Fivefold symmetry as an inhibitor to hard-sphere crystallization

Nikos Ch. Karayiannis,[1] Rohit Malshe,[2] Juan J. de Pablo,[2] and Manuel Laso[1,*]

[1]*Institute of Optoelectronics and Microsystems (ISOM) and ETSII, Universidad Politecnica de Madrid (UPM), ES-28006 Madrid, Spain*
[2]*Department of Chemical and Biological Engineering, University of Wisconsin - Madison, Wisconsin 53706-1691, USA*

Through molecular simulations we investigate the dynamics of crystallization of hard spheres of uniform size from dense amorphous states and the role that hidden structures in an otherwise disordered medium might have on it. It is shown that short-range order in the form of sites with fivefold symmetry acts as a powerful inhibitor to crystal growth. Fivefold sites not only retard crystallization, but can self-assemble into organized structures that arrest crystallization at high densities or lead to the formation of defects in a crystal. The latter effect can be understood in terms of a random polyhedral model.

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I. INTRODUCTION

Random and ordered packings are closely related to processes and applications in colloid science, hard and soft materials science, engineering, biology, and mathematics. Hard spheres represent the simplest, nontrivial model which captures interactions based exclusively on the concept of excluded volume; as such it is amenable to analytic approaches. Kirkwood [1] was the first to predict a hard-sphere phase (disorder-order) transition. His predictions were soon followed by the pioneering simulations of Alder and Wainwright [2] and the experiments of Pusey and van Megen on concentrated colloidal suspensions [3].

Athermal systems, consisting of hard bodies, do not incur into energetic gains or penalties upon configurational change, making entropy the sole driving force for phase transitions. Entropy-driven isotropic-nematic transitions were originally predicted by Onsager for systems of hard rods [4] and confirmed by a series of modeling studies by Frenkel and collaborators [5–7]. Very recently, spontaneous crystallization has also been observed in simulations of dense packings of hard-sphere chains, thus disproving the long-standing belief that chain connectivity suppresses crystallization [8]. It has now been firmly established that, given adequate simulation time, hard-sphere packings eventually crystallize, even at volume fractions near jamming [9,10].

Classical nucleation theory posits that crystal nuclei form spontaneously in a metastable liquid. The system free energy depends on two competing factors: the penalty associated with the creation of a solid-liquid interface and the gain due to the formation of an ordered phase with higher stability than the amorphous material. Once a nucleus attains a critical size, it grows continuously [11]. While spheres represent the geometric shape with the highest volume-to-surface ratio, it has been demonstrated that under certain conditions the shape of the critical crystal nucleus is actually ellipsoidal, rather than spherical [12–15].

Crystallography dictates that fivefold symmetry is incompatible with strict periodicity and thus with crystal structures. Building blocks with fivefold local symmetry ("fivefolds" in the following) may produce structures such as quasicrystals [16] that exhibit long-range order but no translational symmetry [17]. Simulations using anisotropic potentials suggest that local arrangements of sites with pentagonal symmetry are locally favored, thereby causing frustration in the crystallization of glasses [18]. Fivefolds have also been reported to occur in crystal phases [19] and in dense random packings [20] of hard spheres. However, their role in the morphology and dynamics of athermal crystals remains unknown.

In this work, based on results from extensive, event-driven molecular dynamics (ED-MD) simulations, we show that fivefolds play a central role as antagonists of crystallization in very dense hard-sphere packings of uniform sphere size.

II. METHOD

Five (twelve) independent realizations (trajectories) were collected for the large (3000) and small (1200) simulated cells, respectively, at packing densities of $\varphi = 0.56$, 0.58, 0.60, and 0.61. To study the effect of system size we also conducted simulations on systems of 54 000 spheres at selected packing densities. In the present study, we have used the characteristic crystallographic element (CCE) norm [21,22] to determine the point group symmetry of the local environment of each site. The CCE norm can sensitively detect and discriminate between different emerging crystal structures [22]. It also serves to accurately quantify the degree of ordering or crystallinity, τ_c, as the sum of the fractions of sites in hexagonal-close-packed (hcp) and face-centered-cubic (fcc) local environments. Initial configurations were obtained from Monte Carlo trajectories of freely jointed hard-sphere chains [21] by removing all bonds and allowing a short period for the system to relax in the absence of holonomic constraints. All amorphous (random) configurations contained similarly small fractions of ordered sites (either hcp- or fcc-like) and fivefolds, uniformly and randomly dispersed throughout the simulation cell with the initial fivefold fraction, v_{fiv}, increasing linearly with packing density. Clusters of ordered sites were identified by a distance-based algorithm [23] using a threshold of 1.1σ, where σ is the sphere diameter. Further analysis with different radii for the cluster detection revealed no effect on the qualitative trends described here.

