Yield behavior of colloidal aggregates due to combined tensile-bending loads

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In this contribution, the yield behavior of a strongly flocculated colloidal structure subjected to a tensile-bending load is micromechanically modeled. The yielding of a cluster is assumed to be triggered by the failure of one bond (critical bond) and accompanied by massive breakage of further bonds. Thus, identifying the position of the critical bond and evaluating its yield force are the main goals of this study. Interparticle bonds are considered as flexible nanoscale bridges which fail when the force applied on them reaches a critical value. The yield of the critical bonds can result from both tensile and bending stresses. By means of the yield stresses in the critical bonds, the yield force of the whole cluster can be calculated.

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I. INTRODUCTION

A colloidal system is a solution consisting of two separate phases: a dispersed phase (colloids in a solid phase) and a continuous phase (or dispersion medium) which may be solid, liquid, or gaseous. Colloidal systems exhibit a wide range of rheological behavior and are often classified as soft materials. They also appear in a wide range of products, such as food, paints, and polymers. The term "colloid" is specific to individual particles which are larger than atoms but small enough not to immediately settle in the solution (the typical range is from nanometers to a few micrometers). Dynamic behavior of colloidal particles is governed by the Brownian motion and forces of interparticle attraction and sedimentation. Under these forces, the particles may remain suspended in a liquid medium infinitely long. Sedimentation or floating of clusters in a solution takes place when the Brownian forces are not strong enough to overcome the gravitational-hydrodynamic forces. For usual colloid sizes, this can happen only for very large clusters.

Generally, colloids are microscopically dispersed throughout the dispersion medium and form a gel-like structure at high particle concentration or dispersed clusters at low particle concentration. A cluster is a solidlike colony of particles, formed by an aggregation mechanism. In this study, we mainly discuss the yield behavior of single isolated clusters assumed to be completely surrounded by the dispersion medium (see Fig. 1).

Aggregation in colloidal systems is characterized by the magnitude of interparticle forces. If attraction forces are stronger than the thermal forces of particles (that result in the Brownian motion), the particles join together and form irreversibly aggregated clusters. They continue diffusing and aggregating, although their growth rates are limited by the particle diffusion rates. This aggregation mechanism, which can describe the fractal dimensionality of the clusters, is called diffusion limited cluster aggregation (DLCA). Meakin *et al.* [1] proposed a cluster-cluster aggregation (CCA) mechanism which describes the formation of large clusters from a dispersed collection of smaller ones. In this mechanism, the Brownian movement of small clusters and their irreversible flocculation with each other lead to the formation of larger clusters.

Recently, the microrheology, flow, and yielding of colloidal clusters have been subjected to many investigations both theoretically [2–4] and experimentally [5,6]. In spite of that, the yielding mechanism of colloidal clusters has not properly been understood so far. This work addresses the yielding of strongly aggregated clusters under applied tensile forces and bending moments.

The cluster behavior is described by the interparticle forces which are decomposed into centrosymmetric and tangential ones. The mechanical behavior of a bond can be fundamentally different depending on whether the bond is subjected to only central forces or both central and tangential forces.

II. STATE OF THE ART

Different experimental and simulation results show that the centrosymmetric forces play a major role in cluster elasticity [7,8]. Different hypotheses consider the centrosymmetric forces as a result of van der Waals forces [9,10], surface chemistry [11,12], hydrophobic effects [13], depletion interactions [14,15], or local immobilization in the dispersion medium [16].

General understanding of tangential forces which resist the bending moments is quite limited [17–19]. Tangential forces also play an important role in describing the shear resistance of singly bonded clusters formed by DLCA or CCA. The presence of these forces was inferred from the experimental observations of particle deposition [20], differential electrophoresis [21], and laser tweezers [22].

Recently, Pantina and Furst [22] reported experimental results confirming the resistance of the interparticle bonds against bending moments. There are many tangential-force models proposed for cluster simulations (for details, readers are referred to [23]). However, most of them do not consider bending moments between particles. The very first study on this topic was published by Kantor and Webmann [24]. Considering the central and tangential forces between particles, the energy of a chain of particles was approximated. Later, Potanin [25] proposed that the energy of a chain of particles connected by central and tangential forces is identical to the energy of a thin elastic rod of the same length. Quite recently, by means of special shape descriptors the energy of clusters

