Using Monte Carlo simulations, we investigate the equilibrium phase behaviour of a monodisperse system of Mackay icosahedra. We define the icosahedra as polyatomic molecules composed of a set of Lennard-Jones subparticles arranged on the surface of the Mackay icosahedron. The phase diagram contains a fluid phase, a crystal phase and two rotator phases with different degrees of orientational correlations. At high temperatures icosahedral molecules behave similar to hard geometric icosahe-
dra for which the densest lattice packing and the rotator crystal phase have been identified before. We confirm that both phases form at finite temperatures as well. At low temperatures the system forms a rotator face-centered cubic crystal. With increasing temperature there is first a transition to the densest lattice crystal then back to a rotator phase, i.e. the system shows re-entrant behaviour.

I. INTRODUCTION

When a small number of atoms or molecules are forced together they tend to form locally densely packed clusters, in which a central atom is covered by 12 nearest neighbours located at the vertices of an icosahedron. Since these structures posses a five fold symmetry, which is a forbidden crystal symmetry, they can not extend to large length scales. Instead they are often seen as favoured, persisting local structures in supercooled liq-
uids and glass-forming substances [1, 2].

Mackay generalized this construction to larger multiply twinned superlattices of densely packed spherical subpar-
ticles with icosahedral symmetry [3]. These are composed of 20 slightly deformed close-packed tetrahedra which are merged together in such a way that their adjacent planes form twinning crystal domains while their outer planes constitute the 20 faces on the surface of an icosahedron (Fig. 1). If the number of constituent particles is below \( \sim 10^3 \) Mackay icosahedra have been shown to globally minimize the Lennard-Jones potential energy surfaces [4], to result from enthalpy-driven assembly of colloids [5] and to maximize the entropy in spherical confinement of hard spheres [6]. These polyhedral nanocrystals are favoured local structures in diverse systems such as noble gas atoms and molecules [7], gold nanoparticles [8] and clusters of metal atoms [9]. They are thus ubiquitous in nature and constitute an important class of structures.

Interesting from a technological point of view, are in particular the clusters formed by confined colloids, as they could be used as building blocks in hierarchi-
cally structured materials. Confinement of spherical gold nanoparticles inside spherical surfaces of emulsion droplets leads to an assembly of nanocrystals with superlattices corresponding to Mackay icosahedra [8]. The structures of these clusters keep the polyhedral character also for binary mixtures of particles with different attractions [10] while differences in atmospheric pressure can determine the formation of either a complex binary crystal superlattice or core-shell or Janus clusters in dispersions of nanoparticle with binary size distributions [11].

Mackay icosahedra have also been observed for collec-
tions of nanometer- and micrometer-sized hard, spherical colloids in spherical confinement [6]. As such structures have been synthesized, we now aim to use them for bot-
tom up design of functional materials. To determine the properties of these materials an understanding of their equilibrium phase behaviour is a necessary prerequisite.

We thus present here a study of the phase diagram of a suspension of Mackay icosahedra as they would result from a confined colloidal aggregation experiment.

The infinite pressure and temperature boundary of the
phase diagram for geometric icosahedra is already known (at infinite temperature the attractive part of the potential becomes irrelevant, thus the interaction becomes a pure hard-core repulsion). To find the optimal arrangements of congruent objects that do not tile space and their associated maximal density is an ancient mathematical challenge that remains unsolved for all non-trivially shaped objects except for the sphere - the densest packing of which had been conjectured already by Kepler and has only been proven about a decade ago [12]. A more recent conjecture suggests that the densest packings of centrally symmetric Platonic and Archimedean solids are their corresponding optimal Bravais lattice packings [13]. For hard icosahedra (and several other regular polyhedra) the densest lattice packing has been determined using different numerical optimization algorithms [13] [15]. The putative optimal arrangement is a locally jammed packing with density 0.8363574 where each icosahedron contacts 12 neighbors and is represented by a Bravais lattice with a triclinic unit cell where each point contains a single uniformly oriented body (see Fig. 2). Another work has shown that a dense fluid of hard icosahedra assembles into a close-packed (FCC or HCP) rotator crystal where particles are allowed to freely rotate about their lattice positions [16]. Packing small numbers of hard icosahedra in a hard spherical container results in clusters that resemble or match sphere clusters (optimal sphere codes) despite significant faceting of these objects [17].

The bulk behaviour of Mackay icosahedra has not yet been studied systematically although such structures are ubiquitous in nature and they could have technologically important implications for material science. In the present work we explore the equilibrium phase behaviour at finite temperatures and pressures using Monte Carlo simulations. We choose to study the phase behaviour for an icosahedron composed of 55 particles arranged in a Mackay fashion as its size is small enough for the energy computation to be feasible, while it still captures the geometrical features of icosahedra and allows for a description of energetic attributes of such objects. We show that the predicted densest packing and rotator phases for hard icosahedra are also stable at finite temperatures. In the low temperature regime we observe re-entrant behaviour due to the increased importance of energetic interactions which are not captured by the hard icosahedron model.

