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Plastic fluctuations in empty crystals formed by cubic wireframe particles

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We present a computer simulation study of the phase behaviour of colloidal hard cubic frames, i.e. particles with non-convex cubic wireframe geometry interacting purely by excluded volume. Despite the propensity of cubic wireframe particles to form cubic phases akin to their convex counterparts, these particles exhibit unusual plastic fluctuations in which a random and dynamic fraction of particles rotate around their lattice positions in the crystal lattice while the reminder of the particles remains fully ordered. We argue that this unexpected effect stems from the non-convex geometry of the particles in which the faces of a particle can be penetrated by the vertices of the nearest neighbours even at high number densities.

INTRODUCTION

One of the triumphs of statistical mechanics in the past century has been the prediction that colloidal particles interacting via short-range repulsive potentials exhibit complex phase behaviour. Beginning with the theoretical studies of Kirkwood [1], subsequent simulations provided the first evidence of the crystallisation of hard spheres [2–4]. Around the same time, Onsager reported his pioneering work to describe the isotropic-nematic phase transition in systems of thin hard rods and hard discs using a free-energy functional analysis that depends on the single-particle orientation distribution function [5], yet it took several decades for evidence of the formation of stable smectic and columnar phases using computer simulation experiments [6–11]. Much early simulation and theoretical work demonstrated that the shape of colloidal particles is one of the most important features determining their collective phase behaviour [12–16]. By today we know of a host of crystals, liquid crystals, plastic crystals and quasicrystals formed by hard particles of different shapes and sizes [14, 17, 18].

Particular emphasis has been given to the study of colloidal particles with convex shapes such as spheres, rods, discs, polyhedra, etc. However, particles with non-convex geometries have become increasingly important due to advances in synthetic protocols for the fabrication of particles with complex morphologies and sizes [19–23] and tunable interparticle interactions [24]. Simulations of non-convex particles represent a challenge due to the complex interparticle interactions such as interpenetration, shape complementarity, entanglement, and interlocking that can compromise global equilibration. However, it has been demonstrated recently that these complex interactions can be harnessed to design materials with complex structures [25–33]. For example, simulation studies of rigid planar rings demonstrated that interpenetration of the particles promotes the unusual formation of stable smectic phases, provided that both interpenetration and symmetry of the rings are high enough [31]. These liquid crystalline structures are characterised

by extremely large free volume since the non-convex rings are essentially empty, i.e. colloidal rings form smectic phases with unusually high free volumes. Similarly, experimental and simulation studies of branched particles reveal that interlocking effects can promote the formation of ordered superlattices [26].

The aim of this study is to understand the effect of interpenetration in three-dimensional wireframe particles. In particular, we study the phase behaviour of a particle model of hard cubic frames (HCFs) interacting only via excluded volume. Despite the little attention of simulation studies of this kind of particle, the synthesis of three-dimensional wireframe particles is not new. More than 20 years ago Chen and Seeman reported the synthesis of cubic wireframes using DNA [34]. Today, cubic frames and other wireframe polyhedra are readily synthesised across a range of length scales, from materials as diverse as metals [35–39], proteins [40], DNA [41, 42], and polymers and ceramics [43]. In this paper we use Monte Carlo simulations to demonstrate that HCFs, despite their propensity to form simple cubic crystals similar to their convex counterparts [44–47], exhibit an unusual type of plasticity. These cubic crystal phases are characterised by a high degree of translational and orientational order, but a random and dynamic fraction of particles can rotate even at relatively high densities - i.e. a fraction of the particles are dynamically misaligned with respect to the crystal lattice, an effect which is driven by the partial interpenetration that takes place between a particle in the crystal with its nearest neighbours. We define this behaviour as plastic fluctuations, where particles can adopt either aligned or misaligned states separated by a free energy barrier, and we show that this is indeed an equilibrium behaviour. The numerical analysis of the structures reveals that this unusual plasticity is a function of both the thickness of the HCFs and the density of the system.

