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Entropy-Driven Crystallization in Dense Systems of Athermal Chain Molecules

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We describe the direct observation of entropy-driven crystallization in simulations of dense packings of linear hard-sphere chains. Crystal nuclei form spontaneously in the phase coexistence region independently of chain length. Incipient nuclei consistently develop well defined, stack-faulted layered morphologies with a single stacking direction. These morphologies deviate markedly from those of monomeric analogs. The ordering transition is driven by the increase in translational entropy: ordered sites exhibit enhanced mobility as their local free volume becomes more spherical and symmetric.

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Since early times, crystallization [1] has been the subject of intense research, encompassing experimental, analytical, and simulation approaches. While continuum [2] and mean-field [3,4] theories provide an arguably satisfactory description of crystallization, and of the liquid-solid transition, a microscopic, atomistic understanding of the structural and dynamical features of the appearance and growth of crystal nuclei in undercooled liquids requires the use of advanced simulation methods. A considerable body of knowledge from simulations about crystal nucleation and growth has been collected over the last decades, with the most extensive studies focusing, understandably, on the simplest models of matter: monatomic fluids of spherical atoms interacting via soft-core [4,5] or hard-core [6–8] potentials. Because of the simplicity, it is widely accepted that qualitative features displayed by the hard-sphere model are independent of chemical details, and must hence be of general applicability. This last remark is manifestly valid for model macromolecular systems as well [9]. The crystallization of chain molecules is of maximal relevance for the physics and thermodynamics of synthetic and biological polymers, wormlike micelles, and microgels. However, dense, polymer systems present particular challenges to conventional molecular dynamics (MD) methods due to the extremely long relaxation times. For this reason, MD simulations of chain molecules have often considered crystallization from dilute systems [10], or have resorted to coarse-graining approaches [11]. In parallel to atomistic simulations [10,12] and in spite of the simplifications, coarse-graining has provided invaluable insights into, and remarkably realistic descriptions of, nucleation, growth, and reorganization during annealing [11]. Monte Carlo (MC) techniques, both continuum and lattice [13,14], and kinetic MC simulations [15] have also been employed to describe growth and morphogenesis of polymer crystals. It was only recently that an off-lattice MC scheme was developed [16] that can efficiently sample dense packings of hard-sphere chains up to the maximally random jammed state [17], by a combination of chain-connectivity-altering algorithms and localized adaptive-bias moves [16].

In this Letter we report on the direct observation of spontaneous, entropy-driven crystallization in off-lattice MC simulations of linear freely jointed chains of tangent hard spheres. The model contains the fundamental physical mechanism of (strictly) excluded volume but, unlike chemically detailed representations, does not possess any rotational nor bending hindrances, except those caused by the impenetrability of the monomers. In models with rotational hindrance [18], the ‘‘equilibrium’’ crystal typically contains fully extended chains, and is unattainable in practice due to the colossal relaxation time necessary to reach this conformation via thermal agitation [13]. For this reason, results obtained in most studies of crystallization of long linear molecules are unavoidably influenced by both steric (excluded volume) and bonded interactions, even in coarse-grained models. Thus, polymeric, folded-chain crystals are widely accepted as ‘‘nonequilibrium’’ states [19]. However, by eliminating torsional and bending contributions to the system Hamiltonian, while retaining excluded volume, the concept of an ensemble of ‘‘equilibrium’’ crystal configurations acquires a well defined statistical-mechanical meaning. Furthermore, by avoiding the (computationally expedient) limitation of system dilution, the entropic origins of the crystal nucleation and growth can be identified and be cleanly separated from factors originating in chemical particularities. Previous Green function and density functional theory work by Sushko and coworkers [20] had shed valuable light on the effect of chain flexibility, and of the ratio of sphere diameter to bond length (fusion parameter Γ), on chain crystallization. Our contribution explores the limit of tangent, hard spheres ($\Gamma = 1$), and simulation findings for local packing can serve as input for [20].

Our MC simulations were carried out in the isochoric semigrand canonical ensemble [16], and generated long trajectories of uncorrelated system configurations of average length $N = 12$ and 24 of 100 and 50 chains, respectively, for a total of 1200 interacting sites. The effect of polydispersity was investigated by considering two different chain length distributions: (i) uniform ones in the intervals $N \in [6, 18]$ and $N \in [12, 36]$ and (ii) a Flory (most probable) one with a minimum length of $N = 6$. Polydispersity in chain lengths was introduced for computational reasons since a minimum degree of polydispersity is required for the function of the chain-connectivity altering moves [16]. All simulations were performed in cubic cells with periodic boundary conditions. Simulations with larger cells ensured the absence of system size effects on the observed degree of crystallinity, the freezing transition, and the crystal morphology.