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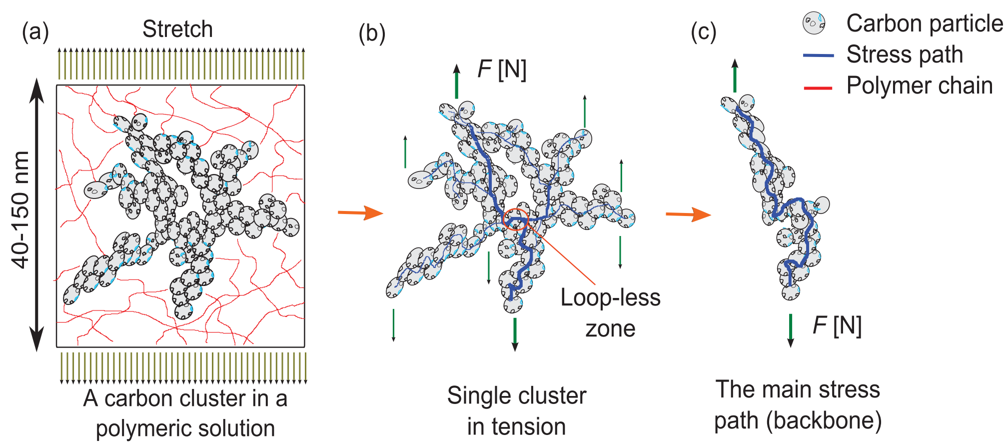

FIG. 1. (Color online) (a) Formation of a backbone chain in an isolated cluster suspended in the polymeric solution. (b) Forces applied on the cluster and the resultant stress paths. (c) The final backbone chain as the main stress path. A loopless zone in the backbone chain is highlighted.

under large deformations was approximated on the basis of the Kantor and Webmann model [26,27]. In another work [19], the central forces are excluded while the tangential forces are assumed to result from tangential springs with limited elasticity range. Although the obtained result was identical to that in [24], the micromechanical approach was fundamentally different.

In order to minimize the computational costs, another model was proposed where particles are replaced by a trimer of particles and, accordingly, the new bonds are defined by the superposition of central forces acting between trimers. Thus, the new bonds can also support bending moments [17]. More recently, Botet and Cabane [18] described an interparticle bond by a number of springs connected to different random sites of the particle surface. Each spring is activated if its end-to-end distance becomes smaller than a specific value. Accordingly, despite the cumbersome procedure of the parameters estimation, the model can successfully take tangential forces into account.

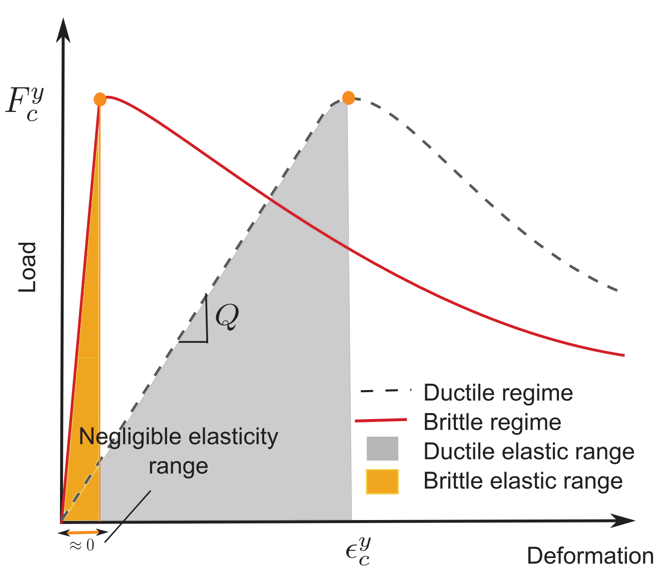

FIG. 2. (Color online) A schematic load-deformation behavior of ductile and brittle materials in central direction.

Klüppel *et al.* [28,29] described the cluster yielding by means of mechanics of interparticle forces. The influence of tangential forces on cluster elasticity was taken into account. Their contribution to yielding was, however, not considered. Thus, a bond is supposed to yield when the centrosymmetric force between particles starts to decrease under tension [16,30]. Experimental results reveal, however, much smaller yield forces than those predicted by the above mentioned theories [31].

Recently, not only centrosymmetric but also tangential forces have been taken into account in order to describe interactions between particles [31,32]. Let us categorize the interparticle interactions in each direction, regardless of their source into two different regimes as follows (see also Fig. 2).

(i) *Brittle regime*. The bond is assumed to rupture without significant deformation in the corresponding direction and yields when the load reaches a maximum value, that is, maximum force F_c^y in the central direction or maximum moment M_t^y in the tangential direction (see Table I). Accordingly, no elasticity in the corresponding direction is assumed, although the bond may exhibit elastic behavior in the other direction.

(ii) *Ductile regime*. The bond yields when the strain in the corresponding direction reaches a specific value, that is, maximum strain ϵ_c^y in the central direction and maximum deflection angle $\Delta\phi_t^y$ in the tangential direction (see Table I). Beyond these values the stress decreases.

Hence, the elastic modulus and the yield strain in each direction can be defined only if the material behavior in that direction is ductile, since in the brittle regime no elasticity range is assumed (see Table I).

TABLE I. Definitions of parameter in central and tangential directions for different regimes.

