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Characterization of sheared colloidal aggregation using Langevin dynamics simulation

Sergiy Markutsya  
Iowa State University

Rodney O. Fox  
Iowa State University, rofox@iastate.edu

Shankar Subramaniam  
Iowa State University, shankar@iastate.edu

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Abstract
Aggregation of colloidal particles under shear is studied in model systems using a Langevin dynamics model with an improved interparticle interaction potential. In the absence of shear, aggregates that form are characterized by compact structure at small scales and ramified structure at larger scales. This confirms the structural crossover mechanism previously suggested by Sorensen and coworkers, that colloidal aggregation occurs due to monomer addition at small scales and due to cluster-cluster aggregation at large scales. The fractal dimension of nonsheared aggregates is scale-dependent. Smaller aggregates have a higher fractal dimension than larger ones, but the radius of gyration where this crossover occurs is independent of potential well depth for sufficiently deep wells. When these aggregates are subjected to shear they become anisotropic and form extended cigar-like structures. The size of sheared anisotropic aggregates in the direction perpendicular to the shear flow is limited by shear-induced breakage because the shear force dominates interparticle attraction for sufficiently large aggregates. Anisotropic aggregates are not completely characterized by a single radius of gyration, but rather by an inertia ellipsoid. Consequently the fractal dimension is no longer an adequate metric to properly characterize them, and to identify changes in their structure from their nonsheared isotropic counterparts. We introduce a new compactness-anisotropy analysis that characterizes the structure of anisotropic aggregates and allows us to distinguish between aggregates from sheared and nonsheared systems. Finally, using the ratio of interparticle force to the shear force $f_{\text{pot,sh}}$ we are able to characterize different outcomes of sheared aggregation as a function of dimensionless well depth and Péclet number.

Disciplines
Biological and Chemical Physics | Biological Engineering | Chemical Engineering

Comments
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I. INTRODUCTION

Aggregation of colloidal nanoparticles is a nonequilibrium multiscale problem that is characterized by a wide range of length and time scales ranging from those associated with a monomer to superaggregates comprising tens of thousands of monomers. Usually colloidal aggregation in real physical systems occurs in the presence of external forces due to gravity [1,2] or shear flow [3–11]. This work is focused on the effects of shear. Shear flow affects the size and structure of aggregates and the rate at which they are formed. A rich variety of phenomena are observed depending on the magnitude of the shear rate, the initiation time [11] (i.e., whether shear is applied after some aggregation has taken place, or right from the onset of aggregation), and the duration of time over which the system is subjected to shear.

These phenomena have been experimentally investigated by studying the influence of externally applied shear on the aggregation of latex nanoparticles [8,11]. If shear is applied after aggregates have already formed, it can change aggregate structure. The magnitude of shear relative to diffusion is characterized by the Péclet number, which can be defined based on the monomer diameter $\sigma$ as

$$\text{Pe} = \frac{G \sigma^2}{4 D_\infty},$$

where $G$ is the shear rate and $D_\infty$ is the diffusion coefficient of the nanoparticle at infinite dilution. In experiments it has been found that moderate shear flow (characterized by $\text{Pe} = 1$–5) results in aggregates with a higher fractal dimension than those found in nonsheared systems [3,8,11].

In these experiments, changes in aggregate structure are inferred from $d_f$, the fractal dimension of aggregates that is obtained from light scattering analysis. However, two-dimensional (2D) Langevin dynamics (LD) simulations of Cerda et al. [12] report that shear changes the effective interaction between monomers by increasing the distance between neighboring monomers in aggregates at initial stages of the cluster nucleation (induction period). These changes in structure are characterized by computing a mean interaction energy attributed to the physical bonds that hold the cluster together [12]. After the induction period ends, shear is observed to compact the initial fractal aggregates. From these studies it is not clear why in some cases shear results in the formation of more compact aggregates, while in others it produces structures where the distance between neighboring monomers is stretched when compared to nonsheared structures.

