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Modeling soft core-shell colloids using stochastic hard collision dynamics

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HIGHLIGHTS

- We characterize the structure and thermodynamics of hard-core soft-shell (HCSS) colloids.
- We extended earlier work to effectively model HCSS colloids while retaining their characteristic properties.
- The SHC model effectively coarse-grains complex long-range interactions in solvents with numerically efficient sampling.
- We determined how softness affects the thermodynamic behavior of a model HCSS colloidal system.

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ABSTRACT

The equilibrium structure and thermodynamic behavior of a soft matter suspension of hard-core soft-shell (HCSS) colloids have been modeled using stochastic hard collision (SHC) dynamics [Craven et al., J. Chem. Phys. 2013, 138, 244901]. SHC dynamics includes the effects of inter-penetrability of soft particles while retaining the computational efficiency of hard collision dynamics. The HCSS colloids are characterized using two parameters: softness parameter (a measure of the propensity toward interpenetration), and core-to-shell ratio. In both, molecular dynamics and Monte-Carlo simulations, the softness parameter is seen to profoundly affect the effective packing fraction and the thermodynamic behavior of the system. Once we accounted for the trivial effects from changes in the reduced volume fraction on changing softness, we found that the inter-particle penetration continues to affect this thermodynamic behavior. The structural origin of this nontrivial effect likely lies in the loss of translational order upon increasing softness.

1. Introduction

Fluids consisting of softly-interacting particles are known to show complex and intriguing self-assembled structural behavior [1–7] including quasicrystalline order [8–11], glassy [12] and clustered crystal [13–15] structures, and dynamical behavior [16–18] resulting from their unique ability to deform and inter-penetrate under mechanical stress or even due to thermal fluctuations. The underlying particles — e.g., polymers, bio-macromolecules (e.g. proteins, DNA, RNA, membranes), or colloids — can give rise to a broad range of behavior useful to scientific and technological applications either because of their individual properties or because of how they behave collectively [19].

Complex fluids consist of well-defined mesoscale structures which are in turn made up of self-assembled molecules or very large single molecules. The large number of atoms required to represent such multi-scale systems necessarily results in a highly computationally intensive molecular dynamics simulation. A widely used method for enhancing the computational efficiency for modeling these systems involves coarse-graining [20–23] as to reduce the intra-molecular degrees of freedom by removing the so-called fine-grained variables and thereby keeping only the relevant coarse-grained degrees of freedom in the computation. Many methods have been developed to efficiently coarse-grain molecular and macromolecular systems [22,24]. Although, coarse-grained models effectively capture equilibrium structural properties, dynamical inconsistency [25] is still a serious limitation of these models [26].

An alternate strategy for (minimal) modeling of complex soft fluids to capture only the generic features of soft particle systems is via bounded or soft core interaction potentials [27–32]. However, ultra-slow glassy dynamics of these systems [33,34] often pose a challenge to access their behavior at higher packing fractions. To overcome this difficulty, Craven et al. [35] recently introduced a stochastic hard collision (SHC) model that effectively represents soft particle interactions with stochastically dressed hard-core interactions. This allows SHC dynamics to include the effects of inter-penetrability exhibited by soft particles while retaining the computational efficiency of hard

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collision dynamics. In SHC dynamics, the outcome of an inter-particle collision is governed by a stochastic rule through a softness parameter which determines the probability of penetration on collision [35]. Consequently, unlike bounded repulsive (such as in the Gaussian Core Model [36]) and soft core potentials, the SHC model is inherently (by construction) stochastic. Nevertheless, the spatial configurations generated by the non-Newtonian SHC dynamics were found to be analogous to those obtained from deterministic bounded potentials [35,37,38].

An important class of soft colloidal system not captured by the initial SHC model is that of hard-core soft-shell (HCSS) colloids. HCSS colloids are soft deformable particles that can be characterized as consisting of a hard solid-particle core inside a soft polymeric network outer layer [39]. They have intermediate properties between those of soft polymers and hard spheres, and can represent block copolymer micelles, star polymers, dendrimers, polymer-grafted nanoparticles, etc. The properties of these colloidal particles can be easily tuned by altering either the core or the nature of the grafted polymeric soft outer shell. The patterned arrays of these systems at surfaces or interfaces [40–45] have applications in various fields of scientific and technological importance, such as plasmonics [46], chemical and biological sensing [47], photovoltaics [48,49].

Despite the many practical applications of HCSS colloids, there have been surprisingly few attempts at modeling and exploring the behavior of these systems using computer simulations. Only recently, for example, a one-dimensional exactly solvable model of HCSS colloids was developed [50], and used to reveal its thermodynamic behavior and self-assembly at interfaces. Given that dimensionality usually has strong effects on the thermodynamic and dynamic behavior, higher dimensional HCSS models remained to be addressed.

In this work, we modeled HCSS colloids using SHC dynamics [35] and explored their structural and thermodynamic behavior. In our model, HCSS colloids are characterized by two parameters: the softness parameter (which characterizes the system's softness and governs whether an inter-particle collision is hard or soft) and core-to-total-radius (or core-to-shell) ratio. Just as in experiments [16], the behavior of these systems can be tuned easily by changing the core-to-shell ratio, softness parameter or packing fraction. Note that, since the SHC model does not entirely remove the infinity of the potential inside the hard sphere radius, it does not give rise to a finite intrinsic energy scale.