### II. SIMULATION METHODS

The Mackay icosahedron shown in Fig. 1 is composed of 55 subparticles arranged in two complete shells around its center. This quasi-spherical arrangement is a particularly stable motif in the minimal energy Lennard-Jones diagrams for binary systems of particles in a wide range of different attraction ratios [16]. Some of its geometrical properties are given in Table I where we see that the volume of the icosahedron fills only 58.2% of the circumscribed sphere. Due to this significant deviation from a spherical shape entropial effects are expected to play an important role in systems of such molecules. (We estimated the volume of the molecule with a Monte Carlo integration using an effective repulsive radius of subparticles, \( r_{\text{rep}} = 2^{1/6} \sigma / 2 \), where \( \sigma \) is the usual Lennard-Jones potential range parameter.)

![Table I](image)

| Geometrical property           | Value   |
|-------------------------------|---------|
| Inradius \( r_{\text{in}} \) / \( \sigma \) | 1.835   |
| Circumradius \( r_{\text{c}} \) / \( \sigma \) | 2.141   |
| Effective circumference \( r_{\text{eff}} \) / \( \sigma \) | 2.702   |
| Effective volume \( V_{\text{eff}} / \sigma^3 \) | 48.091  |
| Equivalent spherical radius \( r_{\text{sc}} \) | 3.637   |
| Scaled exclusion volume \( V_{\text{eff}} / V_{\text{out}} \) | 0.582   |

The interaction energy between two icosahedral molecules depends on the distance between their centers and on their mutual orientation. The icosahedron is a nonlinear, rigid molecule whose configuration is given by a translational vector of its center \( r = (x, y, z) \) and a quaternion \( q = (a, b, c, d) \) specifying its orientation. To calculate the positions of all subparticles after the rotation we use a rotation matrix given by

\[
R = \begin{pmatrix}
  a^2 + b^2 - c^2 - d^2 & 2(bc - ad) & 2(bd + ac) \\
  2(bc + ad) & a^2 - b^2 + c^2 - d^2 & 2(ac - bd) \\
  2(bd - ac) & 2(ac + bd) & a^2 - b^2 - c^2 + d^2
\end{pmatrix}.
\]

(1)

We then calculate a sum of Lennard-Jones terms of all the pairs of subparticles

\[
U(r_{1}, r_{2}, q_{1}, q_{2}) = 4\epsilon \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ \frac{\sigma}{r_{ij}}^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right],
\]

(2)

where \( r_{ij} \) is the distance between subparticles \( i \) and \( j \) and \( N = 42 \). We apply a cutoff of 2.5 \( \sigma \) to the interaction between two subparticles and thus exclude the contribution of the core particles. Additionally a cutoff of 7.0 \( \sigma \) is applied on the interaction between a pair of icosahedra.

The effective (repulsive) diameter of an icosahedron is in a range \( d_{\text{rep}} \in [4.7922 - 5.4046] \sigma \). Taking into account that the Lennard-Jones system compares to square-shoulder system with parameter \( \lambda \sim 1.5 \) [18] we estimate that an icosahedron is comparable to a sphere with a square shoulder potential with an attractive range of \( \lambda \sim 1.1 \). It is expected that the equilibrium behaviour of icosahedra will show qualitative features similar to those in polymer-colloid mixtures of a comparable attraction range which can be tuned by the size ratio of the depletant and colloids [19].

To equilibrate a monodisperse system of icosahedra with periodic boundaries we use a Monte Carlo method [20] in the isobaric-isothermal ensemble with a
variable box size \textsuperscript{21} \textsuperscript{22}. To release the eventual stresses in the orthogonal simulation box we additionally employ Parrinello-Rahman sampling of the variable box shape \textsuperscript{23} \textsuperscript{27}. Deformations of the simulation box are limited to avoid unphysically deformed systems.

Initially we either place the icosahedra in a low density disordered fluid arrangement without any overlaps or on a spherical FCC lattice with arbitrary orientations. Two million Monte Carlo cycles are then performed to equilibrate from several different initial conditions at a given pressure and temperature. Displacement and rotational moves are used to sample configurations, where random orientations of the molecules are generated by sampling quaternions on the surface of the 4D unit sphere \textsuperscript{28}.

We use different structural descriptors to analyze the positional and orientational behaviour. The positional order is monitored by computing the radial distribution function. Steinhardt bond orientational order parameters are used to quantify the bond network of nearest neighbors \textsuperscript{2}. In both quantities the icosahedra are replaced by points lying in their centers (centroids). To measure the amount of orientational order in a system of nonlinear molecules one needs to define a set of characteristic vectors attached to the model molecule. In the case of Mackay icosahedra we chose either the normals of the 20 triangles or the vectors pointing from the center to the 12 vertices on the surface of icosahedron, the results are similar for these choices. The orientational pair correlation function (OPCF) can then be defined as \textsuperscript{29}

\[
g_{\text{opcf}}(r) = \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r - r_{ij}) \left( \sin^2 \alpha_{ij}^{F_1} + \sin^2 \alpha_{ij}^{F_2} \right) / 2}{\sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(r - r_{ij})}
\]

(3)

where $\alpha_{ij}^{F_1}$ and $\alpha_{ij}^{F_2}$ denote the first and the second minimal angles formed by any pair of the characteristic vectors associated to particles $i$ and $j$ such that $\alpha_{ij}^{F_1} \leq \alpha_{ij}^{F_2}$.