	Central direction			Tangential direction		
	Elastic Moduli	Yield def.	Yield load	Elastic Moduli	Yield def.	Yield load
Brittle			F_c^y			M_t^y
Ductile	Q	ε_c^y	F_c^y	$\bar{G}$	$\Delta\phi_t^y$	M_t^y

For example, in a colloidal system where interactions are ductile in the tangential and brittle in the central direction, only the set of parameters $\{F_c^y, \bar{G}, \Delta\phi_t^y, M_t^y\}$ given in Table I is required to describe the material behavior.

Our goal in this study is to define a new yield criterion for single clusters subjected to combined tensile-bending forces by representing the interparticle bonds by solidlike beams. Specifying the interactions between particles in each direction to be of brittle or ductile type, the yield behavior and geometrical properties of the beam can be described.

III. KINEMATICS OF A CLUSTER

A colloidal cluster is an interconnected structure in which a high number of stress paths are usually formed under loading. Experimental studies explicitly show that one stress path (normally the shortest one) transfers most of the applied load [33]. The main stress pathways are then traced while the rest of the cluster is considered to be stress free. This stress path is called the backbone chain. In Fig. 3(a), a cluster subjected to a force $\boldsymbol{F}^T$ at two points and the resulting backbone chain are depicted. The contribution of other stress paths to the mechanical response of the cluster is neglected due to the insignificant amount of transmitted load. Thus, the backbone chain is considered as the principal source of mechanical integrity of the cluster, and its failure results in the yield of the cluster.

Generally, clusters are freely suspended inside the dispersion medium. Thus, except for the cases in which clusters are partially held in stationary traps [3], they do not transmit any moment. Consequently, in the equilibrium state the forces applied to a cluster work along the end-to-end direction of the backbone chain.

In any arbitrary backbone chain, one can identify certain zones where all the stress paths converge and join the backbone chain. These places are called loopless zones (see Fig. 1). Each link of a backbone chain consists of either one or more particles attached to each other.

In the case of yielding, a failure of any single-particle link in the loopless zones would break the cluster into two parts. The failure of the multiparticle links may result in a formation of new backbone chains, in which the multiparticle link is replaced by a new path [34]. In both of these scenarios, considerable energy dissipation is expected, which further results in a notable stress softening of the cluster. Hence, this state can and will be referred to as yield point.

The end-to-end distance of the backbone chain in the virgin state is considered to be equal to the cluster correlation length denoted by ζ. The parameter ζ can be considered as the average distance of two arbitrary points on the cluster surface [35]. Clusters are considered to be fractal at length scales up to ζ and homogeneous at larger length scales. The correlation length is related to the number of particles of the backbone chain N, by

$$N = \left(\frac{\zeta}{l}\right)^{d_b}, \tag{1}$$

where d_b denotes the fractal dimension of the backbone chain and l is the diameter of a cluster particle. d_b characterizes the tortuosity of the backbone chain resulting from the fractal nature of clusters.

Let us assume the same mass and diameter l for all cluster particles and consider the same length l and $\bar{l}$ for all the bonds