METHODS

We use Monte Carlo (MC) simulations to study the packing and phase behaviour of a HCF particle model,

which is shown in Figure 1. Similar to a recent model for tetrahedral frames studied by Ciarella *et al.* [48], the edges of each HCF are represented by hard spherocylinders of diameter σ and length L . This particle model allows one to study the effect of frame thickness t^* defined as $t^* = 1/L^*$, where $L^* = L/\sigma$ is the aspect ratio of the spherocylinders. Note that in this definition, L represents the total length of the spherocylinder including the hemispherical caps as shown in Fig. 1(b). In the limit of $t^* \rightarrow 0$ the particles become infinitely thin frames with sharp vertices, while in the limit of $t^* \rightarrow 1$ the model essentially becomes a hard sphere of diameter σ . Since the vertices of the HCFs are represented by hard spheres, particles comprised of short edges become closely related to rounded cubes and superballs for which the phase diagrams have been reported elsewhere [49, 50]. In this paper we study frame lengths in the range of $5 \leq L^* \leq 100$ which corresponds to a thickness range of $0.01 \leq t^* \leq 0.2$. The upper limit $t^* = 0.2$ is chosen since frames thicker than this value exhibit qualitatively different phase behaviour. An efficient algorithm to detect overlaps between spherocylinders has been reported [12, 51], however, special geometrical tests need to be tailored due to the possibility of unphysical configurations where frames become interlinked as shown in Fig. 1(c). These special tests ensure that while an edge of particle i can penetrate the convex hull of a neighbouring particle j , the opposite situation does not occur simultaneously since mutual interpenetration of convex hulls by HCF edges implies unphysical interlocking. Interparticle interpenetration takes place when the vertex of one HCF passes through the open facet of another HCF. The positions of the eight vertices of a particle i with respect to the position of its centre of mass $\mathbf{r}_i$ is given by

$$\boldsymbol{\nu}_{il} = \mathbf{r}_i + \frac{L}{2} [\pm \hat{\mathbf{e}}_{i1}, \pm \hat{\mathbf{e}}_{i2}, \pm \hat{\mathbf{e}}_{i3}] \quad (1)$$

where $\boldsymbol{\nu}_{il}$ is the position of vertex l of particle i , and $\hat{\mathbf{e}}_{ik}$ is one of the three orthonormal vectors describing the orientation of particle i in the k -direction. Vertex l of particle i is found to be penetrating a particle j if

$$(\boldsymbol{\nu}_{il} - \mathbf{r}_j) \cdot \hat{\mathbf{e}}_{jk} < \frac{L}{2} \quad (2)$$

for each $k = [1, 2, 3]$. Using these tests, we automatically reject any MC move that leads to two or more facets of a particle i being intersected by edges of a second particle j .

Using MC simulations in the isothermal-isobaric NPT ensemble we explore the phase behaviour of HCFs via expansion and compression runs allowing the shape of the simulation cell to change. Free energy calculations, direct coexistence simulations and Gibbs-Duhem integration are also used to determine fluid-solid coexistence point [11, 52–58]. Properties are reported in dimensionless units: pressure $P^* = \beta PL^3$, number density

FIG. 1. Schematic representation of the geometry of a hard cubic frame (HCF) of length L and thickness σ/L . (a) The orientation of a HCF is described by three orthonormal vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$ and $\hat{\mathbf{e}}_3$ that are perpendicular to the empty facets. (b) Each HCF is modelled as sets of 12 spherocylinders of total length L and diameter σ . A special overlap test has been tailored to avoid unphysical (interlinked) configurations as the one shown in (c). This special test is based on the number of intersection of the edges of the HCFs with the planes of the facets, which in the case of HCFs an unphysical overlap takes place when three facets of a HCF are intersected by three edges of a second particle as shown in (d).

$\rho = L^3 N/V$, and volume fraction $\phi = v_f \rho$, where P is the absolute pressure, $\beta = 1/(kT)$, T is the absolute temperature, N is the total number of HCF particles, V is the volume of the system, and v_f is the volume of a HCF. The volume v_f is given by $v_f = 3\pi(L-2\sigma)\sigma^2 + 8v_v$, where the volume occupied by a vertex $v_v = 0.8113\sigma^3$ has been calculated using Monte Carlo sampling.

The orientational order of the system is analysed using the cubatic order parameter, S_4 . For this calculation, we determine the parameter $S_{4,1}$ given by

$$S_{4,1} = \max_{\hat{\mathbf{n}}_1} \frac{1}{N} \sum_{i=1}^N S_{4,1}^i, \quad (3)$$

where $\hat{\mathbf{n}}_1$ is the vector that maximises $S_{4,1}$, and the local orientational order parameter $S_{4,1}^i$ is defined as

$$S_{4,1}^i = \frac{1}{3} \sum_{k=1}^3 \frac{1}{8} \left[35 (\hat{\mathbf{e}}_{ik} \cdot \hat{\mathbf{n}}_1)^4 - 30 (\hat{\mathbf{e}}_{ik} \cdot \hat{\mathbf{n}}_1)^2 + 3 \right], \quad (4)$$