The values of such a pair correlation function can get arbitrarily close to zero for highly orientationally ordered systems while its maximum values are limited by the largest values of the minimal angles which depend on the choice of characteristic vectors.

\section*{III. EQUILIBRIUM PHASE BEHAVIOUR}

We carried out Monte Carlo simulations in the NPT ensemble of 500 monodisperse icosahedra for a range of temperatures and pressures to explore the possible equilibrium phases. We quantify the positional and orientational correlations in the equilibrated systems using the radial distribution function and orientational pair correlation function. Snapshots of the systems with four different structures that were observed as stable phases are shown in Fig. 2. $T$ is given in units $\epsilon/k_B$ and $p$ in units $\epsilon/\sigma^3$. We observe four structural transitions with increasing temperature. A disordered liquid at low temperatures transforms into a FCC rotator crystal and afterwards into a BCC crystal or densest icosahedral lattice depending on the pressure. Further increase in temperature melts a crystal phase into another FCC rotator phase and finally into a disordered liquid at very high temperatures.

In Fig. 3 we analyze the behaviour of positional order in a system at constant pressure for three different temperatures. We see that the icosahedra arrange on a FCC lattice at low temperatures, then transform into a BCC lattice with increasing temperature and then turn back into FCC. This trend was observed at almost all values of the pressure that we studied but became less strong at higher pressures where icosahedra form phases without long range positional or orientational order at low temperatures.

The corresponding orientational pair correlations were computed using the normals of the 20 faces of an icosahedron as characteristic vectors and are shown in Fig. 3 for the same three systems. Small values correspond to high mutual alignments while the strong oscillations are a consequence of regular particle positions as OPCF is defined analogously to the RDF histogram but with dif-
We attempted to categorize the resulting phases into four groups according to the orientational and positional correlations and the bond orientational order parameters \( \rho_{\text{eff}} \). At very low pressures, the box deformation moves in the Monte Carlo algorithm sometimes produced unphysically flattened boxes that induced long-range orientational order, but otherwise no valid equilibrated states with liquid crystalline order were observed. We find a trend of going from a rotator crystal to a crystal and back to a rotator crystal phase with the increasing temperature for a range of pressures. This confirms our expectations that the exact geometrical shape of an icosahedron is relevant only up to some temperature above which icosahedra behave as spheres while at low temperatures energetic interactions become important and destabilize long-range orientational order.

In the analysis of the phase diagram scan we did not precisely categorize different crystal phases, we noticed however, that when positional order was present it was either FCC for rotator phases or BCC and densest icosahedral packing for crystal phases. The densest lattice packing of hard icosahedra was observed at low pressure, \( p = 1 \), and at temperature \( T = 3 \). Both correlation functions of this system are shown in Fig. 6 where a comparison is done with the densest lattice of hard icosahedra [15], the snapshot from the system can be seen in Fig. 2.
IV. CONCLUSIONS

We have investigated the equilibrium phase behaviour of a monodisperse system of Mackay icosahedra composed from Lennard-Jones subparticles. This type of cluster is a representative nanocrystal shape that can be formed in experiments with agglomeration inside emulsion droplets. The analysis of the order by the positional and orientational pair correlation functions has shown a fluid phase, a rotationally disordered crystal with an FCC crystal lattice, and a uniformly oriented crystal phase with either BCC ordering or the densest lattice packing of hard icosahedra.

Some of these phases have already been predicted before for hard regular icosahedra using different approaches but the densest icosahedral lattice packing is yet to be confirmed experimentally. At low temperatures where energetic interactions result in preferred face to face alignment, the system forms a rotator crystal, which is might meta-stable with respect to a yet to be identified, more complex crystalline arrangement. This effect leads to the re-entrant behaviour with increasing temperature where first a transition to the crystal occurs and then the rotator phase is formed again at higher temperatures due to excluded volume effects.

While it takes a considerable amount of time to evaluate all the pair energies of the subparticles within the cutoff range, the model also offers several interesting possibilities to generalize the components under study. For example, interesting structures to study would be those where the vertices have attractions with an increased range or other properties describing functionalised interaction sites in nanocrystals which can be achieved e.g. by DNA-based ligands or inclusion of magnetic subparticles that can assemble under external magnetic fields. This would enable us to evaluate the assembly of the patchy building blocks in the form of binary icosahedral clusters with symmetric or Janus arrangements of interacting sites on the surface of clusters which have been predicted before.

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