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Colloidal Particle gel models using many-body potential interactions

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Many-body effective interactions are commonly used in molecular dynamics simulation study of gel networks formed by colloidal particles. Here, we report a new interaction potential that can be used to investigate the mechanical response of colloidal gel networks under shear deformation. We then investigate the dependence of the numerical simulation results on the form of mathematical expression used to express the interparticle interactions. This work reveals new insight into particle gel models by discussing the physical origins of their mechanical response.

Colloidal gels are ubiquitous in nature and find important engineering applications because of their fascinating material properties. These gels are formed from the aggregation of colloidal particles at low volume fraction [1]. The physical features and mechanical behavior of colloidal gels have been recently investigated using numerical models that are based on the self-assembly of particles [2–5]. Specifically, it has been shown that the minimal particle based model, referred to here as Short Range Gaussian (SRG) model, could generate in silico gel networks whose microstructure resembles what typically observed in experiments [1, 6]. These molecular dynamics (MD) numerical simulations have captured the nontrivial mechanical response of colloidal gels and provided new insight into key aspects of their mechanical response [7–11]. However, only one specific form of interparticle potential function has been used. In particular, N colloidal particles with position vectors \mathbf{r}_i are assumed to interact with each other through the potential energy $U = \epsilon \sum_{i>j} \Phi_2(\mathbf{r}_{ij}/d) + \epsilon \sum_i \sum_{j>k}^{j,k \neq i} \Phi_3(\mathbf{r}_{ij}/d, \mathbf{r}_{ik}/d)$ where ϵ is the energy scale, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, d is the particle diameter, $i, j, k = 1 \dots N$, Φ_2 is a Lennard-Jones type two-body term, and Φ_3 is a three-body potential that confers angular rigidity to the interparticle bonds. The potential U is written as the sum of the two-body and three-body terms in order to form open network structures. Otherwise, phase separation occurs at low volume fraction. One very specific mathematical expression has been used for the three-body term in MD simulations [7–11]. This is a significant drawback because the overall behavior of colloidal gel networks is a function of physical processes occurring at the length scale of interparticle interactions, i.e. the strength and nature of interparticle interactions, represented by the potential energy U in MD simulations, define the overall mechanical properties of colloidal gels. Thus, despite the important contributions of SRG-based models to the field, their findings regarding the relation between the network structure and nonlinear mechanical response of colloidal gels may not be universal. This issue is made even worse by the fact that, besides using a particular form of the potential function U , only one convenient set of parameters, for which colloidal particles self-assemble into persistent network structures,

has so far been used [7, 8, 10]. The primary objective of the present rapid communication is to investigate how this specific interparticle potential, that is not widely accessible to the research community, might have affected the generality of microscopic explanations that MD simulations have provided for colloidal gel network properties at low volume fraction. To this end, we here propose a new effective interaction potential by modifying the Stillinger-Weber (SW) potential function [12]. The three-body SW potential was initially developed for crystalline silicon and then it has been applied to model different materials such as amorphous silicon, glasses, and colloidal gels [13–15]. We choose SW potential because it is well established and has already been implemented in many open source MD packages, i.e. the proposed interaction potential could become a convenient tool for creating particle gel models in future, without complexities involved in defining the SRG model in MD softwares [7]. After confirming that the proposed potential gives colloidal open spanning networks similar to those previously generated using the SRG model, we conduct MD simulations in order to characterize the mechanical response of gel network models under large shear deformation. We then discuss the dependence of the overall properties of in silico gel networks on the potential function used for representing the interactions between colloidal particles.

