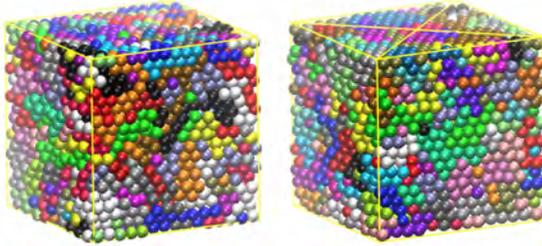# Packing of athermal polymers in the bulk & under confinement

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Snapshots of a 48-chain $N = 100$ system at a packing density $\varphi = 0.60$, (left) in the bulk and (right) under confinement in one dimension. Hard spheres are colored-coded according to the parent chain.
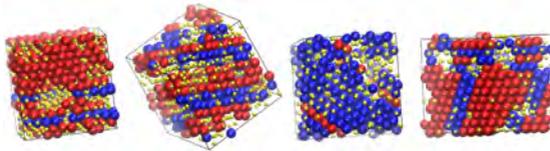
Snapshots of a 100-chain $N = 12$ system in the bulk at $\varphi = 0.5575$ with varied softness of bond lengths. Hard spheres are color coded according to the local structure: red, blue and yellow correspond to fcc, hcp and amorphous structures, respectively. Amorphous (yellow) sites are shown with reduced radii for clarity.

Polymers constitute a distinct class of anisotropic particles with unique dynamical, rheological and mechanical properties[1]. Thus, it is not surprising that during the last decades they have been under the spotlight of intense scientific research. Macromolecular systems, even in dilute solutions and high-temperature

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melts, present a formidable challenge from the modeling perspective as they are characterized by a wide range of characteristic length and time scales.

From the packing aspect, polymer chains are highly anisotropic entities, with the additional characteristic of having shape and size constantly fluctuating over time and with global and local structure being affected by a plethora of factors and conditions. Thus, packing trends and principles, valid and well-established for monomeric counterparts remain under question when it comes to polymer assemblies.

In the present contribution we study the packing properties of athermal polymers through extensive Monte Carlo simulations on freely-jointed chains of hard spheres of uniform size [2]. We examine in detail how factors like volume fraction (packing density), chain length, bond constraints and spatial confinement affect the packing ability of polymeric systems and their phase behavior (crystallization).

We find that the degree of softness of bond lengths has a profound effect on the ability of chains to crystallize, on the structure of the ordered morphologies and on the crystallization rate. Near the melting transition (of monomeric analogues[3]) and below a critical value of bond softness, chains remain amorphous reaching eventually the maximally random jammed (MRJ) state[4].

Confinement is realized through the presence of flat, planar, impenetrable walls in (at least) one dimension. We investigate how chain and monomer packing are affected by confinement, near and far from the surface walls and we compare the established confined polymer morphologies against the ones in the bulk[5].

Present modeling results can be used to aid the design of model polymers (granular/colloidal) with tailored phase behavior and packing properties.

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[4] S. Torquato, T. M. Truskett and P. G. Debenedetti, Phys. Rev. Lett. **84**, 2064 (2000).
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