For clarity of exposition we define the terms we use to characterize aggregates in this work. We always use compactness to refer to the characterization of aggregates in terms of interparticle distance and the magnitude of the potential energy of particles in the aggregate. We denote ramified aggregates as those consisting of smaller compact clusters formed by cluster-cluster aggregation. For isotropic aggregates in nonsheared systems, compact aggregates have high fractal dimension, and ramified aggregates have a lower fractal dimension. Compactness as quantified in this work by the local volumetric potential energy density (LPED) is not scale-dependent and is therefore useful to characterize aggregates in both nonsheared and sheared cases. On the other hand, the fractal dimension is scale-dependent because it depends on the spatial geometry of the aggregates. Therefore, in sheared systems where aggregates are anisotropic, a higher

*Corresponding author: shankar@iastate.edu

1Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, USA
2Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa 50011, USA

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value of compactness as quantified by LPED does not always correspond to a higher fractal dimension.

Computational approaches are well suited to answering the question of how shear affects aggregate structure because one can easily vary parameters such as the dimensionless well depth of the interaction potential and the Péclet number to investigate their effect on aggregation outcomes. In earlier work [13] it was shown that although molecular dynamics (MD) simulations of aggregation in dilute systems with full solvent interactions are still too computationally expensive, mesoscale methods such as LD with modeled solvent interactions scale favorably to larger systems while retaining the capability of representing structure in aggregating systems. A coarse-graining procedure recently developed in our group to specify the potential of mean force in LD for aggregating systems yields time-evolving structure in nonequilibrium aggregating systems that matches very well with MD simulations in both diffusion-limited and reaction-limited regimes [14]. With this improved potential of mean force, the authors have confidence that LD simulations of aggregation can reliably predict important aggregation statistics such as the extent of aggregation, time-evolving solute pair correlation function, and dynamically scaled cluster size distribution that have been compared with MD simulations of smaller model systems [14]. The essential features of this improved LD model that is used to study sheared aggregating systems in this work are described in Sec. II.

The effects of shear on aggregate structure are not easy to characterize because shear affects aggregates differently on smaller length scales (on the order of ten monomer diameters) as compared to larger length scales (on the order of hundred monomer diameters). The reason for this probably lies in the mechanism underlying the formation of aggregates at different scales. As shown earlier [11,15,16], the small-scale structure of aggregates arises from monomer addition, while the large-scale structure corresponds to cluster-cluster aggregation. This scale-dependent modification of aggregate structure by shear also means that a single fractal dimension is not sufficient to characterize the compactness of the aggregate. Expanding on the ideas of Cerda et al. [12], an LPED metric is proposed in Sec. III C to characterize the compactness of anisotropic aggregates that are formed under shear. Aggregate breakage is observed [6,9] when a sufficiently high shear rate is imposed. Thus shear limits the maximum size of aggregates [3,6–9], with the maximum attainable size decreasing with increasing shear rate.

Lekkerkerker et al. [17] have proposed a phase diagram for aggregating systems, and Chakrabarti et al. [18] classified aggregation regimes into (a) equilibrium aggregation, (b) nonequilibrium aggregation, and (c) gelation. Inspired by these aggregation regimes into (a) equilibrium aggregation, (b) nonequilibrium aggregation, and (c) gelation. The ideas of Cerda et al. [12], an LPED metric is proposed in Sec. III C to characterize the compactness of anisotropic aggregates that are formed under shear. Aggregate breakage is observed [6,9] when a sufficiently high shear rate is imposed. Thus shear limits the maximum size of aggregates [3,6–9], with the maximum attainable size decreasing with increasing shear rate.