In this letter, we write the components of potential energy U as $\Phi_2(\mathbf{r}) = A(b r^{-18} - r^{-16}) \exp\left(\frac{1}{r-a}\right)$ and $\Phi_3(\mathbf{r}, \mathbf{r}') = B(\cos \theta + \alpha)^2 \exp\left(\frac{\gamma}{r-a}\right) \exp\left(\frac{\gamma}{r'-a}\right)$ where r is the distance in units of d between any two particles i and j , r' is the distance between particles j and k , and θ is the angle formed by particles j and k at the site of particle i . Furthermore, A , b , a , B , α , and γ are dimensionless quantities that are selected such that colloidal particles could self-assemble into a network structure. Note that the continuity of the interaction potential is ensured by considering an exponential modulation function in the definition of two-body and three-body terms. This modulation function increases exponentially as the distance between particles decreases to their diameter. We select the parameters of the proposed potential such that in silico gel models with geometries similar to those of

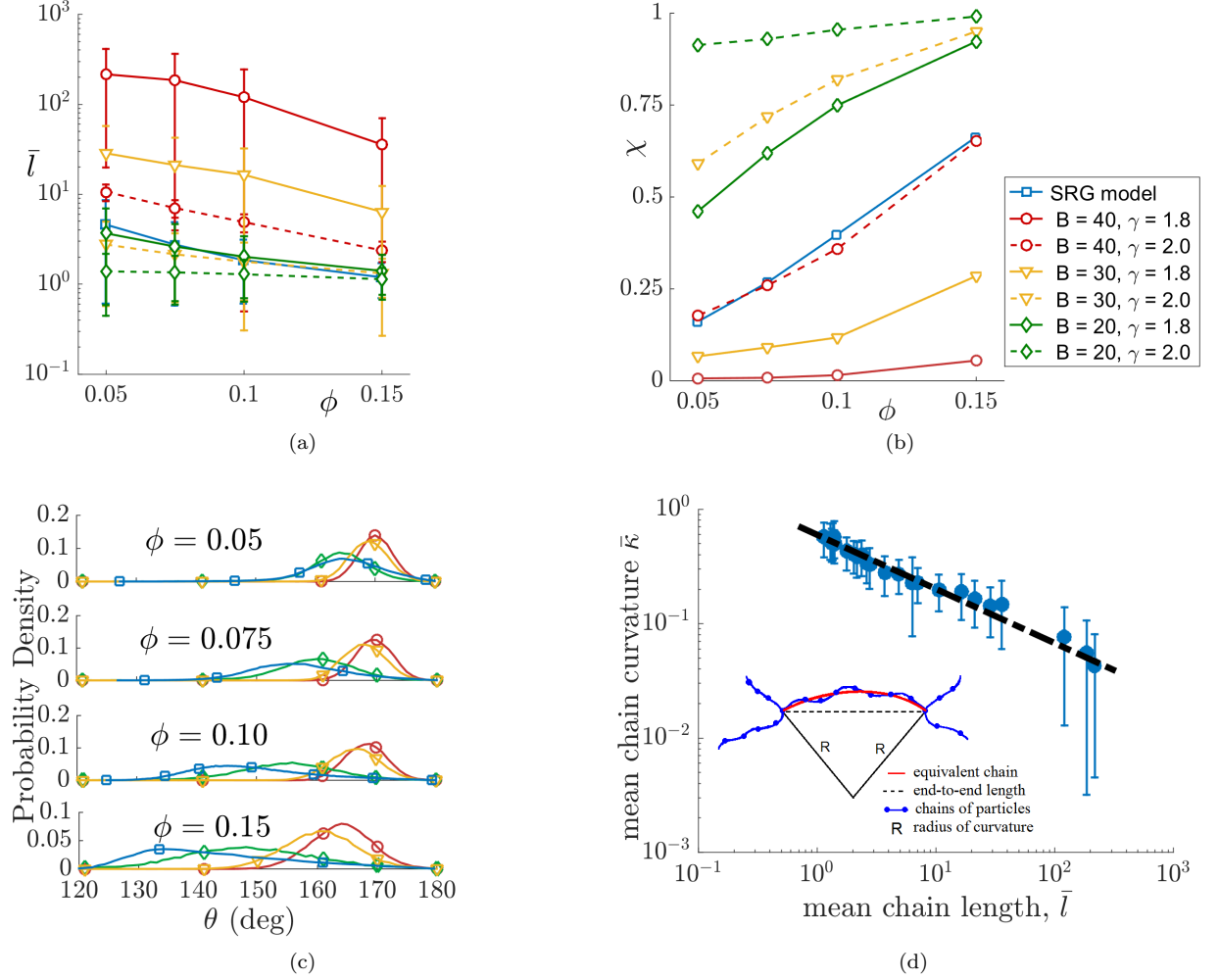


FIG. 1: (a) mean value of the chain length, (b) proportion of bonds χ participating in nodes of coordination 3, and (c) bond angle distribution in chains of particles as a function of volume fraction for gel networks generated by different models. The bond angle distribution for models with $\gamma = 1.8$ is only shown for clarity. (d)

