On the validity of representation of the inter-particle forces of a polymer-colloid cluster by linear springs

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A B S T R A C T

We have investigated the validity of the popular assumption of identical linear spring (ILS) in polymer-colloids aggregated clusters. The ILS assumption suggests that all inter-particle bonds in an aggregated cluster of polymer chains and colloid particles can be represented by identical linear springs. The assumption has been challenged by several experiments that showed the bond stiffness varies across the cluster based on the connectivity of their associated particles. Yet, the predictions of the computational models that used ILS assumption are surprisingly well-aligned with the experiments in some materials. By coupling the coarse-grain Brownian dynamics simulation to a Multi-body dynamics model, a systematic pathway for analyzing the effect of connectivity of particles on elasticity of polymer-colloids aggregated clusters is presented. ILS assumption is found to be valid for systems with a stress path formation mechanism such as close-packed polymer-colloid clusters. We found the assumption irrelevant in systems with wave-like stress distribution mechanism, such as with granular materials, sand piles and jammed systems. Keywords Mechanics; polymer-colloid clusters; Identical springs assumption.

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1. Introduction

Colloidal structures represent an attractive class of soft materials whose properties can be tailored by exploiting the individual and collective properties of the colloids. These structures are assemblies of large numbers of colloids attaching to each other through attractive or repulsive forces. Interestingly, despite different behavior at macro-scale, colloidal systems behave quite similarly in micro-scale. Depending on the types of media and colloids, different forces occur in the assembly of the colloidal structures.

An important class of colloidal systems are polymer-colloid (PC) mixtures, where polymers govern the inter-particle interactions and can be of attractive or non-attractive types.

Apart from the clusters formed by attraction forces between polymers and particles, clusters can also be formed by the depletion induced by the osmotic pressure of non-attractive polymers. In non-attractive mixtures, attractive inter-particle interactions result from entropic exclusion or depletion forces which closely resemble a square-well attractive potential [1–6]. In attractive mixtures, inter-particle interactions exhibit pure attraction at low polymer concentrations, long-range attraction and short-range repulsion at medium concentrations, as well as pure repulsion at higher concentrations [6]. At low polymer concentrations, aggregated structures in attractive PC mixtures strongly resemble those of non-attractive PC mixtures. In high polymer concentrations, polymer bridging between the particles creates permanent bonds and eventually forms entropic aggregates even when the interactions are purely repulsive [7–9].

Here, the main focus is on aggregated clusters formed in low and medium concentrations of attractive polymers. Those aggregates are prevalent in nature [6]. In these clusters, the interactions between colloids are mediated by bridging polymers in a supramolecular fashion.

ILS assumption is designed to simplify the representation of the inter-particle bonds of a cluster. It consists of two parts; (1) assuming all bonds to be represented by linear elastic springs and (2) assuming all bonds to have similar spring constants. Theoretically, the ILS assumption is not valid in highly-connected clusters since the elastic properties of bonds vary considerably throughout

the cluster. However, studies have demonstrated that the ILS model works well, particularly in close-packed structures.

There are two types of load distribution patterns to describe the mechanical response of colloidal systems: (i) wave-like stress distribution in materials such as granular materials, sand piles and jammed systems [10], and (ii) inhomogeneous path-like stress distribution in close-packed clusters such as PC clusters [11—13]. Generally, due to the fractal nature of PC clusters, when they are subjected to a force, several stress paths are formed inside. One stress path, often the shortest one, transfers the most of the applied load [14].

Numerous simulations, experiments and empirical studies on the mechanical behavior of PC composites have provided us with a good understanding of the behavior of these material at macroscales [1,15,16]. So far, no consensus on the micro-mechanics of PC composites, and particularly their clusters has emerged. Mechanics of PC clusters, despite its ubiquity and significance, remains far from understood; even the contribution of inter-particle forces on elasticity of systems are not agreed upon.

At low particle concentrations, scaling and micro-structural models have been advanced to describe the rheological [17—19] and mechanical properties of PC structures [20—22]. At high particle concentrations, more complicated scaling approaches were developed to account for inelastic features that appear at high concentrations [23,15]. In most of the models, ILS assumption was hired.