Langevin dynamics (LD) is a mesoscale simulation method that can capture the effect of shear on aggregate restructuring [14]. The LD model is used to simulate aggregation of solute particles immersed in a liquid solvent that is subjected to steady, uniform (spatially homogeneous) shear flow. LD permits the simulation of larger systems of solute particles than MD [13] because in LD the solvent molecules are not explicitly represented, but the solute-solvent interactions are modeled through frictional and random terms, and through modification of the solute pair interaction potential in the presence of solvent molecules [14]. For the model system considered in this work, the relative magnitude of time scales corresponding to the frictional and pairwise interaction force terms requires evolution of both position and velocity Langevin equations for accurate LD simulations [13,19,20]. The LD equations for evolution of the position $r_i^{(t)}$ and velocity $v_i^{(t)}$ of the $i$th solute particle in a sheared solvent flow are [21]

$$\begin{align*}
dr_i^{(t)} &= v_i^{(t)} dt, \quad \alpha = 1, 2, 3, \\
v_i^{(t)} &= -\gamma v_i^{(t)} dt + \gamma u_n dt + \frac{1}{m_{\alpha}} F^{(t)}_{\alpha} dt \\
&\quad + \sqrt{2\gamma} \sigma v_i \, dW^{(t)}_i, \quad i = 1, \ldots, N,
\end{align*}
$$

where subscript $\alpha$ denotes the Cartesian coordinate direction, $m_{\alpha}$ is the mass of $i$th particle, $u_n = G t^{(t)} \delta_{ia} \delta_{ib}$, $\alpha, \beta = 1, 2, 3$ is the mean fluid velocity (of solvent molecules) due to imposed shear flow evaluated at the solute particle location $r_i^{(t)}$, $G$ is the uniform shear rate, $\gamma = k_B T_{ref}/m^{(t)} D_{\infty}$ is the friction coefficient, $D_{\infty}$ is the diffusion coefficient of solute in solvent at infinite dilution, $\sigma_{\alpha \beta}^{(t)} = k_B T_{ref}/m^{(t)}$ is the stationary velocity variance, $dW^{(t)}_i$ is a Wiener process increment, $N$ is the total number of solute particles, and $F^{(t)} = -\nabla_u U^{LD}$, where $U^{LD}$ is the effective LD potential of mean force between solute particles in the presence of solvent. This effective LD potential is calculated accordingly to a coarse-graining method developed by Markutsya et al. [14] as

$$U^{LD}(r_{ij}) = U^{LD}(r_{ij}) + U_2(r_{ij})$$

$$= \begin{cases} 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + U_2(r_{ij}), & r_{ij} \leq r_{cut}, \\
0, & r_{ij} > r_{cut}, \end{cases}
$$

where $\sigma$ is the particle diameter, $r_{ij}$ is the scalar separation or distance between centers of particles $i$ and $j$, $r_{cut}$ is the cutoff distance chosen to be 2.5 $\sigma$, $U_2$ is the correction term that takes into account the effect of solvent molecules on particle interaction potential [14], and $\varepsilon$ is the well depth of Lennard-Jones interaction potential between solutes.

In this coarse-graining (CG) method for nonequilibrium time-evolving aggregating systems, the effect of solvent can be represented as a correction term $U_2$ to the solute-solute interparticle potential (see Ref. [14] for details). The effective
LD potential $U_{LD}$, the Lennard-Jones potential $U_{LJ}$, and the correction term $\tilde{U}_2$ are shown in Fig. 1 for systems with $\hat{\epsilon} = 8$ and $\hat{\epsilon} = 50$. For the values of potential well depth used in this work, the potential correction is close to zero ($\tilde{U}_2 \approx 0$), and the effective LD potential is practically the same as the Lennard-Jones potential $U_{LD} \approx U_{LJ}$. Nevertheless, for the sake of consistency and for direct comparison with previous work that reported aggregation without shear using the effective potential [14], we have retained the slightly modified effective potential.

The diffusion coefficient at infinite dilution $D_\infty$ and the correction to the interparticle potential $\tilde{U}_2(r_{ij})$ are required input parameters for the improved LD model. The diffusion coefficient at infinite dilution $D_\infty$ is extracted directly from MD simulation of the corresponding system, and the correction to the interparticle potential $\tilde{U}_2(r_{ij})$ is obtained using the semianalytical coarse-graining procedure described previously [14].

The LD simulations are performed using the LAMMPS [22] software package. The initial spatial configuration of the particles is specified to ensure nonoverlapping particles. This is accomplished by spatially distributing the solute particles according to a hard-core Matérn point process [23]. The solute particles are assigned a Maxwellian velocity distribution corresponding to a hard-core Matérn point process [23]. The model system chosen to study aggregation consists of colloidal nanoparticles in a water bath, but it is not as low as in some experiments [3,4,6–8,11] because of computational limitations. System parameters used in the present study are reported in Table I.

