

Polysaccharide clustering in an implicit water solvent

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Summary

A dilute system of equally sized anionic polysaccharides suspended in an implicit water solvent was studied using molecular dynamics. The radial distribution functions were generated for these systems as a function of the polysaccharide chain length (M) and electrostatic strength (η). These simulations indicate that for anionic polysaccharides of equal charge, molecular aggregation or clustering in water is favored as the polysaccharide chain length increases.

Background

Starches, such as maltodextrin, are polysaccharides consisting of repeating glucose monomer units and are commonly used in low concentrations (1 wt%) as hydration inhibitors in cements. Cement hydration occurs under alkaline conditions (pH~12); as such, the polysaccharides are often deprotonated on one (or more, depending on the pK_a) glucose subunits. Importantly, the effectiveness of maltodextrin at inhibiting cement hydration is influenced strongly by the chain length. We hypothesize that the chain length influences clustering of the polysaccharide molecules in aqueous alkaline solutions which, consequently, alters the diffusion of water to particle surfaces and changes the overall rate at which the cement hydrates. Here, we study the effect of the polysaccharide chain length on the clustering of anionic molecules in water using a simplified molecular dynamics simulation.

Simulation Methods

To simulate the system of anionic polysaccharide molecules in water, three pair potentials were used in the canonical ensemble. The linear polysaccharide is modeled as a Lennard-Jones/harmonic spring and the solvent (i.e, water) is modeled implicitly, using the screened Coulomb potential. Combining these potentials and non-dimensionalizing gives the dimensionless interaction potential:

$$u^*(r_{ij}^*) = \underbrace{\frac{k}{2} [r_{ij}^* - r_0^*]}_{\text{bonded (harmonic) interaction}} + \underbrace{4 \frac{\epsilon}{\epsilon_{Coul}} [(r_{ij}^*)^{-12} - (r_{ij}^*)^{-6}]}_{\text{non-bonded (Lennard-Jones) interaction}} + \underbrace{\frac{\eta q_i q_j}{r_{ij}^*} e^{-\frac{r_{ij}^*}{\lambda^*}}}_{\text{electrostatic interaction}}$$

where r_{ij} is the position vector between particles i and j . The corresponding dimensionless parameters, and their estimated values (used in the simulation), are:

$$r_{ij}^* = \frac{r_{ij}}{\sigma_{LJ}}, \quad r_0^* = \frac{r_0}{\sigma_{LJ}} \approx 1, \quad \lambda^* = \frac{\lambda_D}{\sigma_{LJ}} \approx 5, \quad T^* = \frac{k_B T}{\epsilon_{Coul}}, \quad V^* = \frac{V}{\sigma_{LJ}^3}$$

where the hard sphere diameter, σ_{LJ} , is set to 1, and the Debye screening length, λ^* , is set equal to 5 σ_{LJ} .

The parameter η ($\eta = \frac{e_0^2}{4\pi\epsilon_0\epsilon_{water}\sigma_{LJ}}$) is a measure of the electrostatic strength and was varied in

this simulation. The parameter $\epsilon / \epsilon_{Coul}$ was set equal to 1. Simulations were performed with 200 atoms ($N = 200$), while varying the number of monomers, M , (e.g., glucose units) per polysaccharide between $M=1$ (i.e., single glucose molecule) and $M=6$ (i.e., polysaccharide consisting of 6 glucose units). The anionic charge on each molecule was set to -1 (single deprotonation, typical for the solution pH) and the bulk density varied between 0.01 and 0.1. Molecular dynamics simulations were performed at $T^*=1$ over approximately 2000 time steps with $dt=0.001$ and using the velocity Verlet integrator with a rescale frequency of 100 steps. The radial distribution function (RDF) or pair correlation function was used to investigate clustering and computed using a histogram to determine the density of particles at a radial distance, relative to the bulk density.