The organization of the paper is as follows. The computational model of HCSS colloids based on SHC dynamics [35] and computer simulation method details are described in Section 2. Methods used to measure the effective packing fraction of the system at different values of softness parameter and number density of the system is described in Section 3.1. The characterization of the thermodynamic and structural behavior and their dependence on the effective packing fraction and softness parameter is presented in Sections 3.2 and 3.3, respectively. In Section 3.4 we discuss the structural origin of the "non-trivial" effects of softness to the thermodynamic behavior, defined as the change in the thermodynamic behavior on changing the softness parameter at a fixed *effective* packing fraction. Finally, in Section 4, we conclude by summarizing the advantages and efficacy of the extended SHC dynamics to model HCSS colloids, and detailing how its use allows us to tease out the relative effects of softness on their structure and thermodynamics.

2. Model and simulation details

The original SHC algorithm proposed by Craven et al. [35] modeled soft colloids assuming that it had only one effective length scale for the interaction. The existence of both a hard core and soft mid- to long-range interactions in the HCSS colloids necessarily requires at least two characteristic length scales. A natural generalization, accounting for the HCSS structure, is the dual-core SHC potential described by the following form,

$$V_{ij}^{\mathrm{SHC}}(r) = \begin{cases} 0, & r > \sigma_o \\ 0, & \sigma_i < r \leqslant \sigma_o \text{ and } a_{ij}(t_{\mathrm{col}}) < \delta \\ \infty, & \sigma_i < r \leqslant \sigma_o \text{ and } a_{ij}(t_{\mathrm{col}}) > \delta' \\ \infty, & r \leqslant \sigma_i \end{cases} \quad (1)$$

where σ_o is the outer core and σ_i the inner core diameter, respectively. The softness parameter δ describes the probability of penetration when two particles i and j reach the contact distance σ_o. At this putative collision occurring at a given time t_{col}, a random number a_{ij} is generated and compared to the predefined softness parameter δ. If $a_{ij} > \delta$, the pair of particles collides elastically like hard balls [51]. Alternatively, if $a_{ij} < \delta$, the putative pair of colliding particles do not repel and penetrate freely without facing any barrier (like in an ideal gas interaction). Once inside this outer penetration distance σ_o, the particles move freely until they either reach contact at the inner distance σ_i — whereupon they experience an elastic collision while remaining free otherwise — or they escape the outer distance. The degree of penetration depends on the inner core diameter, σ_i. In this model, unlike in deterministic bounded potentials [33,34], the kinetic energy of a colliding pair plays no role in the penetration process. The penetration is solely governed by δ which is an intrinsic property of the system characterizing its softness.

In the limiting case when $\sigma_i = 0$, the dual-core SHC potential (Eq. (1)) reduces to the SHC potential of Craven et al. [35]. When $\delta = 0$ or $\sigma_i = \sigma_o$, the particles behave like a hard sphere with particle diameter σ_o. For $\delta = 1$, the system again behaves as a hard sphere but of particle diameter σ_i, and σ_o becomes moot. The core-to-shell or core-to-total-radius ratio (σ_i/σ_o) is an important control parameter for tuning the properties of core-shell colloidal systems in experiments [52–54]. In this work, we have set the core-to-total-radius ratio equal to 0.7 corresponding to approximately equal area for the core and the shell regions in the 2-dimensional (2D) case. A pictorial representation of the HCSS colloid and its coarse-grained representation along with a plot of the inter-particle SHC potential —Eq. (1)— is shown in Fig. 1.

Time-driven molecular dynamics (MD) [51] and Monte-Carlo (MC) [55] simulations were performed on a system of $N = 1000$ dual-core

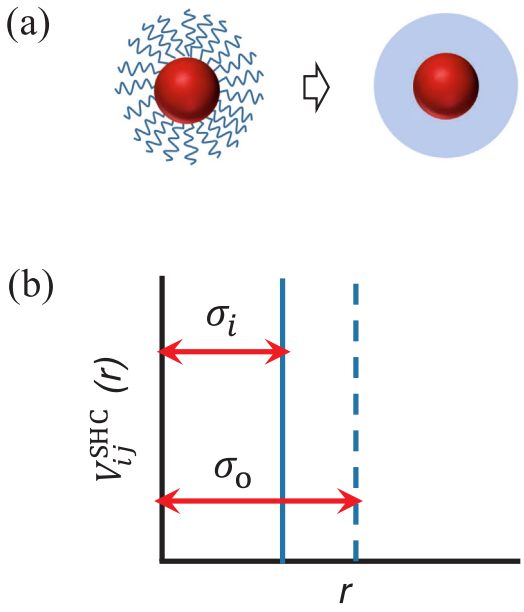

Fig. 1. (a) A pictorial representation of the hard-core soft-shell (HCSS) colloid and coarse-grained representation of the same is shown. In our model, the soft shell is represented by a stochastically penetrable isotropic shell around the hard inner core. (b) The SHC potential (Eq. (1)) showing the partially (stochastically) penetrable outer shell of diameter σ_o (denoted by the dashed line) and the hard inner core of diameter σ_i. The probability of penetration is defined by the softness parameter δ.