



Monte Carlo simulations of densely-packed athermal polymers in the bulk and under confinement

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HIGHLIGHTS

- Identification of the maximally random jammed state for polymer packings.
- Molecular simulation of the phase transition in hard-sphere chains.
- Molecular modelling of the effect of confinement in densely-packed athermal polymers.
- Numerical calculation of the topological constraints in polymeric systems.
- First-principles calculation of the scaling regimes in flexible polymers.

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ABSTRACT

We review the main results from extensive Monte Carlo (MC) simulations on athermal polymer packings in the bulk and under confinement. By employing the simplest possible model of excluded volume, macromolecules are represented as freely-jointed chains of hard spheres of uniform size. Simulations are carried out in a wide concentration range: from very dilute up to very high volume fractions, reaching the maximally random jammed (MRJ) state. We study how factors like chain length, volume fraction and flexibility of bond lengths affect the structure, shape and size of polymers, their packing efficiency and their phase behaviour (disorder–order transition). In addition, we observe how these properties are affected by confinement realized by flat, impenetrable walls in one dimension. Finally, by mapping the parent polymer chains to primitive paths through direct geometrical algorithms, we analyse the characteristics of the entanglement network as a function of packing density.

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1. Introduction

How particles or molecules arrange and assemble at the atomic level, under various conditions, is intimately related to the macroscopic properties and behaviour of the corresponding materials. It is thus very important to develop and employ methods and tools to analyse atomic and particulate packing in a wide range of physical systems including, but not limited to, polymers, colloids, semiconductors, composites, liquid crystals and metallic glasses. Through this a reliable structure–property relation can be established leading to novel materials with tailored characteristics. Such a scientific challenge constitutes an ideal application field for molecular simulation, a modelling field which has experienced an enormous growth since its birth

more than half a century ago. Molecular modelling relies heavily on computers, whose power-to-cost ratio keeps increasing unabatedly. Furthermore, technological advances related to computer hardware are expected to continue their growth for the years to come. In parallel, scientific breakthroughs have been achieved in computational algorithms leading to very efficient numerical and simulation methods allowing the simulation of a diverse class of complex systems. Notwithstanding the obvious shortcomings related to their relatively infant state, computer simulations can robustly address “what if” questions and effectively model extreme processing conditions in an environmentally friendly, non-destructive manner. Thus, it is not surprising that in the last decades molecular simulations play a prominent role in fields as diverse as physics, chemistry, mathematics, materials science, biology and engineering.

In the present contribution we summarize the main results from extensive Monte Carlo (MC) simulations on chain packings of freely-jointed chains of hard spheres of uniform size. The

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simulated range of packing densities covers from dilute polymer packings up to jammed ones. The employed model is the simplest one for the description of polymer systems, bare of chemical details, but still incorporating excluded volume interactions which play a fundamental role in polymer physics (deGennes, 1980; Flory, 1989). The main motivation is to study how the constraints imposed by chain connectivity affect the structure, packing efficiency and phase behaviour of athermal polymer chains with respect to monomeric counterparts.

Starting from the seminal works of Bernal and co-workers in the late 1950s, a wealth of knowledge has been obtained over the years on the structural evolution of random sphere packings with increasing volume fraction ϕ (Bernal, 1959, 1960; Bernal and Finney, 1967; Bernal and Mason, 1960; Scott et al., 1962). It is now widely accepted that the densest possible random packings in a 3D space, generated through different experimental setups and/or modelling protocols, are characterized by densities in the vicinity of $\phi^{\text{MRJ}} \simeq 0.64$, subject to different generation protocols and conditions (Anikeenko and Medvedev, 2007; Anikeenko et al., 2008; Aste, 2005; Aste et al., 2005; Finney, 1970; Jullien et al., 1996; Scott and Kilgour, 1969; Tian et al., 2014). The established value is about 13.5% lower than the corresponding one for regular packings of non-overlapping hard spheres ($\phi^{\text{reg}} \simeq 0.7404$). The later value, initially conjectured by Kepler and proven recently by Hales (Hales, 2005; Hales et al., 2010), corresponds to the packing density of the face-centered cubic (fcc) lattice. While no such proof exists for the corresponding densest limit of random sphere packings the concept of the maximally random jammed (MRJ) state provides a precise mathematical and geometrical definition of the aforementioned state (Donev et al., 2005a, 2005b; Torquato et al., 2000).

Due to its great importance in many fields the unique characteristics of the jammed state have been studied extensively over the last years (Ballesta et al., 2008; Corwin et al., 2005; Donev et al., 2004a, 2004b, 2005a; Goodrich et al., 2012; Keys et al., 2007; Lu et al., 2008; O'Hern et al., 2002, 2003; Zexin et al., 2009). While initial studies focused understandably on dense packing of uniform spheres research has since been extended to objects with complex, anisotropic shapes (Donev et al., 2006; Frenkel et al., 1988; Haji-Akbari et al., 2013, 2011a, 2011b, 2009; Jiao et al., 2009; Jiao and Torquato, 2011; Torquato and Jiao, 2009; Veerman and Frenkel, 1991; Xu et al., 2005; Zeravcic et al., 2009). Athermal polymer packings (of hard-sphere chains) fall in the latter category: while the constituent monomers are well-defined, non-overlapping spheres (of uniform size), the global shape and size of each molecule are highly non-trivial, fluctuate over time, and are distinctly different from one chain to the other.

