Minimal Energy Packings and Collapse of Sticky Tangent Hard-Sphere Polymers

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We enumerate all minimal energy packings (MEPs) for small single linear and ring polymers composed of spherical monomers with contact attractions and hard-core repulsions and compare them to corresponding results for monomer packings. We define and identify “dividing surfaces” in polymer packings, which reduce the number of arrangements that satisfy hard-sphere and covalent-bond constraints. Compared to monomer MEPs, polymer MEPs favor intermediate structural symmetry. We also examine the packing-preparation dependence for longer single chains using molecular dynamics simulations. For slow temperature quenches, chains form crystallites with close-packed cores. As the quench rate increases, the core size decreases and the exterior becomes more disordered. By examining the contact number, we connect the suppression of crystallization to the onset of isostaticity in disordered packings. Our results show that polymer constraints reduce the ways in which hard spheres can be arranged into MEPs, and the strength of this effect varies for different macrostates (i.e., structurally distinct packings). We demonstrate that the large reduction in the number of arrangements may be understood in terms of dividing surfaces. These split polymer packings into disjoint regions and eliminate particle-label permutations that do not correspond to polymer chains. We find that polymer MEPs with intermediate structural symmetry are more frequent relative to the monomer case, where entropy favors low symmetry MEPs [4].

In addition, using molecular dynamics (MD) simulations of temperature quenches at various rates $T$, we show that single chains display glassy dynamics during collapse, and that the final polymer packings depend on $T$. In the slow quench rate limit, the chains undergo a sharp [9] transition to crystallites, with a jump in the energy and number of contacts $N_c$ (including covalent bonds) at temperature $T = T_{\text{melt}}$. The crystallites possess a close-packed core surrounded by a “surface” whose size and disorder increase with $[T]$. For slow quenches, $N_c$ at $T_{\text{melt}}$ jumps from below the minimal number $N_c^{\text{min}} = 3N - 6$ required for mechanical stability [11] to $N_c^{\text{low}}$, where a significant fraction of the monomers possess 12 contacts. In the large $[T]$ limit, the clusters are disordered with $\leq N_c^{\text{min}}$ contacts even as $T \rightarrow 0$, showing that rigidification can hinder crystallization.

We first describe exact enumeration methods for monomer and polymer MEPs [12]. To generate possible packings for a given number of spheres $N$ and contact number $N_c$, we iterate over all $N \times N$ adjacency matrices $\tilde{A}$ satisfying $\sum_{j \neq i} A_{ij} = N_c$. The elements of $\tilde{A}$ are 1 for contacting particles and 0 for noncontacting particles and diagonal entries. Covalent bonds link sticky spheres to form a polymer chain with length $N$; $A_{i,i+1} = 1$ for $1 \leq i < N$ for linear chains, and additionally $A_{i,i} = 1$ for
rings. The distinction between permanent covalent and thermally fluctuating noncovalent bonds is not important for static packings; we include both types in \( N_c \).

We enumerate all adjacency matrices satisfying the above conditions and then identify those that also fulfill hard-sphere and minimal rigidity constraints. Hard-sphere constraints imply that the center-to-center distances \( r_{ij} \) between unit spheres \( i \) and \( j \) obey \( r_{ij} \geq 1 \), where the equality holds for contacting pairs. Necessary conditions for rigidity are that each monomer possesses at least three contacts and \( N_c \geq N_{\text{min}}^{\text{rigid}} \) [13].

To enforce these constraints, we implemented geometrical rules developed by Arkus et al. [2,3] that eliminate invalid adjacency matrices. For the remaining configurations, we solved the system of quadratic equations

\[
|\vec{r}_i - \vec{r}_j|^2 = d^2_{ij} \quad (1)
\]

for sphere positions \( \vec{r}_i \) to an accuracy of \( 10^{-9} \). We also calculated the dynamical matrix [all second derivatives of the energy in Eq. (2) with respect to monomer displacements] for all configurations, which allowed us to identify rigid (with \( 3N - 6 \) nonzero eigenvalues) and floppy configurations [13] (with fewer nonzero eigenvalues) [12].

From this procedure, we obtain microstates and macromstates for a given \( N \) and \( N_c \) that satisfy hard-sphere and minimal rigidity constraints and the relevant polymeric constraints. Each macromstate is characterized by an adjacency matrix that is nonisomorphic to and a set of interparticle distances \( \{r_{ij}\} \) that is different from those characterizing other macromstates [12]. With this definition, no macromstate can be rotated or reflected such that it yields a different macromstate. Every connected sticky hard-sphere macromstate admits a linear polymer macromstate [14]. Thus, sticky-sphere and linear polymer packings have identical macromstates. We have also verified this for ring packings for \( N \leq 10 \).