which represents the sum of the fourth-Legendre polynomial evaluated for the cosine of the angles made between $\hat{\mathbf{n}}_1$ and the three orthonormal vectors $\hat{\mathbf{e}}_{ik}$ associated to particle i . The vector $\hat{\mathbf{n}}_1$ is obtained using a

similar methodology reported in reference 59. A second indicator of global orientational order is available in $S_{4,2}$, which is given by finding $\hat{n}_2$, the vector orthogonal to $\hat{n}_1$ that maximises $S_{4,2}$. For simple cubic crystals the ensemble averages of $S_{4,1}$ and $S_{4,2}$ are found to be equivalent, and for brevity $S_{4,1}$ is reported as S_4 . The distinction between the two order parameters becomes useful when considering local orientational order. Using the vector $\hat{n}_1$ we can find $S_{4,1}^i$ using Eq. 4, while $S_{4,2}^i$ is calculated in the same way by replacing $\hat{n}_1$ with $\hat{n}_2$. $S_{4,1}^i$ and $S_{4,2}^i$ are found to differ for disordered particles, so the local orientational order of particle i is found as the average of the two quantities, i.e.,

$$S_4^i = (S_{4,1}^i + S_{4,2}^i)/2. \quad (5)$$

As HCFs are essentially empty particles with open facets, the degree of interpenetration between a pair of particles is a useful metric that needs to be quantified. A particle interpenetration takes place when a vertex of one HCF crosses the open facet of a second particle. Since a HCF has 8 vertices, it is hypothetically capable of penetrating 8 HCFs at the same time, though we observe that 6 is the maximum number of interpenetrations for a single particle due to steric effects. In this way, we measure the penetration frequency as $\bar{\chi}_n = N_{pen}/N$, where N_{pen} is the number of penetrating vertices. If an interpenetration takes place, we also measure the distance from the penetrating vertex to the centre of mass of the second particle and this is then normalised by dividing by the circumscribed radius of a HCF to get χ_d . The average penetration depth $\bar{\chi}_d$ is the sum of all χ_d divided by N_{pen} , i.e. $\bar{\chi}_d = N_{pen}^{-1} \sum \chi_d$. Finally to measure the local orientational fluctuations of the system we calculate the fraction f_d of misaligned particles with respect to a perfect crystal lattice. We consider particle i to be misaligned if its local orientational order is below a cut-off, $S_4^i < 0.6$, and aligned otherwise. This cut-off is chosen based on the minimum observed in histograms of S_4^i at various densities where this cut-off clearly separates the two peaks representing the aligned and misaligned states.

Equations of state are obtained from compression and expansion runs using MC-NPT simulations. Compression runs start from a very low density (ideal gas) state and continue up to close-packing. Long simulations are required near the coexistence points to allow crystals to fully equilibrate. Expansion runs start from either a close-packed simple cubic crystal or an equilibrated crystal configuration. For the simulations involving crystalline phases, the shape of the box is allowed to change to aid the relaxation of the lattice by varying the box vectors independently [52, 60]. A total of $N = 216$ HCFs, corresponding to a total of 3072 spherocylinders, are used for the calculations of the equations of state. Potential finite size effects are analysed studying larger systems

comprising up to $N = 1728$ HCFs. For compression and expansion runs about 10^6 MC cycles are used for equilibration and another 10^7 MC cycles are used to collect statistics. Each cycle involves N moves with the following probabilities: translation, 47.5%; rotation, 42.5%; assign a new random orientation, 5%; and volume change, 5%. At least 200 configurations are saved for post-processing analysis. MC-NVT simulations for systems comprising of up to $N = 10^4$ are also used in order to study the plasticity of crystals formed by HCFs in more detail for selected high-density states.

Finally, we have also performed calculations of the potential of mean force (PMF) between a pair of particles in isolation using MC simulations. During the simulations, random particle orientations are assigned to the particles at a fixed interparticle distance r_{ij} , and then histograms of the relative local orientational order parameter S_4^{ij} are accumulated in small bins. The PMF for a set of values r_{ij} and S_4^{ij} is then obtained as

$$\text{PMF}(r_{ij}, S_4^{ij}) = -\beta^{-1} \ln \langle e^{-\beta U(r_{ij}, S_4^{ij})} \rangle. \quad (6)$$