The variation of mean chain curvature as a function of mean chain length for different particle gel models. A power law dependence with an exponent of about 0.45 is observed. The inset is a schematic showing how the curvature of wavy chains is computed

the SRG model are obtained. In particular, particle gel models with geometries similar to that of the SRG model were found using $A = 29.215$, $b = 0.896$, $a = 1.9$, and $\alpha = 1$. The parameter B , which determines the strength of the three-body term, and the parameter γ , which controls the rate of variation of the modulation function, are varied in separate studies in order to investigate how variation of model parameters could affect the results of MD simulations.

LAMMPS MD software is used to create numerical gel networks with different volume fractions from N randomly placed colloidal particles in a simulation box [3, 16]. For this purpose, the Nosé - Hoover thermostat over 5×10^6 timesteps is first used to bring the systems to temperature $\epsilon/k_B T = 20$. With decreasing the tempera-

ture, it is seen that the particles aggregate into clusters and form arrested networks spanning the entire simulation box. These gel networks are persistent because the thermal energy $k_B T$ is small compared to the energy scale of the potential interactions ϵ , i.e. thermal fluctuations cannot break the bonds between particles. After performing a thermostatted run at the final temperature, the systems are quenched using the damped dynamics with the damping parameter $\sqrt{md^2/\epsilon}$ until the thermal energy becomes negligible compared to the potential energy [9, 10]. In the following, the length, mass, and energy are given in reduced units of particle diameter d , particle mass m , and energy scale ϵ , respectively.

The mean length of chains, \bar{l} , (Figure 1a), the ratio of bonds connected to nodes with coordination 3, χ , (Fig-