III. RESULTS

In the course of the ED-MD evolution, all systems considered here exhibit consistent qualitative trends, regardless

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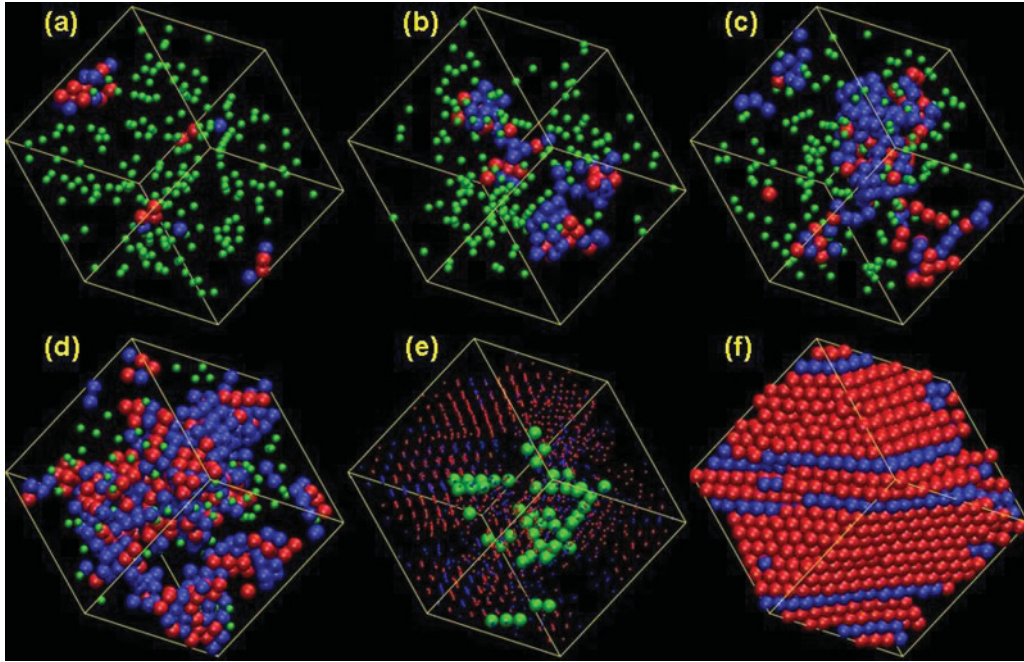*Author to whom correspondence should be addressed: mlaso@etsii.upm.es

FIG. 1. (Color online) System snapshots as obtained from ED-MD simulations on a sample at $\varphi = 0.61$. Each panel shows the largest cluster (nucleus) of ordered sites and fivefold sites as identified by the CCE norm. fcc-, hcp-like, and fivefold sites are shown in red (gray), blue (dark gray) and green (light gray), respectively [gray, dark gray, and light gray in printed version]. (a) after 10^7 collisions, $\tau_c \cong 0.077$, $\nu_{\text{fiv}} = 0.069$; (b) after 1.08×10^8 collisions, $\tau_c \cong 0.12$, $\nu_{\text{fiv}} = 0.056$; (c) after 2.36×10^8 collisions, $\tau_c \cong 0.14$, $\nu_{\text{fiv}} = 0.063$; (d) after 3.30×10^8 collisions, $\tau_c \cong 0.27$, $\nu_{\text{fiv}} = 0.031$; (e) after 4.50×10^8 collisions, $\tau_c \cong 0.52$, $\nu_{\text{fiv}} = 0.018$; and (f) after 8.00×10^8 collisions, $\tau_c \cong 0.89$, $\nu_{\text{fiv}} = 0$. Sphere diameters are scaled for visualization purposes: in a 2:5 ratio for fivefold sites in panels (a), (b), (c), and (d), and in a 1:5 ratio for fcc- and hcp-like sites in panel (e). Image created with the VMD software [32].