RESULTS

We first examine the phase behaviour of HCFs in the two limiting cases, i.e. $L^* = 5$ ($t^* = 0.2$) and $L^* = 100$ ($t^* = 0.01$). The results for the phase behaviour of both systems are shown in Fig. 2. For the first case with HCFs of $L^* = 5$, the system exhibits a phase transition from the isotropic phase ($\rho = 0.55$, $S_4 \sim 0$) to a simple cubic (SC) crystal ($\rho = 0.61$, $S_4 \sim 0.72$) at a pressure of $P^* \sim 9.52$. The large value of S_4 in the crystal phase denotes at high degree of orientational order. This value of S_4 is similar to the one reported for the SC crystal formed by convex cubes at coexistence where it was observed that $S_4 \sim 0.73$ [44]. It is evident from Figures 2(e,g) that as the density increases the system converges towards perfect order with $S_4 \rightarrow 1$ and $f_d \rightarrow 0$. At high densities the system undergoes a solid-solid phase transition from the SC crystal to a sheared simple cubic (ShSC) crystal in which the cubic lattice is deformed into a rhombic lattice. The rhombic lattice of this ShSC phase is a consequence of the particle vertices being round, which is an effect that is more prominent in thicker HCFs. The formation of ShSC crystals have also been reported for the case of rounded cubic particles and superballs [50, 61, 62].

The system of HCFs of $L^* = 100$ also form a similar SC crystal as in the previous case, in which the system crystallizes from a fluid state ($\rho = 0.55$) to a SC crystal ($\rho = 0.61$) at $P^* = 8.94$. Close to their corresponding coexistence points, the SC crystals of both $L^* = 5$ and $L^* = 100$ systems exhibit similar structural properties (see Fig. 2 (e-f)), but as the density in the solid phase increases the behaviour diverges considerably. The differ-

FIG. 2. Representation of hard cubic frames of lengths (a) $L^* = 5$ and (b) $L^* = 100$. In (c) and (d), the corresponding equations of state in the P^* - ρ representation are presented. In (e) and (f) the order parameters S_4 (global orientational order), $\bar{\chi}_n$ (penetration frequency) and $\bar{\chi}_d$ (average penetration depth) are shown against number density, ρ . The fraction of disordered particles, f_d , against ρ is also presented in (g) and (h). Vertical dashed lines indicate phase boundaries.

ent order parameters for the system of HCF of $L^* = 100$ are shown in Fig. 2 (f,h) where, in particular, it is observed that the frequency of interpenetrations, $\bar{\chi}_n$, increases with density. Furthermore, the average penetration depth, $\bar{\chi}_d$, appears to have a minimum at $\rho = 0.7$, while as the density increases S_4 reaches a maximum of $S_4 = 0.8$ at $\rho = 0.79$, and the fraction of disordered particles has a minimum of $f_d = 0.12$ at $\rho = 0.76$. This indicates that upon compression, the global orientational order of the systems actually decreases slightly along the SC branch. These order parameters show that while the system is still highly ordered, there is a large fraction of particles which are orientationally misaligned from the crystal lattice. We refer to this phenomenon as plastic fluctuations in which all the particles are predominantly aligned with respect to the crystal lattice, but every particle is still able to rotate and this event takes place spontaneously. Representative configurations for two SC phases exhibiting a degree of plastic fluctuations are shown in Figures 3(a-b). While the effect is evident in both snapshots, the clear distinction between aligned and misaligned particles is more evident in the high-density state shown in Fig. 3(b). Further compression of the system to $P^* = 31$ and $\rho \sim 0.85$ results in a solid-solid

phase transition between the SC crystal and an offset simple cubic (OfSC) crystal, which is represented in Fig. 3(c). The main difference between both lattices is that in the former the orientations of the particles are on average aligned with the cubic lattice vectors, while in the latter the orientations of the particles are slightly tilted with respect to the cubic lattice. In Figure 2 (h) is observed that the fraction of misaligned particles in the OfSC is very small but non-zero indicating that there are still plastic fluctuations occurring up to reduced densities as high as $\rho = 0.95$. As the system approaches the limit of maximum packing both $\bar{\chi}_n$ and $\bar{\chi}_d$ tend to zero, and at sufficiently high pressures the ShSC phase emerges.

We explore now the structural properties of thin frames ($L^* = 100$) in more detail to gain more insight into the plastic fluctuations taking place in the crystalline phases. Three crystalline states are shown in Figure 3 along their orientation distribution plots represented as histograms of the orientations of HCFs projected onto a unit sphere. These orientation distributions describe not only the orientations of high and low probability but also provide information of the rotation mechanism (paths) taken by the particles during the evolution of the simulation. A representative configuration of the SC crystal formed by thin frames near the fluid-solid transition is shown in Fig. 3(a). In this configuration it is observed the particles prefer to be aligned mainly along the three orthogonal axes characterising the cubic phase, but about 18% of HCFs on average are misaligned. Tracking down the orientations of the misaligned particles shows that these particles eventually realign with respect to the cubic lattice confirming these events are dynamic in nature. As the density is increased close to the SC-OfSC coexistence we can observe in Fig. 3(b) the particles in the system seems to be strongly separated into either aligned or misaligned configurations. The orientation distribution plot now displays a striking network of orientations of higher or lower probability, indicating that disordered particles rotate along specific routes. These networks, however, disappear at sufficiently high densities as shown in Fig. 3(c) for the case of the OfSC crystal in which the system is limited to exploring just a few orientations corresponding to small interpenetration depths. Nonetheless it is still remarkable to see these orientational fluctuations at a packing fraction close to maximum packing.