The controversy concerning the realism of the ILS assumption goes back to the 1980s, when the assumption was widely adopted in analytical models to reduce their computational cost [19,24—27]. Early studies on ILS assumption were mainly focused on the role of the local connectivity and stress homogeneity in the mechanics of gels, percolation networks and amorphous solids [28—31]. In a pioneering work, Alexander [32] summarized several studies on the mechanics of amorphous solids, and rejected the second part of the ILS assumption by suggesting that the bonds may be linear elastic but not identical throughout the cluster. Using the first part of the ILS assumption, he proposed a generalized formulation for the elasticity of PC clusters which is applicable in different colloidal systems. The model was computationally expensive as it calculated the energy of a cluster by summing up the energies of each individual bond. More recent studies on non-affine mechanics of disordered solids such as gels, glasses, etc. have also shown that the stresses and bonds developed under aggregation or solidification are unbalanced and non-equivalent [6,33].

In the first targeted study on the validity of the ILS assumption, Zaccone et al. developed a simplified aggregation model to explore the role of heterogeneity and connectivity of bonds in the elasticity of dense gels. The study showed that heterogeneity of inter-particle stiffness plays a major role in the elasticity of aggregated structures and thus cannot be neglected [34,35]. Similar observations reported for disordered fiber networks [36], granular solids, and particulate packings [37] confirmed that the bonds' stiffness varies across the cluster based on the colloid-colloid and colloid-media interactions [11,17,38,39].

Although ILS assumption contradicts experimental and theoretical studies, many models that adopt this assumption show good agreement with experiments [18,19,40—45]. The ILS assumption is still widely popular, adopted by many multi-scale models, and often acts as a coupling assumption between atomistic and continuum-scale models. Yet, there is no understanding of the error of the ILS assumption in different material systems or load conditions. As the assumption is increasingly being utilized in the modeling of gels, composites and biological systems [6,10,15], understanding the validity, and error range of the ILS assumption in different material settings is of true interest.

Here, two fundamental questions on ILS assumption are investigated.

1 How can the ILS assumption be effective despite being rejected by experiments?
2 What is the error associated with it in PC clusters?

To this end, a Lattice Boltzmann implemented with coarse-grained Brownian Dynamics simulation method, previously developed to describe blood-clotting procedure [16,46,47], has been used for the assembly of the clusters in attractive polymer-colloid solutions. The polymers are modeled by using bead-spring model, and colloids by Raspberry model. Although the simulation procedure is not the focus of this paper, a description of the simulation and testing procedure is provided to clarify the model validation process. The elasticity of each bond is derived from the thermal vibrations of the particles associated to it. Three loading types are considered to be transferred by each bond; (i) centrosymmetric, (ii) bending, and (iii) torsion loads. The vibrations of the bonds when subjected to each of these loads are derived by performing uni-axial tests on simulated PC clusters. Having the response of the bonds at hand, the load transfer pattern inside the cluster is derived and correlated to the variance of the bond stiffness. By characterizing the connectivity of the particles, we show that the mechanical behavior of inter-particle bonds is strongly governed by the connectivity and spatial position of particles. The results suggest that in the close-packed clusters (CPC) where the behavior of the clusters is governed by a small number of bonds, the behavior of the contributing bonds are identical.

2. Simulation method

PC clusters are first assembled and then subjected to uni-axial tensile test. The assembly of PC clusters is achieved under shear flow using Lattice Boltzmann method (LB) and Brownian Dynamics (BD) simulations. The behavior of polymer and colloids are described by BD whereas the contribution of solvent is depicted by fluctuating LB method [48]. Once the PC clusters is assembled, those transient clusters are transformed into the permanently linked stable clusters. There are different approaches to transfer the transient aggregates into permanently linked aggregates by e.g. photolithographic polymerization [49]. Although variations can occur due to the change of polymer-colloid link treatment, the permanent linked CPC will serve as a close approximation of the transient CPCs. In many mixtures, like carbon-black filled elastomers, the aggregation takes place in the mixing process due to a shear flow and high temperature. The mixing process will result in formation of permanent PC aggregates which can sustain large deformations after the compound is cooled down [42,50—54]. Next, they are subjected to uni-axial tension to measure the inter-particle force. To minimize the computational costs of coupled Brownian Dynamics and LB method simulation and to avoid the complex superposition of the shear and tensile loads, The tensile test simulations are carried out using only free draining BD without LB. This is because LB is computationally costly and the effect of hydrodynamics interactions between colloid particles within the same rigid cluster can be neglected. Therefore, LB method is not implemented for performing the tensile test.

2.1. Fluctuating lattice boltzmann method and Brownian dynamics

Polymers and colloids are simulated with standard simulating techniques under the framework of the fluctuating Lattice Boltzmann (LB) equation [55] in three-dimensional grids with