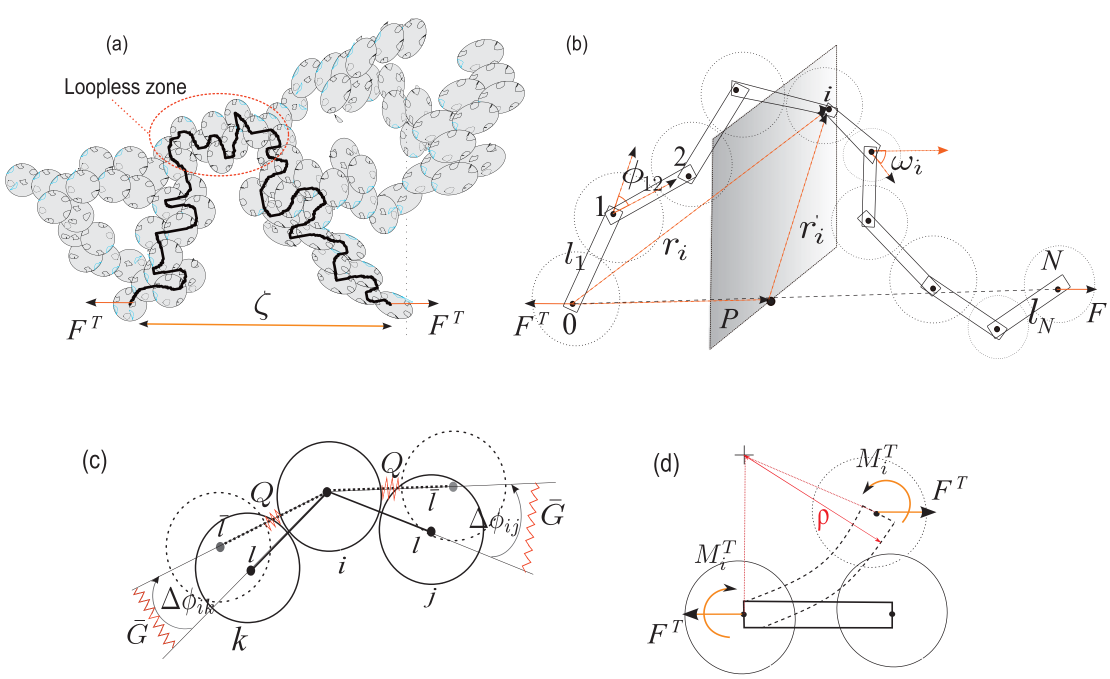

FIG. 3. (Color online) (a) A schematic view of a cluster subjected to a tensile force and the corresponding backbone chain. (b) Vectorial representation of the backbone chain with N bonds and illustration of the implemented angles and vectors. (c) The initial and deformed positions of three adjacent particles within the backbone chain. Interactions between two particles are represented by two linear springs. (d) Representation of interparticle bonds with solidlike beams and the deformation of these beams due to the applied combined loads.

in reference and current configuration, respectively. Further, $\boldsymbol{l}_i$ $(i = 1,2,\ldots,N)$ denotes a vector connecting the centers of particles $i-1$ and i in the backbone chain as shown in Fig. 3(b). Then, the vector $\boldsymbol{r}_i$ connecting 0th particle with the ith particle is expressed by

$$\boldsymbol{r}_i = \sum_{j=1}^{i} \boldsymbol{l}_j. \tag{2}$$

The angle between the bond i and the force direction $\boldsymbol{F}^T$ is represented by ω_i, while ϕ_{ij} denotes the angle between the bonds i and j [see Fig. 3(c)].

IV. YIELD OF AN INTERPARTICLE BOND

Let us ideally represent an interparticle bond by an isotropic, homogeneous solidlike beam of constant cross section, as shown in Fig. 3(c). Due to the large tangential displacements of adjacent particles, finite bending theory is applied for the calculation of the yield stress [see Fig. 3(d)]. Accordingly, the normal stress in the cross section of a bond is calculated by using the extended version of Euler-Bernoulli beam theory for large bending deformations (see, e.g., [36]). To this end, we consider the curvature radius ρ to be relatively small $\rho < 10h$ and assume the sections of the beam remain flat under deformation.

Consequently, the maximum normal stress in the beam is reached at the outer surface of the bond. In an arbitrary bond i subjected to a combined tensile-bending load (F^T, M_i^T), the maximum stress is thus given by

$$\sigma = \frac{F^T \cos\omega_i}{A_b} + M_i^T \left(\frac{1}{\rho A_b} + \frac{1}{I}\frac{\rho h}{\rho + h} \right), \tag{3}$$

where ρ and h represent the local bending radius in the deformed state and half of the beam thickness along the bending radius (see Fig. 4). I is the modified area moment of inertia along the central axis given by

$$I = \rho \int_A \frac{h^2}{\rho + h} dA \tag{4}$$

at the ρ place.

Further, M_i^T is the bending moment applied to bond i and A_b denotes the cross-sectional area of the bond. By considering an identical yield stress σ^y for all bonds of the backbone chain, the position and the yield force of the critical bond can be determined by force and moment balance equations.

As mentioned above, interactions between particles can be of ductile and brittle types depending on the type of particles. For this reason, we study in the following each of these regimes, separately.

A. Brittle regime

Apparently, a bond fails when the applied bending moment exceeds M_t^y in the absence of the tensile force or the applied tensile force exceeds F_c^y in the absence of the bending moment [see Figs. 4(b) and 4(b)]. Accordingly [Eq. (3)], we obtain

$$\sigma^y = \frac{F_c^y}{A_b}, \quad \text{or} \quad \sigma^y = \frac{M_t^y}{\mathcal{I}}, \tag{5}$$

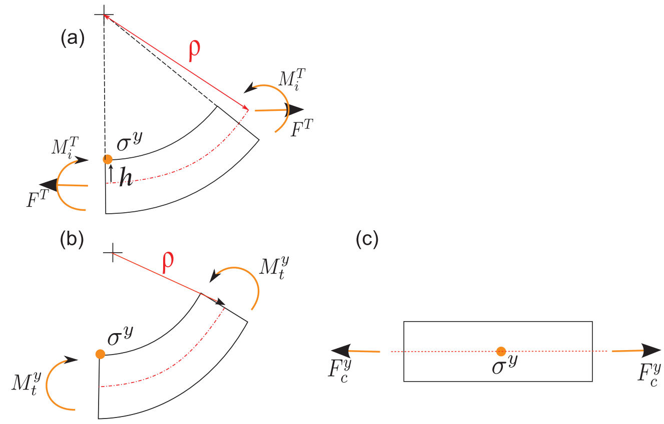

FIG. 4. (Color online) Calculation of the yield stress as a result of (a) combined tensile-bending load, (b) only bending moment, and (c) only tensile force.