In order to investigate the effect of system size, systems with $N = 10\,000$ and $N = 300\,000$ solute particles were considered. No significant difference in aggregation statistics (fractal dimension $d_f$, and inflection point $R^2_g$) was observed between these two systems for both sheared and nonsheared cases. The results in this paper are reported from the system with $N = 300\,000$ solute particles in a cube with sides of length $\sim 210\,\sigma$ because that yields better statistics of aggregate properties.

### Table I. Parameters used to define model aggregating systems for LD simulations.

<table>
<thead>
<tr>
<th>$\hat{\epsilon}$</th>
<th>$\text{Pe}$</th>
<th>$N$</th>
<th>$D_\infty \times 10^{-9} \text{m}^2/\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>0.0, 2.1, 8.0</td>
<td>300 000</td>
<td>1.95</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0, 2.1, 8.0</td>
<td>300 000</td>
<td>1.54</td>
</tr>
</tbody>
</table>
The effect of shear flow on aggregation was studied by imposing different shear rates corresponding to two Péclet number values \( \text{Pe} = (2.1; 8.0) \), representative of moderate shear flow \([11,12]\). The strength of the interparticle interaction potential in Eq. (4) is controlled by varying the dimensionless well depth \( \hat{\varepsilon} \) of the Lennard-Jones interaction potential. Its value was chosen based on experience with aggregating systems in previous work \([14]\).

### A. Aggregation without shear

Aggregates were determined based on a distance criterion, according to which two particles are assigned to the same cluster if the distance between their centers is less than a specified distance \( r_{cl} \), which is typically in the range \( 1.1\sigma < r_{cl} < 1.5\sigma \). In the present study \( r_{cl} = 1.4\sigma \), which corresponds to the location of the first minimum in the radial distribution function \( g(r) \), which is approximately the same for both \( \hat{\varepsilon} = 8 \) and \( \hat{\varepsilon} = 50 \). Aggregation in the absence of shear was analyzed by plotting the size of the aggregate (characterized by the number of solute particles in the cluster \( N_{cl} \)) as a function of the nondimensional radius of gyration \( R_g/\sigma \) on a logarithmic scale as shown in Figs. 2(a) and 2(b). The fractal dimension \( d_f \) is related to the number of monomers \( (k) \) in a cluster, and to the radius of gyration of the cluster \( R_g \) by the fundamental relation

\[
k = k_0 \left( \frac{R_g}{a} \right)^{d_f},
\]

where \( a = \sigma/2 \) is the particle radius, \( \sigma \) is the particle diameter, and \( k_0 \) is a constant. For a statistically isotropic system, the radius of gyration for each cluster can be calculated as

\[
R_g^I = \left[ \frac{1}{k} \sum_{i=1}^{k} (r_{cm}^{(i)} - r^{(i)})^2 \right]^{1/2},
\]

where \( r_{cm} \) denotes the position of the center of mass of the cluster, and \( r^{(i)} \) denotes the position of the i-th particle in the cluster. The radius of gyration given by Eq. (6) is a good measure of aggregate size for statistically isotropic systems, and so for the nonsheared cases we use Eq. (5) with \( R_g = R_g^I \) to calculate \( d_f \).

The fractal dimension of the aggregates is obtained according to Eq. (5) by fitting the data from Figs. 2(a) and 2(b) with the power function and extracting the power term. The two values of fractal dimension shown in the figures are obtained by splitting the data at the inflection point \( R_g^I \). The statistical