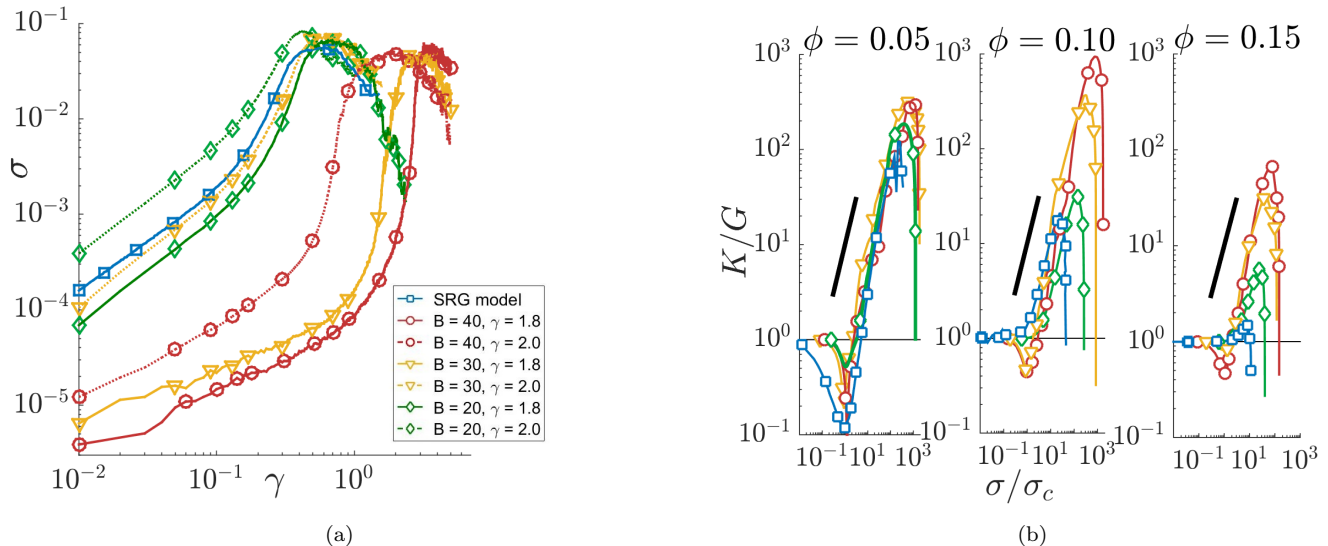


FIG. 2: (a) Homogenized shear stress-strain curves for gels with $\phi = 0.10$, all models have an almost similar maximum stress; (b) normalized differential modulus as a function of σ/σ_c where σ_c is the stress corresponding to γ_c . An initial softening at low volume fraction followed by strain hardening is observed in all models; black lines have a slope of one. The softening response disappears with increasing the volume fraction. The results for models with $\gamma = 1.8$ are only shown for clarity.

ure 1b), and the distribution of bond angles, θ , (Figure 1c) are used to characterize the fibrillar topology of gel networks as a function of volume fraction ϕ . It is noted that these quantities are correlated; for example, a network of short chains is also densely connected. However, the breakdown is not unique and depends on the model parameters. The present model with $B = 40$ and $\gamma = 2$ gives networks with nearly identical proportion χ as the SRG model but with longer chains. Moreover, the present model with $B = 20$ and $\gamma = 1.8$ or $B = 30$ and $\gamma = 2.0$ generates gels with chains of similar length as those generated using the SRG model but with larger connectivity. The important message of Figure 1 is that the present model gives researchers the flexibility to numerically generate particle gel models of different topologies. It is desirable to have a general framework for this purpose; nevertheless, the complex form of the potential energy U makes this task very difficult and future efforts are required to pursue this important objective. Despite this, it can be stated that with decreasing the 3-body prefactor B , the repulsion between particles becomes less strong allowing the formation of denser regular assemblies of short chains. The effect of parameter γ in adjusting the mean chain length becomes more important when the three-body term is strong, i.e. $B = 40$. Increasing γ from 1.8 to 2.0 in models with $B = 40$ generates gels with shorter but higher connectivity because the modulation function prevents formation of long chains, Figure 1. The existing flexibility in

generating particle gel models with different topological features makes the proposed model suitable to be used in synergistic experimental and computational efforts. In such studies, imaging techniques will provide the essential information about the distribution of particle chains inside the gel. Such information can then be used to guide the numerical model parameter selection process. The distribution of bond angles in the chains is relatively similar for all models. We use the probability measure 'mode of the distribution function' for representing the dominant bond angle in chains of coordination 2 (Figure 1c). At low volume fraction, the mode is large and distributions are narrow, which implies that local equilibrium prevails and loosely connected long chains adapt an almost straight configuration. Densely connected networks at high volume fractions have more constraint in their configurations because of neighboring particles. As a result, chains tend to be less straight, i.e. the mode for these gels decreases and the distribution broadens. Models with $B = 40$ have longer chains, a narrower distribution, and larger mode for all volume fractions, confirming the interrelation between the chain length and curvature. In order to support this statement further, we plot the mean chain length and mean chain curvature for all models in Figure 1d, showing that shorter chains have larger curvature regardless of the model parameters.

Next, the nonlinear response of gel network models under strain-controlled simple shear kinematics is investigated. The shear deformation γ is applied incrementally

($\delta\gamma = 10^{-2}$) until failure. The systems are first deformed affinely at each increment before relaxing them to equilibrium by performing the damped dynamics using a finite shear rate $\dot{\gamma} = 10^{-5}\tau_0$ with $\tau_0 = \xi d^2/\epsilon$ [9]. The virial stress at each loading increment is taken as the homogenized mechanical stress σ [17]. Figure 2a shows that the overall shape of the stress-strain response is in agreement with experimental results obtained for soft gels under direct shear [18–20] and with that was previously reported using the SRG model. This further highlights the validity of our approach and demonstrates that different potential formulations can be used to model the mechanical behavior of soft gels. At small strains, systems show an almost linear response, represented by their initial shear modulus G . They then exhibit initial softening where the differential modulus K , corresponding to the slope of the stress-strain curve, decreases. The softening response continues up to the strain γ_c where K reaches a local minimum. Afterwards, the response enters a non-linear strain-hardening phase until the maximum strength is reached. In the final yielding phase, the stiffness decreases because of the presence of irreversible mechanisms and damage accumulations caused by local interparticle bond breakings. Beyond that phase, the systems undergo the shear flow [19].