where

$$\frac{1}{\mathcal{I}} = \frac{1}{\rho A_b} + \frac{1}{I}\frac{\rho h}{\rho + h}. \tag{6}$$

Due to the absence of elastic range in the brittle regime, the following geometrical identity is obtained from (5)

$$\frac{A_b}{\mathcal{I}} = \frac{F_c^y}{M_t^y}. \tag{7}$$

By the definition of the backbone chain, forces applied on different bonds are equivalent and denoted by $\boldsymbol{F}^T$. Since clusters are assumed to transmit no moments, the bending moment applied to a bond M_i^T results solely from the tensile force F^T. Thus,

$$M_i^T = F^T r'_i. \tag{8}$$

The parameter $r'_i = \|\boldsymbol{r}'_i\|$ represents the length of the vector rejection of $\boldsymbol{r}_i$ from the force direction so that [see Fig. 3(b)]

$$\boldsymbol{r}'_i = \boldsymbol{r}_i - \left(\boldsymbol{r}_i \cdot \frac{\boldsymbol{F}^T}{F^T} \right) \frac{\boldsymbol{F}^T}{F^T}. \tag{9}$$

Hence, for an arbitrary bond i, one can introduce a critical force F_i^y leading to the bond failure. The magnitude of this critical force is obtained implicitly from

$$F_i^y = \left\{ F_i^y \,\middle|\, \sigma^y = \frac{F_i^y}{A_b}\cos\omega_i + \frac{F_i^y r'_i}{\mathcal{I}} \right\}. \tag{10}$$

B. Ductile regime

By considering the interparticle behavior to be ductile in the central, tangential, or both these directions, one can represent the elastic material behavior in the corresponding direction(s) by an averaged elastic modulus Q for the central direction, $\bar{G}$ for the tangential directions, or both. For the central direction, the elasticity equation for the bond i [see Fig. 3(c)] gives

$$\sigma = Q\epsilon \Leftrightarrow \frac{\boldsymbol{F}^T}{A_b} \cdot \frac{\boldsymbol{l}_i}{l} = \frac{F^T}{V_b} l \cos\omega_i = Fl\cos\omega_i = Q\epsilon, \tag{11}$$

where $\epsilon = \frac{\bar{l}-l}{l}$ represents the bond strain and $F^T = \|\boldsymbol{F}^T\|$. The parameter $V_b = A_b l$ denotes the volume of an interparticle bond. The elasticity equation in the tangential direction gives

$$M_i = V_b \bar{G} \Delta\phi_{ij} \Leftrightarrow \boldsymbol{F} V_b \cdot \boldsymbol{r}_i = F r_i' V_b = V_b \bar{G} \Delta\phi_{ij}, \quad j = i+1, \tag{12}$$

where $\Delta\phi_{ij}$ refers to the changes in the angle between bonds i and j ($j = i-1$ in case of bending, and $j = i-2$ in case of torsion). Accordingly, simplifying (11) gives

$$F r_i' = \bar{G}\Delta\phi_{ij}, \quad F\cos\omega_i = \frac{Q}{l}\epsilon, \quad j = i+1. \tag{13}$$

The magnitude of the maximum load in each direction can be calculated by means of the elastic moduli as

$$F_c^y = Q\epsilon_c^y, \quad M_t^y = \bar{G}\Delta\phi_t^y. \tag{14}$$

Similarly, representing a bond by a solidlike beam, its deflection and elongation due to a combined tensile-bending load are obtained by

$$\Delta\phi = \frac{M_i^T \bar{l}}{EI}, \quad \epsilon l = \frac{\boldsymbol{F}^T \cdot \boldsymbol{l}_i}{E A_b}, \tag{15}$$

where E represents the elastic modulus of the beam. By substituting (13) into (15), one gets

$$\bar{G} = \frac{E}{V_b}\frac{I}{\bar{l}}, \quad Q = E, \tag{16}$$

which further yields the following identity for the beam geometry:

$$\frac{A_b}{I} = \frac{Q}{\bar{G}}\frac{1}{\bar{l}^2}. \tag{17}$$

C. Critical force

Having F_c^y and M_t^y at hand for both regimes, we can represent the bond yield stress as a result of tensile load, bending load, and combined tensile-bending force in both regimes as

$$\frac{F_c^y}{A_b} = \frac{M_t^y}{\mathcal{I}} = \frac{F_i^y}{A_b}\cos\omega_i + \frac{F_i^y r_i'}{\mathcal{I}}, \tag{18}$$

which can be simplified to

$$\frac{1}{F_i^y} = \frac{1}{F_c^y}\cos\omega_i + \frac{r_i'}{M_t^y}. \tag{19}$$

Using (17) or (7), Eq. (19) can be implemented for the brittle or ductile regime, respectively.