![FIG. 2. (Color online) The fractal dimension \( d_f \) from LD simulations with effective potential \( U_{LD}^{\text{eff}} \) at time \( \hat{t} = 3244 \): (a) \( \hat{\varepsilon} = 8.0 \), (b) \( \hat{\varepsilon} = 50.0 \). Snapshots for typical aggregate for \( \hat{\varepsilon} = 50.0 \) at time \( \hat{t} = 3244 \) for (c) aggregate containing 150 monomers with the radius of gyration \( R_g = 2.8\sigma \); (d) aggregate containing 966 monomers with the radius of gyration \( R_g = 7.1\sigma \).]
variability in the fractal dimension $d_f$ measurements (arising from variability in the initial configuration of the particle ensemble) is estimated from three independent simulations (data points from one simulation are shown for clarity). These plots indicate a multifractal structure corresponding to a phenomenon called structural crossover [24], and suggests the presence of aggregates with two different fractal dimensions with the transition marked by an inflection point $R^m_f$ that corresponds to the number of monomers in an aggregate $N_{cl}$ at the inflection point. Aggregates with $R_g < R^m_f$ and with $N_{cl} < N_{cl}^m$ [see Fig. 2(c) for an example] are characterized by a higher fractal dimension $d_f \approx 2.4$ for both dimensionless well depth values (8 and 50) in Table I. Larger aggregates with $R_g > R^m_f$ and $N_{cl} > N_{cl}^m$ [see Fig. 2(d) for an example] are characterized by a lower fractal dimension $d_f \approx 1.5$ for both dimensionless well depth values. The fractal dimension of the aggregates, the location of the inflection point in the $N_{cl}$ versus $R_g$ plot, and the underlying mechanisms that are responsible for the formation of these aggregates all merit explanation, especially because the nonsheared system is the reference state to which the sheared system will be compared.

In the diffusion-limited regime, large aggregates (with $R_g > R^m_f$) are typically characterized by a fractal dimension $d_f \approx 1.8$ [25], and the formation of aggregates with a fractal dimension $d_f \approx 1.5$ as in Fig. 2 is not expected. This difference in the structure of large aggregates is attributed to the fact that the Lennard-Jones potential used in the present study is a long-range potential. Therefore, with a very deep potential well ($\hat{\varepsilon} = 50$) “fat fractals” are formed [26] that are characterized by a higher fractal dimension at small scales, and a lower fractal dimension at larger length scales. If short-ranged potentials (such as AO or DLVO potentials) are used, then much thinner aggregates form on small length scales, and the large-scale cluster structure is characterized by a fractal dimension $d_f \approx 1.8$. In order to check this hypothesis, the same LD method was used with the short-ranged DLVO potential (results not shown here) for the same aggregating system, and a fractal dimension $d_f \approx 1.73$ was obtained, which is close to the expected value of 1.8.

The nonsheared systems exhibit the structural crossover phenomenon wherein aggregates initially form due to monomer addition, but as clusters grow they can also form superaggregates through a mechanism called cluster-cluster aggregation [16,24]. The higher fractal dimension of the small aggregates with $d_f \approx 2.4$ appears to correspond to monomer addition. Snapshots of the large aggregates shown in Fig. 2(d) reveal a more ramified structure (df ≈ 1.5) that appears to correspond to cluster-cluster aggregation. The formation of different aggregate structures at different length scales is also observed [27] using 2D Brownian dynamics simulations

From this perspective, the inflection point $R^m_f$ identifies a change in the physical mechanism of aggregation and the maximum size of small aggregates (in terms of geometrical size $R^m_g$ and in terms of number of monomers $N_{cl}^m$). It is observed that for nonsheared aggregating systems the location of the inflection point $R^m_g \approx 4\sigma$ does not depend on the potential well depth $\hat{\varepsilon}$, for potential wells deep enough to be in the DLA regime (Fig. 2).

### B. Shear-induced aggregation

Starting from a nonsheared aggregated system described at the beginning of this section, aggregation in moderate shear flow ($Pe = 2.1$) is simulated to a dimensionless time $\hat{t} = 113$ in $a^2/D_\infty$ units. The fractal dimension, scale-dependent modification of aggregate structure, and behavior of the inflection point are analyzed and compared to the nonsheared case. Since shear flow results in anisotropic aggregates, Eq. (6) is not used for the radius of gyration calculation. For anisotropic aggregates, the radius of gyration $R^m_g$ is calculated using the inertia ellipsoid for each cluster according to the procedure described in Appendix A. From these radius of gyration values, the fractal dimension $d_f$ was calculated using Eq. (5) with $R_g = R^m_g$ and is shown in Fig. 3.