While Fig. 3 gives a simple visual description of the orientational behaviour of the system, a more complete analysis can be drawn from the set of probability distributions presented in Fig. 4. In Fig. 4(a) we present probability distributions of the local orientational order parameter, S_4^i , effectively reframing the information used in the orientation distribution plots. For $\rho \leq 0.85$ there is a peak in $\mathcal{P}(S_4^i)$ at $S_4^i = -0.5$, indicating that this level of disorder results in particularly favourable configurations. As the density increases to $\rho = 0.85$, $\mathcal{P}(S_4^i)$ becomes strongly bimodal, indicating that particles cross a high

FIG. 3. Snapshots of two representative configuration SC crystals formed by HCF of length $L^* = 100$ at (a) $P^* = 10$ ($\rho = 0.65$, $S_4 = 0.74$, $f_d = 0.186$) and (b) $P^* = 32$ ($\rho = 0.85$, $S_4 = 0.79$, $f_d = 0.147$), and (c) a representative configuration of an OfSC crystal at $P^* = 100$ ($\rho = 0.95$, $S_4 = 0.99$, $f_d = 0.0007$). For each snapshot, orientation distribution plots are displayed in the Mollweide projection; the scale bar indicates the relative probabilities of the orientations adopted by the particles. In (c), θ is the average angle made between the HCF orientations and the SC unit cell vectors.

FIG. 4. Probability distributions describing the plastic fluctuations for HCF of $L^* = 100$: (a) local orientational order, S_4^i ; (b) penetration depth χ_d ; (c) fraction of time a particle spends in a disordered state within 2×10^5 MC cycles, τ_d ; (d) length of time a particle stays in a misaligned state before becoming aligned, τ_{MC} . The results correspond to the states shown in Fig. 3.

free energy barrier to transition from aligned state to misaligned state and vice versa. Potential of mean force calculations for two isolated particles also reveal that HCFs achieve the smallest interparticle distance when one particle has $S_4^i = 1$ and the other has $S_4^i \sim -0.5$, which coincides with the first peak observed in $\mathcal{P}(S_4^i)$. For $\rho = 0.65$ the probability distribution of penetration depths shown in Fig. 4(b) reveals that at lower densities HCFs can penetrate across a wide range of depths. Above $\rho = 0.72$, however, $\mathcal{P}(\chi_d)$ also becomes bimodal and by $\rho = 0.85$ particles are packed so close that they are only likely to either interpenetrate corner-to-corner (aligned state with low values χ_d) or interpenetrate deeply (misaligned state with high values of χ_d). These bimodal probability distributions explain why plastic fluctuations become even more apparent at higher densities due to the clear distinction between aligned and misaligned states adopted by the particles. It is important to stress that this behaviour is not a result of particles becoming kinetically trapped due to a fast compression; the results presented in Fig. 4 (c-d) were obtained from MC simulations in the NVT ensemble for systems comprising $N = 10^5$ HCFs with perfectly ordered crystals as initial configurations. In order to quantify the dynamic behaviour of particles moving between aligned and misaligned states we present two measures. The first one is the fraction of time τ_d that a particular HCF spends in the misaligned state, as measured in a simulation of 2×10^5 MC cycles - if particles are able to rotate then τ_d should approach the value of f_d for sufficiently long simulations. The second measure is the length of time τ_{MC} that a HCF stays in the misaligned state before switching to an aligned state. For $\rho = 0.65$ Fig. 4 (d) shows that HCFs only stay in misaligned states for short periods of time, and in Fig. 4 (c) $\mathcal{P}(\tau_d)$ is peaked at the equilibrium fraction of misaligned particles, $f_d = 0.18$. For $\rho = 0.85$ the system can still switch between states as demonstrated by the broad distribution for $\mathcal{P}(\tau_{MC})$ in Fig. 4 (d), though the dynamics are much slower. Given the high free energy barrier between the aligned and misaligned states at $\rho = 0.85$, if a particle becomes misaligned it remains in that state for a long time.