The onset and evolution of crystallization was monitored by means of the characteristic crystallographic element (CCE) norm [16,21]. The CCE norm is a strictly monotonic and structure-discriminating measure of order based on the point symmetry group [22] of the local environment of a site. The CCE norm has been shown to sensitively and quantitatively detect changes in local ordering, while identifying the emerging ordered structure with high specificity [21]. In this Letter, the CCE-norms for the face-centered cubic (fcc) $\varepsilon_i^{\mathrm{fcc}}$ and hexagonal close packing (hcp) $\varepsilon_i^{\mathrm{hcp}}$ point symmetry groups for each site i were continually computed. Additionally, all sites were tested for fivefold and higher-order symmetries by computing the corresponding CCE norm. For a given configuration an order parameter s^X (X is either hcp or fcc) was calculated from the distributions $\xi(\varepsilon^X)$ over all sites as $s^X = \int_0^{\varepsilon^{\mathrm{thres}}} \xi(\varepsilon^X) d\varepsilon^X$, where norms below the threshold value $\varepsilon^{\mathrm{thres}} = 0.245$ correspond to a well ordered local environment [16,21]. The degree of crystallinity τ_c is calculated as the sum of the norms ($\tau_c = s^{\mathrm{hcp}} + s^{\mathrm{fcc}}$).

In the absence of any external influence, hard-sphere chain systems were observed to systematically and spontaneously develop crystalline nuclei in the range $\varphi \in [0.58, 0.61]$. Our observation of spontaneous crystallization also parallels the finding by Rintoul and Torquato [7] that, given sufficient time, monomeric hard spheres will crystallize at all packing densities above the melting point. Figure 1 shows the spontaneous evolution of crystallinity, for systems of different average chain lengths ($N = 12$ and 24) and chain length distributions (Flory and uniform) and at various packing densities. The results of Fig. 1 demonstrate that, at a given volume fraction, statistically independent MC trajectories converge to very similar degrees of crystallinity, for both the Flory and uniform distributions, and for different chain lengths. Crystallization is thus a robust phenomenon and virtually insensitive to chain length and polydispersity. Furthermore, crystallinity is observed to increase with increasing packing density. At the highest volume fraction ($\varphi = 0.61$), four out of five sites ($\tau_c \simeq 0.83$) possess a highly ordered, nearly perfect crystalline environment. By far the most salient feature of the ordered structures [Fig. 2(b)] is the presence of a randomly stack-faulted, layered morphology with a single stacking direction. Thus, the incipient nucleus consists of parallel, two-dimensional–compact layers of either hcp or fcc character in random alternation. It is remarkable how, starting from disordered, liquidlike configurations [Fig. 2(a)], the MC algorithm is able to generate nuclei of incipient crystallization for chain molecules while fully respecting their connectivity, and correctly sampling from the statistical-mechanical ensemble. The structure of the incipient crystalline nuclei of chains of hard spheres can thus be understood as crystals of monomeric hard spheres on which self-avoiding random walks have superimposed. This result is, with the benefit of hindsight, quite plausible. Much less obvious, and up to the present work unknown, is the determination of the arrangement of chains in the crystal so that they remain random walks, and yet are able to entirely cover the highly regular structure of the crystal of mono-

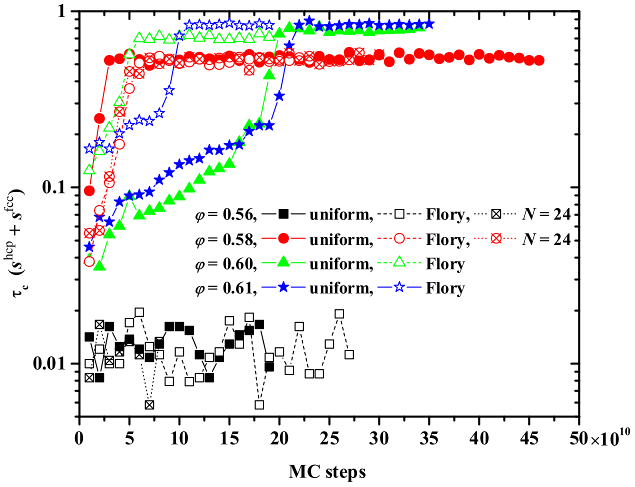

FIG. 1 (color online). Evolution of degree of crystallinity τ_c with MC steps for systems characterized by uniform (for average chain lengths $N = 12$ and 24) and most probable chain length distributions at various packing densities φ.