A macromstate is a particular labeling of the particles 1 through \( N \) that comprise an \( N \)-particle macromstate with \( N_c \) contacts. Many microstates correspond to each macromstate due to particle permutations for monomer packings [4], and for polymers, the multiple possible paths through a given macromstate. The total number of microstates \( \Omega_m \), \( \Omega_p \), and \( \Omega_r \) is given by the sum of microstates for each macromstate for monomers, linear polymers, and rings, respectively [12]. For monomer packings, which lack covalent bonds, the number of microstates for each macromstate (ignoring chirality) is given simply by a geometric factor

\[
\Omega_m = \mathcal{P}_i, \quad \text{where} \quad \mathcal{P}_i = \text{the number of allowed permutations of particle indices for macromstate} \ i \quad [3].
\]

For polymer packings, the number of microstates is not given by this relation since one must ensure that particle indices are consecutive.

Exact enumeration results are displayed in Table I, which shows the number of macromstates \( M \), fraction \( f \) of adjacency matrices with \( N_c \) contacts obeying minimal rigidity that also satisfy hard-sphere constraints, and \( \Omega_m \), \( \Omega_p \), and \( \Omega_r \) for \( 5 \leq N \leq 10 \). \( f \) corresponds to the probability to obtain a packing for an “ideal” protocol that samples adjacency matrices uniformly. From Table I, we see that \( f \) decreases approximately exponentially with \( N \) for \( N \geq 5 \), and even faster for \( N > 9 \). Part of the reason for the strong decrease in \( f \) between \( N = 9 \) and 10 is the decrease in macromstates from 52 to 3. This occurs because \( N = 10 \) MEPs possess \( N_c = N_{\text{rigid}}^{\text{rigid}} + 1 \), which exceeds the number of degrees of freedom. Equation (1) is then overconstrained, and its solutions possess special symmetries. The increase in \( N_c \) signals the onset of crystal nucleation and the formation of a close-packed core. The ability to enumerate the numbers of isostatic \( (N_c = N_{\text{rigid}}^{\text{rigid}}) \) and hyperstatic \( (N_c > N_{\text{rigid}}^{\text{rigid}}) \) packings will yield insight into systems where glass and crystallization transitions compete.

For the \( N \) studied here, hard-sphere constraints are more difficult to satisfy for minimally rigid polymer packings compared to monomer packings: \( f_r < f_p < f_m \) [17]. A key mechanism for the reduction in \( f \) is the occurrence of “dividing surfaces” in polymer packings. A dividing surface is any minimal subset of a connected cluster of contacting monomers that geometrically splits it into two. Any polymer path that traverses a dividing surface that does not also topologically divide the polymer is blocked and invalid. Specifically, if \( m \) consecutive monomers...
with \( N_c = N_c^\text{min} \)), rearrangements into MEPs will be slow because of their low entropy. Thus, glassy dynamics in single polymer chains should be observable in systems quenched at varying rates. For \( k_B T \gg |\epsilon| \), where \(-\epsilon\) is the contact energy, polymers adopt random-coil configurations with \( N_c \ll N_c^\text{min} \). As the polymer is cooled, one expects quench rate effects to become important when \( N_c \approx N_c^\text{min} \) [18].

To demonstrate glassy dynamics for single linear polymer chains, we employ MD simulations in which monomers interact via the potential energy

\[
U_{\text{harm}}(r) = \begin{cases} 
-\epsilon + \frac{k}{2} (r - 1)^2 & r < r_c \\
0 & r \geq r_c
\end{cases}
\]

where \( k \) is the spring constant and \( D = 1 \) is the monomer diameter. The temperature \( T \) is controlled via a Langevin thermostat. The unit of time is \( \tau = \sqrt{mD^2/\epsilon} \), where \( m \) is the monomer mass. The cutoff radius \( r_c/D = \infty \) for covalently bonded monomers and \( 1 + \sqrt{2\epsilon/k} \) for noncovalently bonded monomers. \( U_{\text{harm}} \) reduces to the energy for tangent sticky hard spheres [19] in the limit \( k \to \infty \) and possesses the same MEPs. For \( N \leq 10 \), the MEPs from

FIG. 2 (color online). (a) Potential energy per particle (-\( U/Nc \)), (b) number of particles with 12 contacts \((N_{12})\), and (c) total number of contacts \((N_c)\) versus \( k_BT/\epsilon \) for single linear polymers with \( N = 100 \) at different quench rates. Data [top to bottom, (b),(c); bottom to top, (a)] are for quench rates \( k_BT/\epsilon = -10^{-3}, -10^{-4}, -10^{-5}, -10^{-6}, \) and \(-10^{-7}. \) The critical quench rates are \([k_BT/\epsilon] \approx 10^{-7}/\tau \) and \([k_BT/\epsilon] \approx 10^{-3}/\tau \). All results are averaged over several independent initial configurations. The horizontal (vertical) dotted lines indicate \( N_c = N_c^\text{min} \) \((k_BT/\epsilon = 0.37)\).
We also performed MD simulations of single linear chains with larger $N$, which link glassy dynamics to the onset of rigidity. This work sets the stage for future studies that investigate whether cooperative dynamics from chain connectivity and uncrossability constraints improves or impedes the glass-forming ability of single polymers compared to colloidal systems.

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