V. YIELD OF A CLUSTER

Failure of the first bond (critical bond) in the backbone chain is supposed to be accompanied by massive breakage of further bonds, which finally leads to the cluster failure. Thus, the yield force of the cluster $\mathcal{F}^y$ is considered to be the yield force of the critical bond. Accordingly, $\mathcal{F}^y$ is formulated by

$$\mathcal{F}^y = \min\left\{F_i^y \middle| i \in \mathbb{N} : n \leqslant N\right\}. \tag{20}$$

In view of (6) and (10), the magnitude of the yielding force is strongly influenced by the direction and position of the critical bonds. These bonds are placed far away from the end-to-end vector and have the same direction with it. In the case of large clusters, the minimal critical force is obtained when the particles roll on each other. In this case, the following identities hold:

(i) $\rho = \bar{l}$ direct movement of particles on each other;

(ii) $h = \frac{\bar{l}}{2}$ by assuming that the neutral axis remains in the middle of the beam during deflection;

(iii) $r_i' = \frac{\zeta}{2}$ by considering a cluster to be a sphere of the radius $\frac{\zeta}{2}$;

(iv) $\cos\omega_i = 1$ by assuming the bond to be in the direction of the applied force.

Accordingly, using (19), the yield force of a cluster $\mathcal{F}^y$ is obtained by

$$\mathcal{F}^y = F_c^y \frac{2M_t^y}{2M_t^y + F_c^y \zeta}. \tag{21}$$

By excluding the tangential forces ($\lim_{\Delta\phi_t^y \to \infty} M_t^y = \infty$), the obtained yield criteria (21) reduces to the simple tension failure criteria [28], where $\mathcal{F}^y = F_c^y$. If interactions between particles in both directions are considered to be ductile, in view of (6), (17) gives

$$\frac{A_b}{\mathcal{I}} = \frac{1}{\bar{l}} + \frac{Q}{\bar{G}}\frac{1}{3\bar{l}}. \tag{22}$$

For the ductile regime, (19) can be further simplified by means of (22) and (7) into

$$\mathcal{F}^y = F_c^y \frac{2}{2 + \frac{\zeta}{l}\left(1 + \frac{1}{3}\frac{Q}{G}\right)}. \tag{23}$$

VI. EXPERIMENTAL VALIDATION

The model presented above assumes that the structure breaks at a single bond. This is possible for clusters formed by DLCA kinetics where most of particles in the backbone chain act as single-bond links. In compact clusters formed by other mechanisms, due to the existence of many stress paths, one may find more than one backbone chain transmitting load. Accordingly, in these clusters, the moments and forces at yield may be divided up over several backbone chains. Moreover, yielding of a backbone chain from a bond that is placed in a loop may result in formation of another backbone chain. The experimental observations, however, do suggest that the aggregated clusters break in parts that are used by several stress paths [17] [see Fig. 3(a)].

In order to validate the proposed model, its predictions are compared against experimental values of the yield stress for a colloidal gel network provided by Buscall *et al.* [5,37] for several particle sizes and particle concentrations. In these experiments, the mean yield stress T_y of strongly aggregated polystyrene lattices in solution of barium chloride ($BaCl_2$) has been measured and reported.

When the network is formed by fractal clusters, the mean cluster size of the network is approximated with respect to the particle volume fraction ϕ by