After describing the phase behaviour of the two limiting cases, we proceed to discuss the behaviour of HCF for lengths in the range $5 < L^* < 100$. Fig. 5 (a) shows the phase behaviour in the aspect ratio-number density plane, $L^*-\rho$, which is useful for comparing across the range of L^* studied. It is evident that systems of HCFs consistently crystallise from an isotropic fluid to a SC crystal at $\rho \sim 0.55$. This means that the fluid-solid coexistence observed in HCFs is shifted to higher densities compared to convex cubes which start to crystallise at $\rho = 0.45$. We only observe the appearance of the ShSC crystal phase in frames with lengths in the range $5 \leq L^* \leq 9$, though since it is known that rounded convex cubes pack most efficiently in the ShSC phase we expect

FIG. 5. Phase diagrams of HCFs in (a) the aspect ratio - number density ($L^*-\rho$) plane and in (b) the thickness - volume fraction ($t^* - \phi$) plane. The colour code indicating the different stable phases in (b) is the same as in (a).

that it is stable at maximum packing as long as the HCF edges are curved [61]. The OfSC phase only becomes stable for $L^* > 11$ as the HCFs must be thin enough to maintain SC structure while also allowing the corners of HCFs to interpenetrate. Fig. 5 (b) shows the same information as Fig 5 (a), but as a function of HCF thickness and volume fraction, $t^*-\phi$. As the particles are essentially empty, the volume fraction converges to zero for infinitely thin particles leading to the formation of ordered structures with unusually high free volumes (porous ordered structures).

Finally, it is important to mention that the present study has not considered explicitly the effect of vacancies on the phase behaviour and stability of the ordered phases formed by HCFs. The reports of Smalenburg et. al. [46] and van Damme et. al. [47] showed that vacancies in simple cubic crystals formed by hard convex cubes near the isotropic-solid phase transition enhance the stability of the crystalline order. Indeed, the results presented in reference 46 show that vacancies as high as 6% are observed in the most stable crystals, but this fraction decreases as the density of the system is increased. The results of Smalenburg et. al. [46] suggest that the enhanced stability of the vacancy-rich crystal phase is due to the delocalization of the vacancies in the crystals, i.e., vacancies are not strongly bound to a particular lattice

site thus allowing strings of particles to move cooperatively along one of the three orthonormal directions of the crystals. We do not expect that vacancies will affect considerably the results for HCFs presented in this work for two reasons. The first reason is due to the effect of interpenetration itself. The partial interpenetration can in principle reduce the cooperative diffusion of particles in a single direction of the crystal since the interpenetrations act as weak “entropic” bonds which will cause the particles and vacancies to be bound in some degree to the lattice sites. The second reason is with respect to the difference in the position of the phase coexistence region between convex cubes and cubic wireframes. Smallenburg *et al.* determined that the lowest-density cubic crystal phase formed by convex cubes has a density of $\rho \sim 0.50$ with a vacancy concentration of 6%. The concentration of vacancies is at its highest at this lowest-density crystal state and decreases to about 0.5% as the density of the crystal reaches a value of $\rho \sim 0.6$. As reported in the present study, the lowest density simple cubic phase formed by cubic wireframe particles takes place at a density of $\rho \sim 0.61$ (the phase behavior is shifted to higher densities) thus we expect by simple analogy that the concentration of vacancies will be extremely low. It is for these two reasons that we conjecture that the role of vacancies in wireframe particles will be less important than in the case of convex cubes. Nevertheless, additional simulations considering explicitly vacancies are needed to probe this argument.

CONCLUSIONS

In conclusion, we have studied the phase behaviour of particles with cubic wireframe geometry using Monte Carlo simulations and a customised overlap algorithm. We found that as these particles become thinner they increasingly tend to exhibit plastic fluctuations. This behaviour takes place when particles in an ordered crystal spontaneously switch between aligned and misaligned states. While the dynamics of this switching slows down as the density is increased, this phenomenon still occurs at high densities. This behaviour mirrors to an extent the phase behaviour of convex cubes, where large concentrations of extended vacancies are present near solid-fluid coexistence, resulting in a fraction of positionally disordered cubes. One would expect that the absence of solid facets in the frames would change the phase behaviour of the particles dramatically. However, we observe that in our case the cubic geometry is still the dominant feature leading to the formation of cubic phases and the only effect the open facets have on the system is an enhancement of the rotational dynamics of the particles in the solid phases. In other words, the symmetry of the particles control the translational order of the crystal while the open facets control the local orientational

order. What is striking about this feature of HCFs is the range over which plastic fluctuations are evident; that is, a relatively large fraction of particles continue to be able to rotate up to number densities of $\rho = 0.85$. This phenomenon is made possible by the wireframe geometry - the ability to interpenetrate allows more ways to pack efficiently and rotate which increases the orientational entropy of the system. It is important to note that while hard, rigid particles as thin as $t^* = 0.01$ are unlikely to be synthesised in the near future, one may observe these plastic fluctuations in HCF particles as thin as $t^* = 0.1$ ($L^* = 10$).

