimes the phase is not stable at its minimum energy. As seen in Fig. 3, the stability regions of Pen/Pen2 and Xi/Xi2 are shifted to lower $r_0$ values due to competition with Hex.

An important aspect of the two-dimensional LJG system is the fact, that all phases can actually be grown as single crystals in simulations, if the cooling time is slow enough. When heating the system up, the complex crystal often reversibly transform into quasicrystals. This is the case for Xi [24], but also for Pen/Pen2 and Sig [25], and means that these phases are not accessible from the melt, but have to form via a solid-solid transformation from the quasicrystal [26].

3 The sigma phase and a glass in three dimensions

In this section, first results for the three-dimensional LJG system are presented. Its full $T = 0, p = 0$ phase diagram is not known. Nevertheless as we show now, the LJG potential allows to grow at least one complex crystal in simulations. We ran 11 simulations with $\epsilon = 1.8, \sigma^2 = 0.02, \Delta r_0 = 0.1$. Standard molecular dynamics (MD) with a Nosé-Hoover thermo-/barostat and periodic boundary conditions were applied. The cubic simulation box contained 2744 particles with an initially amorphous configuration.

We searched for temperatures close to, but below the melting point for rapid crystallization. We were successful to achieve crystallizations for all $r_0$ values except 1.4. After a few $10^5$ MD steps, six different crystals have been grown: fcc (cF4, $r_0 = 1.0$), hcp (hP2, 1.6),...
Figure 4: Single crystal of the sigma phase grown with molecular dynamics using 15 625 particles. (a) Projection along the four-fold symmetry axis. (b) Diffraction image. (c) Fourier-filtered structure image with tiling superimposed.

bcc (cI2, 1.1-1.2, 1.7-1.9), shl (hP1, 1.3), pzt (tP5, 2.0), sig (tP30, 1.5). Here, shl is the simple hexagonal lattice (prototype: $\gamma$-HgSn$_{6-10}$, disordered), pzt the tetragonal perovskite structure (PbZr$_x$Ti$_{1-x}$O$_3$), and sig the sigma-phase ($\beta$-uranium).

It was observed that the particles cannot relax effectively with periodic boundaries, since point defects and dislocations do not heal out. Therefore, the simulations were repeated with open boundaries, i.e. the particles form a solid sphere floating in vacuum. The structures are the same, but this time single crystals were obtained. The possibility to simulate at zero pressure is an advantage of the LJG potential. For the Dzugutov potential, external pressure usually has to be applied, because of the repulsive bump in the interaction.

For $r_0 = 1.5$, the sigma phase was observed. To study its formation in detail, we simulated a large system of 15 625 particles at $T = 1.7$ (as usual $k_B = 1$), which is about 90% of the melting temperature. After less than $10^5$ MD steps, local crystallization started and a polycrystal with dodecagonal quasicrystallites appeared. Ordering proceeded in two steps: first to a bicrystal at $10^6$ steps and then to a single crystal at $2 \cdot 10^6$ steps. At the same time, rearrangements within each crystallite transformed the quasicrystal state into the sigma phase. After $3 \cdot 10^6$ steps the system was relaxed to $T = 0$.

Fig. 4(a) shows the configuration of the particles projected along the four-fold axis. The width of the Bragg peaks in the diffraction image (Fig. 4(b)) is determined by the system size. By selecting only the twelve inner strong reflections for an inverse Fourier transform, we obtain a Fourier filtered structure image (Fig. 4(c)). It allows to easily detect the underlying tiling. Cylindrical columns with pentagonal shape forming squares and triangles in a ratio 1:2 are characteristic for the sigma phase.

We note that the sigma phase is unstable at $T = 0$, because fcc has a lower energy than sig. To test the stability at $T = 1.7$, we initiated a simulation of a fcc crystal in contact
with a sigma crystal. Quickly, the whole system transformed into a single fcc phase. Hence, the sigma phase is also not stabilized entropically. The reason for its appearance in our simulations is the huge nucleation radius of fcc. The local order of sig is much closer to the melt. Further details will be reported elsewhere.

In the case \( r_0 = 1.4 \), all attempts to crystallize the system failed. One reason is the comparably low melting temperature: the ground state fcc melts around \( T = 0.9 \). In various MD runs over several \( 10^6 \) steps in the range \( 0.5 \leq T \leq 0.9 \) no nucleation was observed. We conclude that the choice \( r_0 = 1.4 \) is interesting for studying a monatomic glass. Our results indicate that this LJG glass is more resistant against crystallization than the Dzugutov glass [27], which forms the dodecagonal quasicrystal rather quickly [9, 10, 28].

4 Discussion

How does the LJG system compare to experiments? In metals, multi-body terms can only be neglected in a first approximation. Effective potentials often have Friedel oscillations, which are mimicked by double-wells. It should be kept in mind that fixed pair interactions between all atoms might not be applicable in complex phases, since the atoms are found in different local environments. Furthermore, the interaction is expected to change during crystallization.

Isotropic pair potentials are more applicable to macromolecular self-assembly, because the molecules as a whole interact almost classically. It has been suggested [29] that their complex arrangements originates from the competition of two length scales, which appear due to soft repulsion and strong interpenetration. The micelles forming the dodecagonal quasicrystal in [15] have two natural length scales: the inner one corresponds to the backbone of the dendrons and the outer one to the end of the tethered chains. Our simulations suggest that the ideal ratio of the scales is close to 2:3.

The cylindrical phases (T-shaped molecules and ABC-star polymers) can be understood as two-dimensional tilings with an effective interaction within the plane. Although not isotropic anymore, the particles still have two length scales. The tilings observed so far [30, 31] consist of hexagons, squares, and triangles only. If it will be possible to stabilize pentagons or decagons, then the phases Pen/Pen2, Xi/Xi2 might appear.

We finish with a challenge: Can monodisperse icosahedral quasicrystals be grown in simulation or experiment? As of today, none have been found.

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