of density. An "incubation" period is initially observed where fivefolds and ordered sites coexist, and their populations either remain constant or increase slightly. This very short (compared to the time required for the ordering transition) period is followed by a continuous decrease in the number of fivefolds and a parallel increase of ordered sites. In early stages, crystal nuclei consist of a few sites (precritical clusters) and remain isolated, surrounded by fivefolds [Fig. 1(a)]. An intriguing feature of these incipient crystal clusters is their tendency to adopt highly nonspherical shapes, reminiscent of elongated ellipsoids [Fig. 1(b)]. This highly anisotropic growth can be traced back to a tendency of ordered clusters to avoid proximity with existing fivefold sites [Figs. 1(a) and 1(b)]. This avoidance stems from the geometric frustration to crystallization due to fivefold local symmetry and is responsible for the highly anisotropic shapes of precritical and critical crystal nuclei. As ordered clusters progressively grow in size [Figs. 1(c) and 1(d)], fivefolds become increasingly unstable in spite of their symmetry being preferred at a local level. As a result, fivefold population declines sharply. In some cases, a small number of the remaining fivefold sites continue to hinder crystal growth by adopting linear arrangements [Fig. 1(e)]. At long simulation times, the highly ordered final states display typical self-assembled crystal morphologies. In the final configuration in Fig. 1, no fivefolds exist, and the crystal morphology corresponds to alternating stack-faulted layers of predominant fcc character with a single stacking direction.

The systems considered here crystallize as stacks of close-packed layers, whose proper symmetry is described by the

layer group $P(6/m)mm$. The stacking is, however, random, and cannot be described in the usual Ramsdell notation. Thus, although the immediate environment of a given site has a definite cubic or hexagonal character, the complete structure has a lower, trigonal symmetry [24]. The appearance of such structures is in agreement with past experiments [15,25,26] and simulations [7,13,19]. Given the minute entropic advantage of strictly hcp or fcc structures with respect to such randomly alternating structures in athermal systems [27,28] the observed abundance of random stackings nicely illustrates Ostwald's rule of stages, according to which metastable intermediate phases may hinder the attainment of the thermodynamically stable phase [29].

In some samples, during crystallization fivefold sites form striking patterns consisting of intersecting linear aggregates (Fig. 2). These alignments of fivefolds remain stable for extended periods of time, acting as particularly effective inhibitors of crystallization. Structures containing such well-organized linear aggregates do not reach high crystallinity ($\tau_c \leqslant 0.6$). In parallel, these fivefold assemblies do not disappear throughout the entire, extremely long simulations considered here.

In order to characterize crystallization kinetics, we have analyzed the time required for the fraction of fivefolds to decrease to half its maximum value (one half-life $t_{1/2}^{\text{fiv}}$) and to a quarter of its maximum value (two half-lives $t_{1/4}^{\text{fiv}}$). These lifetimes can be directly compared to the time required for the attainment of the final, maximum crystallinity, t^{ord}. We find that $t_{1/2}^{\text{fiv}}$ and $t_{1/4}^{\text{fiv}}$ are significantly shorter than t^{ord} in all
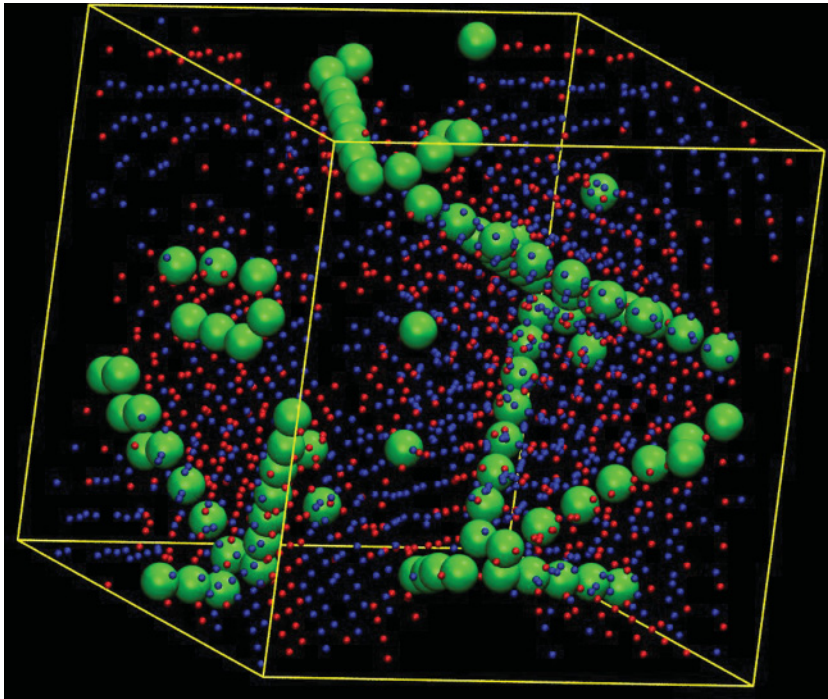
FIG. 2. (Color online) Same as in Fig. 1 but for a sample at 0.60 after 9.20×10^8 collisions, $\tau_c \cong 0.56$, $\nu_{\text{fiv}} = 0.033$. Sites with fivefold symmetry have formed linear aggregates, significantly prolonging their half life and consequently delaying the phase transition to a single ordered morphology. Fivefold aggregates remained stable for the whole simulation time, which exceeded by one order of magnitude the time required for the ordering transition in all other samples at the same packing density. Sphere diameters of fcc- and hcp-like sites are scaled in a 1:5 ratio for visualization purposes.