In the simplest polymer representation, that of the freely-jointed chain model, connectivity is solely imposed by bonds restricting the allowed distance between successive monomers along the chain backbone; bending and torsion angles for triplets (1–3 interactions) and quartets of monomers (1–4 interactions), respectively, can fluctuate freely, limited only by the condition of excluded volume. The non-overlapping condition further dictates all non-bonded interactions between pairs. An apparent fundamental question thus arises on how polymer connectivity affects the packing efficiency, phase behaviour and jammed state compared to monomeric hard spheres. Additionally, chain connectivity endows macromolecular systems with exceptional dynamical, rheological and mechanical properties. This unique behaviour is intimately related to the uncrossability of chains which effectively leads to topological constraints between chains in the form of entanglements (deGennes, 1980; Doi and Edwards, 1988). The original reptation theory, based on the tube model, and more recent theoretical concepts have captured qualitatively and quantitatively the effect of entanglements on polymer dynamics and

rheology (deGennes, 1980; Doi and Edwards, 1988; Kroger, 2004; Likhtman, 2005; Likhtman and McLeish, 2002; Marrucci, 1996; Marrucci and Ianniruberto, 2004; McLeish and Larson, 1998; Ramirez et al., 2007; Stephanou et al., 2011; Wang et al., 2012). Additionally, density is one of the key factors which affect profoundly the static, dynamic and rheological properties of entangled polymers (Daoud et al., 1975; Doi and Edwards, 1988; Edwards, 1966; Fleer et al., 1993).

Molecular simulations, based on the simple athermal model, can be employed to study how packing density (volume fraction) affects not only local and global polymer structure but also the underlying entanglement network. Primarily, by exploring the whole concentration range from infinite dilution up to the MRJ state a robust definition can be provided to quantify “dense” in the commonly used term of “dense polymer”. Once the jammed state is reached it is equally important to study the dependence of various quantities (for example chain size/shape, entanglement spacing, knot complexity, pair distribution function, contact network) on packing density. Such analysis will further allow the identification of the distinct scaling regimes, of the corresponding characteristic exponents and of the cross-over concentration thresholds.

Besides the physical significance in addressing the aforementioned fundamental topics there is an additional practical aspect in simulating athermal polymer packings. During the last years momentous progress has been made in the synthesis and characterization of colloidal and granular polymers (Brown et al., 2012; Palberg et al., 2009; Vutukuri et al., 2012; Zou et al., 2009). Colloidal macromolecules, by sharing key features with their atomic analogues, allow the direct experimental observation of corresponding quantities at a macroscopic level. Thus, experimental advances in colloidal polymers can greatly benefit from insights gained from detailed simulations on dense athermal polymers. Concepts like jamming (and the MRJ state), observed in computer-generated athermal polymers or in synthesized granular chains, can be related with the glass formation in polymers leading to a unified description and to an improved understanding of the phenomenon.

The phase behaviour of monomeric hard-sphere packings has been extensively studied since the earliest Molecular Dynamics (MD) simulations (Alder and Wainwright, 1957). While originally met with great scepticism and criticism, the pioneering work of Alder and Wainwright unmistakably showed, for the first time, that under specific conditions hard-sphere packings crystallize spontaneously. It is now well established that once a critical density is met and given enough observation time an initially amorphous packing of hard spheres crystallizes (Rintoul and Torquato, 1996). The entropic origins of phase transition date back to the classical work of Onsager (Onsager, 1949) on the isotropic–nematic transition of hard rods and have been analysed in detail over the last years for athermal systems (Eldridge et al., 1993; Frenkel, 1988, 1999, 2000; Stroobants et al., 1987). It is now well-established that the face-centered cubic (fcc) is marginally thermodynamically more stable than the hexagonal close packed (hcp) crystal structure (Bolhuis et al., 1997; Woodcock, 1997). In spite of this, different ordered morphologies can also be observed in experiments and simulations like the random hexagonal close packed (rhcp) layered structure or close packed crystallites, randomly oriented with defects being strongly correlated with twinning planes (Anikeenko et al., 2007; Auer and Frenkel, 2001; Bagley, 1970; Bolhuis et al., 1997; Cheng et al., 2002; Frenkel, 1999; Harland and van Megen, 1997; He et al., 1997; Henderson and van Megen, 1998; Karayiannis et al., 2011, 2012; Kawasaki and Tanaka, 2010; Leocmach and Tanaka, 2012; O'Malley and Snook, 2003; Pusey and Vanmegen, 1986; Pusey et al., 1989, 2009; Rintoul and Torquato, 1996; Russo and Tanaka, 2012; Schilling et al., 2010;

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