$$\zeta \approx l\left(\frac{\phi}{\phi_e}\right)^{\frac{1}{3-d_f}}, \tag{24}$$

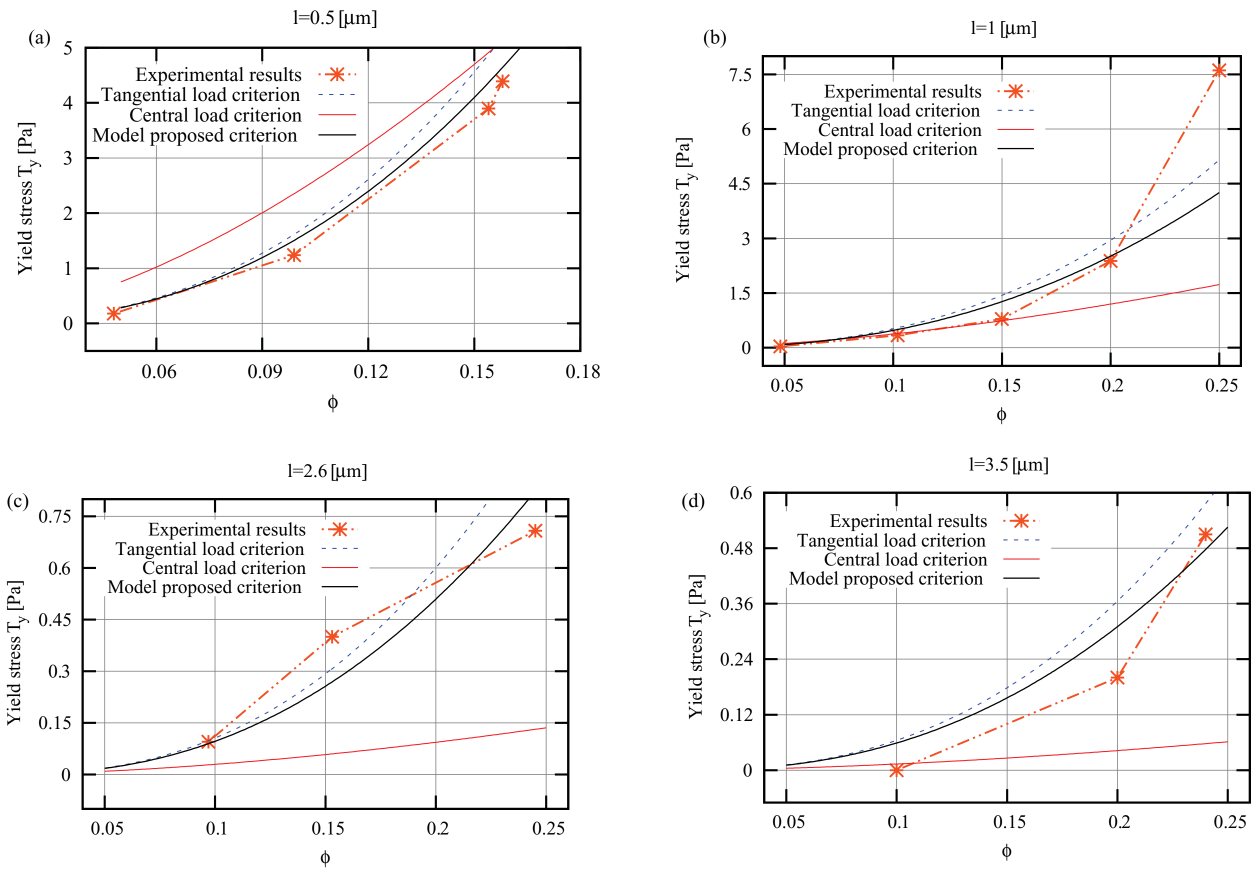

FIG. 5. (Color online) Rheological measurements of the yield stresses of the polystyrene aggregated structures in $BaCl_2$ [5,37]. The yield stress is measured with respect to particle concentration for different sizes of particles: (a) $l = 0.5$ (μm), (b) $l = 1$ (μm), (c) $l = 2.6$ (μm), (d) $l = 3.5$ (μm). The experimental data are then compared with the tangential load criterion (26), central load criterion (28), and the combined load criterion proposed here (29).

where d_f is the fractal dimension of clusters, and ϕ_e denotes the particle volume fraction of a cluster which is determined by cluster aggregation kinetics.

In order to show that the bond failure is more likely to result from a combined tensile-bending load rather than from pure tensile or pure bending load, we plotted and compared the yield stresses estimated from these three methods against the measured values from experimental results in Fig. 5.

Tangential load criterion. The influence of tangential loads on the yield behavior of an interparticle bond was studied in detail in [3]. By measuring deflections of polystyrene aggregates in magnesium chloride solution, the authors identified a critical bending moment M_t^y which expresses the limit of the linear elastic response of the cluster. Having M_t^y at hand, the yield stress of the gel network was further obtained by

$$T_y \propto \frac{M_t^y}{\zeta^3} \propto \frac{M_t^y}{l^3}\left(\frac{\phi}{\phi_e}\right)^{\frac{3}{3-d_f}}. \tag{25}$$

In order to normalize the influence of the particle size on the measured yield stresses T_y, the measured values are scaled by $l^{\frac{5}{3}}$. However, the magnitude for scaling exponent is also reported by some authors, such as $l^{\frac{3}{2}}$ [31] or l^2 [37]. Finally, (25) gives

$$T_y\left(\frac{l}{l_{\rm ref}}\right)^{\frac{5}{3}} = a_1\frac{M_t^y}{l_{\rm ref}^3}\left(\frac{\phi}{\phi_e}\right)^{\frac{3}{3-d_f}}, \tag{26}$$

where a_1 is a fitting constant, and $l_{\rm ref}$ (m) is considered as a reference particle size.