systems considered here. Remarkably, even though t^{ord} and $t_{1/2}^{\text{fiv}}$ (or $t_{1/4}^{\text{fiv}}$) are determined in completely independent ways, a strong correlation exists between fivefold half-life and the time required for crystal formation (Fig. 3). Another striking feature is that the relationship between t^{ord}, $t_{1/2}^{\text{fiv}}$, and $t_{1/4}^{\text{fiv}}$ is valid over the entire range of packing densities that we have examined, independently of system size. These results provide further evidence that the local symmetry of fivefold sites frustrates hard-sphere crystallization.
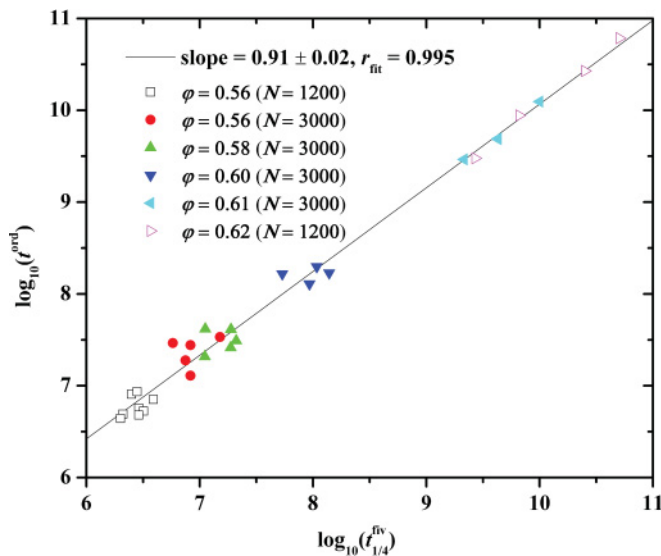

FIG. 3. (Color online) Logarithm of the time required for the establishment of crystal morphology (t^{ord}) versus logarithm of two half lives ($t_{1/4}^{\text{fiv}}$) of sites with fivefold symmetry from systems with 1200 and 3000 spheres. Also shown is a line as obtained from best fit over all simulation data with r_{fit} being the corresponding correlation coefficient.

The presence of fivefolds, even at small concentrations, in the final, predominantly ordered state also affects the resulting morphology and its deviation from a perfect crystal. This effect can be explained by means of a simple geometric model: once crystalline clusters reach their critical size, they grow by accretion of sites from their amorphous environment. In this growth phase, the shape of critical crystal clusters is markedly anisotropic. Growing clusters eventually impinge on each other and in some cases (proper alignment of the stacking vectors) merge. Disordered (amorphous) sites become increasingly confined between growing clusters. Cluster growth and merging continue until final crystallinity is reached, at which point only a few large and well-ordered clusters or crystallites remain, and take up most of the volume. The system can thus be conveniently understood as a tightly packed collection of randomly sized, nondendritic, roughly polyhedral, crystalline domains which are separated by amorphous regions of very low aspect ratio, i.e., approximately two dimensional. These amorphous regions become thinner as crystallinity increases. Fivefold sites, if any, are confined to the boundaries between two or more crystallite faces (Fig. 2). A more detailed analysis of the structural characteristics of the interfaces between the crystallites will be presented elsewhere. Additionally, transition path sampling calculations [30] will provide more information on the crystal nucleation along with the inhibition effect of fivefolds.