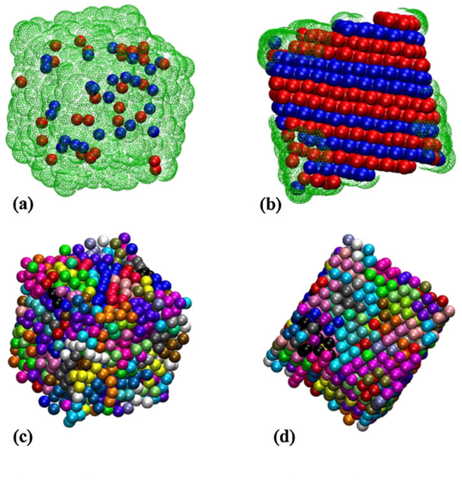

FIG. 2 (color online). System configurations ($\varphi = 0.61$), at (a) early stage of simulation (amorphous packing) and (b) late stage where the majority of sites possess a highly ordered local environment ($\tau_c \simeq 0.83$). Grey and black spheres correspond to sites with hcp-like and fcc-like local order, respectively. Sites with high CCE norms are shown as parts of a mesh cloud. (c) and (d) Same as in (a) and (b) but all sites colored according to the parent chain. Image created with VMD software [31].

meric hard spheres. As seen in Fig. 2(d) chains typically extend across several layers and adopt irregular conformations. Although a detailed description of the structure is outside the scope of this Letter, structural and configurational analyses of the resulting nuclei unambiguously identify the entropic mechanism of the disorder-order transition. On the one hand, chain conformational entropy decreases upon crystallization: the accessible conformational states are reduced, as evidenced by peak narrowing in the bending and torsional angle distributions (not shown). Orientational entropy also undergoes a small decrease due to loss of isotropy in the distribution of the chain end-to-end vector (not shown). However, these two entropy losses are compensated for by a larger increase in translational entropy. To understand better the driving mechanism we have studied the rearrangement of local (free) volume around each site through the transition. We have determined the local density of each site as the reciprocal of the volume of the corresponding Voronoi polyhedron. By construction, since the Voronoi cells completely fill the volume of the simulation box, the average local density remains constant over the MC trajectory. We further find that the second moment of the distribution of local density remains practically unaltered during the simulation. However, a significant change occurs in the shape of the Voronoi polyhedra as the system transits towards the ordered state. We quantify the shape through two principal measures: asphericity b and relative shape anisotropy k^2, which can be readily calculated from the eigenvalues I_1, I_2, and I_3 of the moment of inertia tensor of the Voronoi cell [23]. The lower the value of b the closer the resemblance of the shape to sphere. The higher the value of k^2 the higher the anisotropy of the shape. We observe that both measures decrease significantly through the transition so that the local environment around each chain site becomes more spherical and more symmetrical. Figure 3 presents the evolution of b along with τ_c as a function of MC steps. It is evident that especially in the transition regime the decrease of b towards sphericity is very sharp. It is thus established that the local environment undergoes drastic shape rearrangement. To elucidate how this shifting towards symmetry and sphericity increases the mobility of chain monomers, we have quantified their ability to "jiggle" (rattle) around by employing the concept of "flippers" as we have done in the past to calculate proximity to the maximally random jammed state for chain assemblies [16]. Here, a chain monomer is considered as a "flipper" if it is able to perform flip moves of amplitude $d\phi$ clockwise or counterclockwise with respect to the rotation axis defined by its nearest bonded neighbors without resulting in overlaps with any other sphere in the system. We find that, independently of the flip amplitude $d\phi$, in all cases the fraction of flippers increases significantly through the ordering transition. This is vividly shown in Fig. 3 where the fraction of flippers ($d\phi = 1°$) is plotted along τ_c and b versus MC steps. The strong correlation between all three quantities is very pronounced. Furthermore, we find that the distribution of the amplitude of the maximum allowed flip ($d\phi_{\max}$) for each hard sphere is shifted to much higher values in the ordered phase compared to the amorphous. It is thus clear that the increase in translational entropy is a consequence of an increase in the accessible volume around each monomer, as the free volume around it changes significantly in shape through the transition. This finding for model chain molecules is in perfect qualitative agreement with the seminal work of Onsager for rodlike colloidal particles [24] and the more recent studies by Frenkel and collaborators of entropy-driven phase transitions [25]. Interestingly, in the case of chain molecules the existence of bonds frustrates, but does not stop, the redistribution of free volume. However, we should note that because of the frustration caused by the divergence in the gap lengths of the nearest neighbors from the reference site (two neighbors should be tangent as a result of chain connectivity but the rest in principal are further apart), the local environment around each site is well ($\varepsilon^i \leq \varepsilon^{\mathrm{thres}}$) but not perfectly ($\varepsilon^i \to 0$) ordered.