Central load criterion. In order to simulate the yielding of a colloidal bond due to the maximum central load F_c^y, the value of F_c^y is approximated by the theory of particle adhesion by Johnson, Kendall, and Roberts [38]. For equal-sized particles in the absence of tangential loads, the central yield force of an interparticle bond $F_c^y = \frac{3}{2}W_{sl}\pi l$ gives the yield stress of the network as

$$T_y \propto \frac{F_c^y}{\zeta^2} \propto \frac{F_c^y}{l^2}\left(\frac{\phi_e}{\phi}\right)^{\frac{2}{3-d_f}}, \tag{27}$$

where W_{sl} is the adhesion energy per unit area of particles [39]. Considering the particle size dependence of T_y, one has

$$T_y\left(\frac{l}{l_{\rm ref}}\right)^{\frac{5}{3}} = b_1\frac{F_c^y}{\zeta^2}\bigg|_{l=l_{\rm ref}}, \tag{28}$$

where b_1 is also a fitting constant.

Proposed combined criterion. By means of F_c^y and M_t^y, the critical force $\mathcal{F}^y$ can be calculated using (21). Then, the yield stress of the gel network is obtained by virtue of (28) and (26) as

$$T_y\left(\frac{l}{l_{\rm ref}}\right)^{\frac{5}{3}} = b_1 \frac{\mathcal{F}^y}{\zeta^2}\bigg|_{l=l_{\rm ref}} + a_1 \frac{\mathcal{F}^y r_i'}{l_{\rm ref}^3}\left(\frac{\phi}{\phi_e}\right)^{\frac{3}{3-d_f}} = \left(\frac{a_1}{2}+b_1\right)\frac{F^y}{\zeta^2}\bigg|_{l=l_{\rm ref}}, \quad (29)$$

where $r_i' = \frac{\zeta}{2}$. This criterion agrees best with experimental results when compared to the two other criteria for different particle sizes and volume fractions (see Fig. 5).

For evaluation, we consider common values for the parameters of the close packed clusters formed by DLCA kinetics, that is, $l_{\rm ref} = 1$ (μm), $d_f = 1.8$ and $\phi_e \approx 0.64$ [40]. The maximum tangential and central loads are set to $M_t^y = 6 \times 10^{-6}$ (nm) [3] and $W_{sl} = 11(\frac{l_ref}{l})$ (μ nm^{-1}), respectively. Accordingly, the corresponding values obtained for F_c^y are consistent with the experimental observations about the minimum tensile yield force of the aggregates, which should be above 15 (pN) (see [22]).

Under cluster yielding, the bonds mostly fail due to the combined tensile-bending loads, or sometimes due to pure bending loads. Generally, a pure tension rarely results in a bond failure [19]. Moreover, in the yielding procedure of a cluster, it is unlikely that a single bond fails due to pure tension, whereas pure bending failures and failures due to combined tensile-bending loads do occur more frequently. In line with previous studies, we claim that combined tensile-bending load is the major factor for bond failure in strongly aggregated clusters, as shown in Fig. 5. We believe that this is due to the fact that a small tensile force can cause a large bending moment in the curvilinear path of a backbone chain. Thus, bending plays a major role in yielding of clusters in low particle fractions, where most of the particles in a backbone chain act as single-particle links.

If the predictions of the tangential and central load criteria are close, both forces have notable contributions to the yielding procedure. Thus, neglecting one of these criteria may result in overestimation of the final result. Accordingly, the actual yield stress is expected to be, and regularly is, somewhat lower than the predicted values [see Fig. 5(a)].

Generally, in smaller clusters, the contribution of bending is less than that one of tensile loads. Thus, at higher particle concentrations (smaller clusters), the actual yield stress of clusters is considerably higher than that predicted by pure tensile loads and lower than that predicted by bending loads [see Figs. 5(c) and 5(d)].

Thus, a combination of both loads is expected to influence the yield behavior. The proposed combined load model shows good prediction abilities in this regard.

Here, the predicted curves of tangential, central, and combined load criteria are all fitted to the available experimental points by means of one fitting parameter. Thus, despite the limited number of points available, Fig. 5 represents a comprehensible but concise comparison between the prediction abilities of the three different criteria. The experimental validation presented here can be improved in the future by more detailed experimental data.

VII. CONCLUSION

In this contribution, a new micromechanical yielding criterion for strongly aggregated colloidal clusters is proposed. This criterion is based on the interactions between colloids. These interactions are decomposed into centrosymmetric and tangential directions. Thus, the failure load of an interparticle bond is formulated as a function of both these load types. To this end, an interparticle bond is represented as a nanoscale solidlike bridge. The yield force required to break the bonds is derived as a function of the position and deformed geometry of the cluster bonds. Accordingly, the critical bonds are identified as the bonds with the least yield forces. By means of the failure force of critical bonds, the yield force of the cluster is derived.

The proposed approach is independent of the nature and source of the interactions between colloidal particles and thus can be generalized to various colloidal systems.

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