Results and Interpretation

The clustering of the polysaccharides molecules was probed using the radial distribution function for different chain lengths, M , at constant density. Figure 1 shows a plot of the RDF for a bulk density of 0.10 and deprotonation resulting in a charge of -1 for each molecule (with the anionic charge located on the terminal monomer). These curves are typical of an RDF: specifically, there is an initial peak (in this case, at $r/\sigma \sim 2$), followed by oscillations at greater distances that eventually converge to values of 1 and indicate that there is no long-range order in the system. Notably, as the chain length of the polysaccharide increases, so do the values of $g(r)$. This indicates that under these conditions, longer polysaccharide chain lengths increase clustering in solution significantly. The observation arises due to the influence of electrostatic interactions in the system. Specifically, when $M=1$ (i.e., glucose molecule) all molecules and monomer species are negatively charged and therefore repulsive electrostatic forces between molecules prevent clustering to a significant extent. As the chain length increases, all molecules remain negatively charged, but only 1 monomer species within the polysaccharide is charged. As such, when $M=4$, within each molecule there are 3 uncharged monomers and 1 charged monomer. The uncharged monomers effectively ‘screen’ the repulsive interactions between the negatively charged monomers, which leads to increased aggregation or clustering of the molecules in solution (see Figure 1, inset). This simple model suggests that larger deprotonated polysaccharides are more likely to aggregate or cluster in alkaline solutions than smaller polysaccharides with the same degree of deprotonation. This may help explain the observation that the effectiveness of maltodextrin at inhibiting cement hydration is influenced strongly by the chain length. It is hypothesized that as the size of the polysaccharide increases (e.g., maltodextrin chain length), increased polysaccharide aggregation delays hydration in cements by reducing water diffusion to particle surfaces.

This model is necessarily simplified but the approach could be improved to simulate behavior in real systems. The implicit solvent model isn’t particularly accurate as it neglects the complex rearrangement of the solvent due to the solute. An explicit solvent model would be desirable to more accurately model solute-solvent interactions (e.g., Poisson-Boltzmann Solvent Accessible Surface Area Method, Generalized Born Solvent Accessible Surface Area Method). Secondly, a more detailed study of the anionic nature of the charged polysaccharide species under hydrating cement conditions (e.g., location of charges, degree of deprotonation) would help provide more meaningful results.

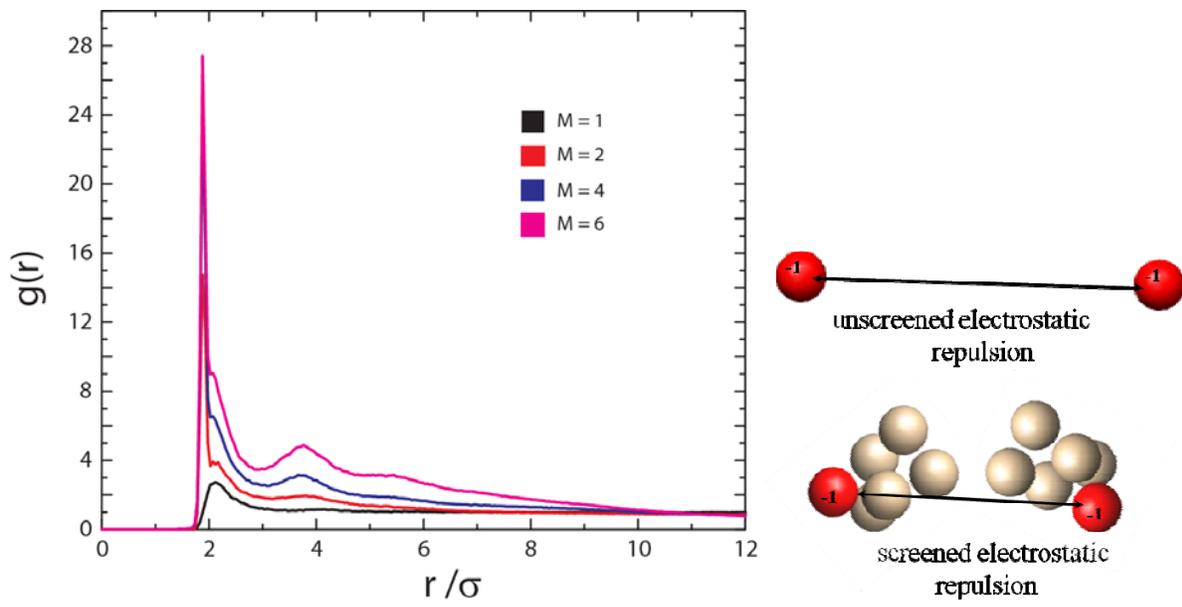


Figure 1: The radial distribution function plotted for different polysaccharide chain lengths, M . Simulation parameters: $N = 200$, $k = 3000$, $\eta = 100$, density = 0.10, charge/molecule = -1. The inset illustrates an ‘unscreened’ and ‘screened’ electrostatic repulsion corresponding to $M=1$ and $M=6$.