Figure 2 shows that all models have almost the same maximum stress, suggesting other mechanisms other than the allowable variations in the mathematical expression used for the interaction potential control the strength. The stiffness, however, behaves differently, i.e. the maximum stress is reached at different strain values for different models. This plot shows that the model parameters significantly influence the exact shape of the stress-strain response. Furthermore, the behavior of systems built using $B = 30$ and $\gamma = 2.0$ is very similar to that of the SRG model. Although it is desirable to find a master curve for the stress-strain response in terms of model parameters, such studies are beyond the scope of the present work. Nevertheless, several conclusions can be made. At constant B , increasing the parameter γ shifts the shear strain corresponding to the maximum stress to the left. The normalized differential modulus K/G is plotted against the normalized stress σ/σ_c for present models with $\gamma = 1.8$ (Figure 2b); this plot clearly shows the different phases of the mechanical response. There exists a strain-softening response for low volume fraction gels in which the normalized differential modulus strictly decreases to values less than 1. This strain softening response has been also observed experimentally and numerically in soft gels of different nature and under various loading conditions as well as systems whose microstructure is fibrillar such as polymer fiber networks [7, 10, 15, 21–26]. Similar to the SRG model, the variation of the normalized shear stiffness is significant at the lowest volume fraction $\phi = 0.05$ and becomes less significant with increasing the volume fraction. Considering

the results shown in Figure 1a, it can be stated that softening is controlled in part by the particle chain length and should be due to uncoiling and straightening of long curly chains in the initial stages of deformation. Figure 2b also shows that the differential modulus K is initially constant when $\phi = 0.15$, indicating purely linear response at small strain. The shift to the strain-hardening phase occurs earlier with increasing volume fraction. During the strain-hardening phase, the differential modulus scales as a power-law with the stress $K \sim \sigma^{\nu \gtrsim 1}$; a typical feature of structures with nonaffine behavior [24, 27–29]. Interestingly, the scaling seems to depend only on the volume fraction and is similar for all models. At $\phi = 0.05$, the exponent is larger than one while $\nu = 1$ at $\phi = 0.10$ and 0.15 . The yield strain and the maximum value of differential modulus during the strain hardening phase also decrease with increasing the volume fraction. These observations indicate that microstructural reorganizations are more important at low volume fractions where gel networks are loosely connected and more fibrillar. At higher volume fractions, networks become denser and their deformation becomes more affine. The maximum strain reduction also indicates a transition toward a more brittle behavior. In addition to the volume fraction, this transition directly depends on the potential model parameters that are used to describe the interaction between colloidal particles. For example, gel models with $B = 40$ and $\gamma = 1.8$ remain fairly ductile even at high volume fractions.

We will now discuss fundamental mechanisms behind the initial strain softening response of colloidal particle gel networks by quantifying chain rearrangements in gel network models during the deformation. Geometric reorganization, i.e. rotation, uncoiling, and stretching, of particle chains influences gel topology and in turn their overall mechanical response. A new measure $\Theta = |\hat{\mathbf{r}} \cdot \mathbf{v}_I|$ is defined for determining the contribution of individual bonds in bearing the applied deformation. This measure quantifies the alignment of bonds, with unit bond vector $\hat{\mathbf{r}} = \mathbf{r}/r$, in the direction \mathbf{v}_I of the maximum principal stress σ_I . It indicates the degree to which one particular bond can participate in the overall response, i.e. bonds with $\Theta = 1$ are perfectly aligned in \mathbf{v}_I direction and could directly participate in resisting the applied shear strain. The participation of a bond in the overall response also depends on whether that bond belongs to the force chain formed in the structure. In other words, bonds that both belong to the force chain and are aligned in \mathbf{v}_I direction are expected to carry a significant amount of stress, i.e. the axial stretch r/d for these bonds will be large. We compute the Pearson correlation coefficient (PCC) between the bond alignment measure Θ and the bond stretch r/d for all interparticle bonds (Figure 3). Note that isotropic systems show no correlation between the stretch and alignment. Upon increasing the strain, network chains are rearranged causing PCC to become