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- [1] J. E. Kirkwood, in *Phase Transformations in Solids*, edited by M. Smoluchowski and Weyl (Wiley, 1951).
- [2] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).
- [3] W. W. Wood and J. D. Jacobson, *J. Chem. Phys.* **27**, 1207 (1957).
- [4] W. G. Hoover and F. H. Ree, *J. Chem. Phys.* **49**, 3609 (1968).
- [5] L. Onsager, *Ann. N. Y. Acad. Sci.* **51**, 627 (1949).
- [6] M. Hosino, H. Nakano, and H. Kimura, *J. Phys. Soc. Jpn.* **47**, 740 (1979).
- [7] D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants, *Nature* **332**, 822 (1988).
- [8] R. Eppenga and D. Frenkel, *Mol. Phys.* **52**, 1303 (1984).
- [9] J. A. C. Veerman and D. Frenkel, *Phys. Rev. A* **45**, 5632 (1992).
- [10] S. C. McGrother, D. C. Williamson, and G. Jackson, *J. Chem. Phys.* **104**, 6755 (1996).
- [11] P. Bolhuis and D. Frenkel, *J. Chem. Phys.* **106**, 666 (1997).
- [12] M. P. Allen, G. T. Evans, D. Frenkel, and B. M. Mulder, *Adv. Chem. Phys.* **86**, 1 (1993).
- [13] F. A. Escobedo, *Soft Matter* **10**, 8388 (2014).
- [14] G. van Anders, D. Klotz, N. K. Ahmed, M. Engel, and S. C. Glotzer, *Proc. Natl. Acad. Sci. U. S. A.* **111**, E4812 (2014).
- [15] V. N. Manoharan, *Science* **349**, 1253751 (2015).
- [16] M. A. Boles, M. Engel, and D. V. Talapin, *Chem. Rev.* **116**, 11220 (2016).
- [17] S. C. Glotzer and M. J. Solomon, *Nat. Mater.* **6**, 557 (2007).
- [18] M. A. Boles, M. Engel, and D. V. Talapin, *Chem. Rev.* **116**, 11220 (2016).
- [19] C. J. Hernandez and T. G. Mason, *J. Phys. Chem. C* **111**, 4477 (2007).
- [20] S. Sacanna and D. J. Pine, *Curr. Opin. Colloid Interface Sci.* **16**, 96 (2011).