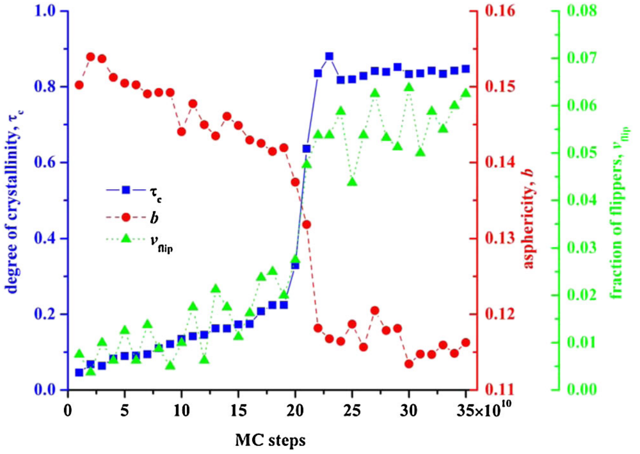

FIG. 3 (color online). Evolution of degree of crystallinity τ_c, average asphericity of the Voronoi polyhedra b, and fraction of flippers v_{flip} of amplitude $d\phi = 1°$ as a function of MC steps ($N = 12$, $\varphi = 0.61$).

The resulting crystal is thus the thermodynamically favorable phase. This process parallels crystallization in monomeric athermal systems [7,8,26], but with enriched configurational freedom. The observed spontaneous emergence of the crystal nuclei is, to the best of our knowledge, the first direct observation of a purely entropy-driven phase transition in off-lattice, dense macromolecular systems. It sheds light on a long standing controversy regarding the structure of crystals in athermal chains: layers are found to stack unidirectionally in all cases. A CCE-based analysis of the nuclei shows that hcp and fcc appear with equal probability (within statistical uncertainty). Determining any entropic advantage of fcc versus hcp, assuming such an advantage exists in chain systems, needs specialized techniques [27] and cannot be resolved by the present MC method, nor is it the goal of the present study. Very remarkably, no traces of twins or multiply twinned nuclei were identified, nor could any vestige of decahedral or twisted icosahedral symmetry be detected. The explicit search for fivefold rotation axes was also unsuccessful in all cases. This complete absence of sites with fivefold symmetry is a major departure with respect to the morphologies observed in experiments and in MD calculations of monomeric hard spheres, where multitwinned structures with pentagonal symmetry appear copiously [8]. We surmise that two independent factors are responsible: MD-based crystallization dynamics are widely recognized to more closely adhere to Ostwald's rule of stages [2(a),28], in which metastable intermediate phases may hinder the evolution of the thermodynamically stable phase [29]. However, a second, equilibrium factor, more substantial than the previous kinetic argument, is responsible for the absence of twins and of extended chains in crystalline nuclei of athermal polymers: unlike monoatomic hard spheres, athermal chains crystallize while simultaneously respecting chain connectivity. Highly irregular, compact chain conformations are favored entropically: there are many more ways to build a crystal using coiled, compact chain conformations than using extended ones. These conformations are also observed to favor specific bending and torsion angles, which stem from an underlying, loosely polytetrahedral structure [23] and are essentially incompatible with any point symmetry group that includes one fivefold rotation axis. Hence, the observed statistical weight of configurations containing fivefold axes is negligible. Any method able to generate truly equilibrated structures will consequently produce a minuscule, in practice unobservable, fraction of entropically penalized morphologies. In this respect, chain-molecule nuclei differ greatly from monomeric-sphere nuclei: the latter are free from connectivity constraints, and can incorporate a few sites of fivefold symmetry in incipient nuclei with a small entropic penalty, so that they readily appear in experiments and in MD simulations [8]. On the other side our MC study strongly supports the view that in a perfect crystal of hard-sphere chains, the positions of the sphere centers correspond to those of the monomeric-sphere crystal, but there is an entire distribution of microstates (chain conformations) that can be ''overlaid'' on the fixed coordinates of the sphere centers. These numerous microstates make the classical ground state of the crystal of hard-sphere chains highly degenerate [30].

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