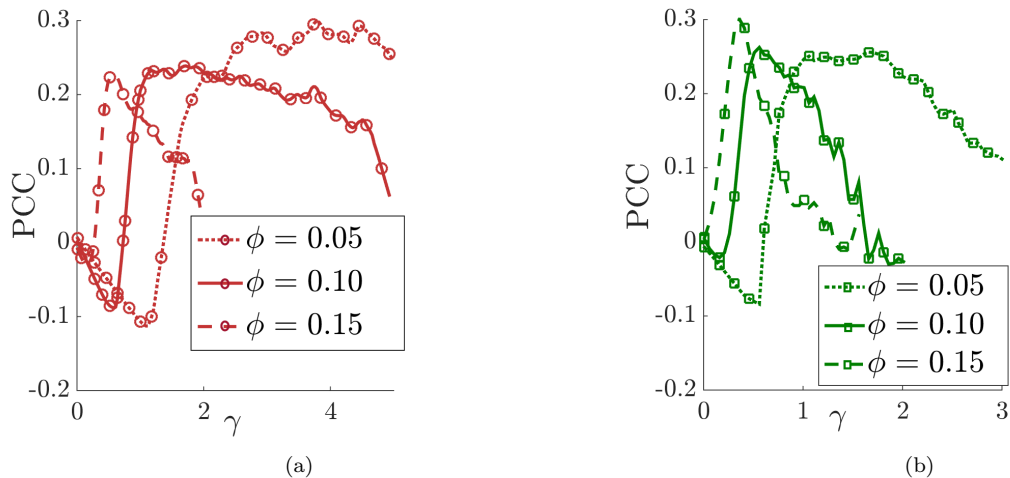


FIG. 3: Pearson Correlation Coefficient between alignment Θ and stretch r/d for all interparticle bonds in models with (a) $B = 40$ and $\gamma = 1.8$, and (b) $B = 20$ and $\gamma = 1.8$.

negative, i.e. an anticorrelation between the amount of chain stretch and their alignment in the principal stress direction exists. This anticorrelation provides additional support for possible enthalpic origin of the initial softening phase observed in the stress-strain response, Figure 2. In particular, gels showing the most softening (Figures 2b) also have the largest anti-correlation (Figure 3). The shear softening may therefore be, in part, due to the disturbing the initial configuration of curly chains whose preferred equilibrium form is straight. The potential strain energy stored in curly chains is released as their initial configuration is changed during the deformation; note that these new configurations do not necessarily align with the direction of the principal stress. The important role of chain length is also validated by the response of gels generated using $B = 20$ and $\gamma = 1.8$ model at $\phi = 0.15$; these systems have short chains and show no initial anti-correlation. The PCC for these gels is a strictly increasing positive function of γ (Figure 3). Thus, the enthalpic contribution to the strain softening includes nonaffine processes as well as the release of residual stress of curly chains. Following the initial phase, the PCC for all models increases to positive values and reaches a maximum value when straight chains are primarily aligned in the direction of principal stress. Upon failure, major reorganizations occur due to interparticle bond breaking and forming; thus, the PCC decreases.

In summary, this work introduces a new particle gel model based on the Stillinger-Weber potential and confirms that it can successfully reproduce geometric and mechanical features of existing numerical models in the literature. Furthermore, this study demonstrates that different mathematical formulations of the interparticle interaction potential can be used in numerical simulation studies of colloidal gel networks [7–11]. New insight

into microscopic origins of shear softening has also been provided by quantifying the correlation between bond stretch and bond alignment in the direction of principal stress. The present simulations suggests that the relaxation of residual stress in curly chains plays a significant role in the initial shear softening behavior of gels. Although the present work determines the influence of effective interaction parameters and quantifies their influence on the gel mechanical response, it does not provide a complete recipe, i.e. the model parameters are selected such that disordered percolating networks are self-assembled at temperature $\epsilon/k_B T = 20$. Future work is needed to extend this study and explore the possibility of developing a general framework in which the macroscopic properties of gels can be expressed in terms of physically observables such as mean chain length and proportion of three-coordinated nodes.

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