This highly simplified model leads to a relationship between the fraction of fivefold sites observed at a given fixed time in a simulation, and the difference in crystallinity at that time with respect to the maximum achievable crystallinity: at intermediate and high levels of crystallinity, it is reasonable to assume that the number of clusters stabilizes at a value N_{cluster}, i.e., further growth in crystallinity is due to the growth of this fixed number of clusters. If the clusters follow a random *polyhedral* distribution, and occupy a total, fixed volume
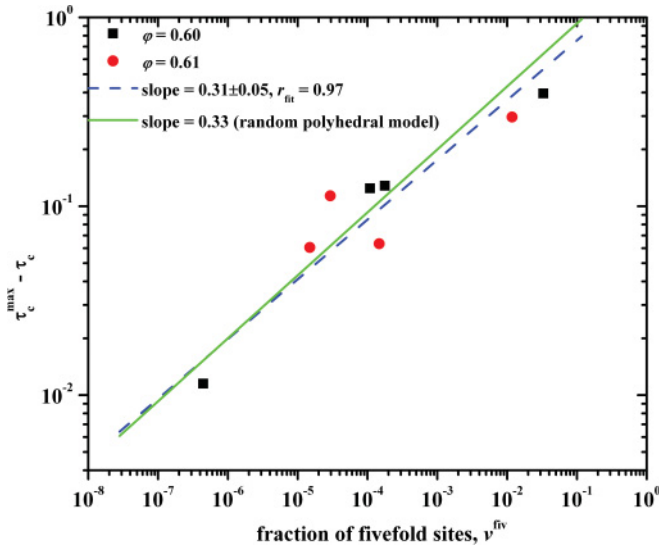
FIG. 4. (Color online) Deviation from maximum degree of ordering ($\tau_c^{\max} - \tau_c$) versus fraction of sites with fivefold symmetry in the final (ordered) state. $\tau_c^{\max}$ is defined here as the maximum value of crystallinity, observed in present simulations, in the total absence of fivefolds at $\varphi = 0.60$ and 0.61. Scattered points correspond to simulation data. Also shown are (i) a line with a slope of $1/3$ as predicted by the random polyhedral model proposed here and (ii) a line as obtained from best linear fit on simulation data with r_{fit} being the corresponding correlation coefficient.

(the volume of the simulation cell V_{cell}), the distribution average of a characteristic cluster size (e.g., an average edge length) must scale as $L \propto \sqrt[3]{V_{\text{cell}}/N_{\text{cluster}}}$. Since the amorphous sites are confined to the regions between clusters, the fraction of amorphous sites $\tau_c^{\max} - \tau_c$ must scale as the distribution average of the area of a polyhedral face, times the number of faces (which scales as $\propto N_{\text{cluster}}$):

$$\tau_c^{\max} - \tau_c \propto (\sqrt[3]{V_{\text{cell}}/N_{\text{cluster}}})^2 N_{\text{cluster}} \propto N_{\text{cluster}}^{1/3}.$$

Since fivefolds are located at, and therefore scale with, the number of edges in the system, and the random polyhedra obey

Euler's relation between faces, edges, and vertices, the number of fivefolds must then scale as $N_{\text{fiv}} \propto N_{\text{cluster}}$, hence

$$\tau_c^{\max} - \tau_c \propto N_{\text{fiv}}^{1/3}.$$

Thus, if this simplest random polyhedral model holds, the number of fivefold sites must scale with the exponent $1/3$ of the difference between maximum achievable crystallinity and crystallinity at the given time. This simple scaling is strongly confirmed by the results of our simulations (Fig. 4) over the observed fivefold concentration. This also implies that the alternative dendritic growth model [31] cannot possibly apply, for it would predict quite a different scaling exponent, whose value would depend on the assumed fractal dimension of the dendritic structure. In addition, a dendritic model would provide no natural explanation for the observed linear arrangements of fivefold sites.

Building on the observed behavior of fivefold sites as antagonists to crystallization, it is suggested that the inclusion of tailored nanoparticles that mimic the fivefold effect could be potentially used to control the crystallization kinetics and in general, the phase behavior of novel dense materials.

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