- [21] H. Li, A. G. Kanaras, and L. Manna, *Accounts Chem. Res.* **46**, 1387 (2013).
- [22] S. Sacanna, M. Korpics, K. Rodriguez, L. Colon-Melendez, S.-H. Kim, D. J. Pine, and G.-R. Yi, *Nat. Commun.* **4**, 1688 (2013).
- [23] Y. Xia, K. D. Gilroy, H.-C. Peng, and X. Xia, *Angew. Chem.-Int. Edit.* **56**, 60 (2017).
- [24] A. Yethiraj and A. van Blaaderen, *Nature* **421**, 513 (2003).
- [25] C. Avendaño and E. A. Müller, *Phys. Rev. E* **80**, 061702 (2009).
- [26] M. Marechal, R. J. Kortschot, A. F. Demirors, A. Imhof, and M. Dijkstra, *Nano Lett.* **10**, 1907 (2010).
- [27] K. Miszta, J. de Graaf, G. Bertoni, D. Dorfs, R. Brescia, S. Marras, L. Ceseracciu, R. Cingolani, R. van Roij, M. Dijkstra, and L. Manna, *Nat. Mater.* **10**, 872 (2011).
- [28] J. de Graaf, R. van Roij, and M. Dijkstra, *Phys. Rev. Lett.* **107**, 155501 (2011).
- [29] S. Atkinson, Y. Jiao, and S. Torquato, *Phys. Rev. E* **86**, 031302 (2012).
- [30] D. J. Ashton, R. L. Jack, and N. B. Wilding, *Phys. Rev. Lett.* **114**, 237801 (2015).
- [31] C. Avendaño, G. Jackson, E. A. Müller, and F. A. Escobedo, *Proc. Natl. Acad. Sci. U. S. A.* **113**, 9699 (2016).
- [32] C. Avendaño and F. A. Escobedo, *Curr. Opin. Colloid Interface Sci.* **30**, 62 (2017).
- [33] N. Pakalidou, D. L. Cheung, A. J. Masters, and C. Avendano, *Soft Matter* **13**, 8618 (2017).
- [34] J. H. Chen and N. C. Seeman, *Nature* **350**, 631 (1991).
- [35] X. Lu, L. Au, J. McLellan, Z.-Y. Li, M. Marquez, and Y. Xia, *Nano Lett.* **7**, 1764 (2007).
- [36] X. Hong, D. Wang, S. Cai, H. Rong, and Y. Li, *J. Am. Chem. Soc.* **134**, 18165 (2012).
- [37] C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, *et al.*, *Science* **343**, 1339 (2014).
- [38] M. McEachran, D. Keogh, B. Pietrobon, N. Cathcart, I. Gourevich, N. Coombs, and V. Kitaev, *J. Am. Chem. Soc.* **133**, 8066 (2011).
- [39] J. Nai, B. Y. Guan, L. Yu, and X. W. Lou, *Sci. Adv.* **3**, e1700732 (2017).
- [40] Y.-T. Lai, E. Reading, G. L. Hura, K.-L. Tsai, A. Laganowsky, F. J. Asturias, J. A. Tainer, C. V. Robinson, and T. O. Yeates, *Nat. Chem.* **6**, 1065 (2014).
- [41] R. Inuma, Y. Ke, R. Jungmann, T. Schlichthaerle, J. B. Woehrstein, and P. Yin, *Science* **344**, 65 (2014).
- [42] R. Veneziano, S. Ratanalert, K. Zhang, F. Zhang, H. Yan, W. Chiu, and M. Bathe, *Science* **352**, 1534 (2016).
- [43] L. R. Meza, A. J. Zelhofer, N. Clarke, A. J. Mateos, D. M. Kochmann, and J. R. Greer, *Proc. Natl. Acad. Sci. U. S. A.* **112**, 11502 (2015).
- [44] U. Agarwal and F. A. Escobedo, *Nat. Mater.* **10**, 230 (2011).
- [45] P. F. Damasceno, M. Engel, and S. C. Glotzer, *Science* **337**, 453 (2012).
- [46] F. Smalenburg, L. Filion, M. Marechal, and M. Dijkstra, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 17886 (2012).
- [47] R. van Damme, B. van der Meer, J. J. van den Broeke, F. Smalenburg, and L. Filion, *J. Chem. Phys.* **147**, 124501 (2017).
- [48] S. Ciarella, O. Gang, and F. Sciortino, *Eur. Phys. J. E* **39**, 131 (2016).
- [49] R. D. Batten, F. H. Stillinger, and S. Torquato, *Phys. Rev. E* **81**, 061105 (2010).
- [50] R. Ni, A. P. Gantapara, J. de Graaf, R. van Roij, and M. Dijkstra, *Soft Matter* **8**, 8826 (2012).
- [51] C. Vega and S. Lago, *Comput. Chem.* **18**, 55 (1994).
- [52] D. Frenkel and B. Smit, *Understanding molecular simulation: from algorithms to applications*, Vol. 1 (Academic press, 2001).
- [53] D. Frenkel and A. J. C. Ladd, *J. Chem. Phys.* **81**, 3188 (1984).
- [54] B. Widom, *J. Chem. Phys.* **39**, 2808 (1963).
- [55] A. Fortini, M. Dijkstra, M. Schmidt, and P. P. Wessels, *Phys. Rev. E* **71**, 051403 (2005).
- [56] E. G. Noya, C. Vega, and E. de Miguel, *J. Chem. Phys.* **128**, 154507 (2008).
- [57] D. A. Kofke, *J. Chem. Phys.* **98**, 4149 (1993).
- [58] P. J. Camp, C. P. Mason, M. P. Allen, A. A. Khare, and D. A. Kofke, *J. Chem. Phys.* **105**, 2837 (1996).
- [59] B. S. John, C. Juhlin, and F. A. Escobedo, *J. Chem. Phys.* **128**, 044909 (2008).
- [60] R. Najafabadi and S. Yip, *Scripta Metall.* **17**, 1199 (1983).
- [61] M. Marechal, U. Zimmermann, and H. Löwen, *J. Chem. Phys.* **136**, 144506 (2012).
- [62] Y. Jiao, F. H. Stillinger, and S. Torquato, *Phys. Rev. E* **79**, 041309 (2009).