The fractal dimension $d_f$ has two distinct values with an inflection point $R^m_g$ [see Fig. 3(a)] that is similar to previously observed behavior [Figs. 2(a) and 2(b)] in the nonsheared case. The fractal dimension and its statistical variability are computed in an identical manner to the nonsheared cases. Shear increases the fractal dimension of small-scale aggregates ($R_g < R^m_g$) from $d_f \approx 2.4$ to $d_f \approx 3.0$. On the other hand, the fractal dimension of larger aggregates ($R_g > R^m_g$) decreases from $d_f \approx 1.5$ [Figs. 2(a) and 2(b)] to $d_f \approx 1.1$ [Fig. 3(a)]. Shear also changes the shape of large clusters from their original ramified structure in the nonsheared case [Fig. 2(d)] to cigar-like structures [Fig. 3(b)]. These cigar-like aggregates are characterized by a smaller radius of gyration $R_g$ when compared to more isotropic aggregate shapes. Thus, moderate shear applied to an aggregating system manifests as higher fractal dimension at small length scales and results in elongation of aggregates to cigar-like shapes at larger length scales. However, as we discuss later, the fractal dimension is not an adequate descriptor of anisotropic aggregates because it does not reveal the different ways in which shear modifies aggregate structure.

Shear also affects the location of the inflection point $R^m_g$, which is now found to change with the nondimensional interparticle potential well depth $\hat{\varepsilon}$ [see Fig. 3(a)]. The inflection occurs at lower $R^m_g$ for $\hat{\varepsilon} = 8$ than for $\hat{\varepsilon} = 50$, suggesting different length scales of aggregates for different nondimensional well depth values $\hat{\varepsilon}$. For $\hat{\varepsilon} = 8$, shear reduces the radius of gyration at the inflection point $R^m_g$ from $R^m_g \approx 4.0$ for the nonsheared system to $R^m_g \approx 3.0$. The number of particles in a cluster at the inflection point $N^m_{cl}$ decreases from $N^m_{cl} \approx 300$ to $N^m_{cl} \approx 80$.

The decrease in the number of particles in a cluster at the inflection point $N^m_{cl}$ from $N^m_{cl} \approx 300$ to $N^m_{cl} \approx 80$ for the system with $\hat{\varepsilon} = 8$ in the sheared case suggests that the effect of shear dominates interparticle force causing an increase in fractal dimension for small aggregates due to formation of more compact, smaller aggregates and decrease of $R^m_g$ (thinning of the local structure due to loss or rearrangement of surface particles that decreases the size of aggregates). When shear is applied to the system with $\hat{\varepsilon} = 50$ the inflection radius of gyration increases ($R^m_g \approx 7.0$) and the inflection number of particles also increases from $N^m_{cl} \approx 300$ to $N^m_{cl} \approx 1000$. This suggests that the interparticle forces are strong enough to withstand the effect of shear flow (thus no thinning of local structure was observed). The fractal dimension of large
aggregates with $R_g > R_g^{in}$ further decreased to $d_f = 1.08$ on shearing, and the formation of aggregates with cigar-like shapes is observed [see Fig. 3(b)]. This suggests that when shear is applied, all the aggregates in the system are compacted. Moreover, in addition to compaction those aggregates with ramified structure in the non-sheared case [see Fig. 2(d)] are rearranged due to mechanical stress created by the shear to form cigar-like aggregates.

From these results, it is possible to conclude that shear flow significantly changes aggregate structure on both small and large length scales. These changes are observed through changes in metrics such as the fractal dimension $d_f$, and through visual observation when large ramified aggregates change to cigar-like structures under shear. It is worth noting here that shear-induced anisotropic aggregates are not completely characterized by a single radius of gyration, but rather by an inertia ellipsoid, and consequently the fractal dimension is no longer an adequate metric to properly characterize anisotropic aggregates and distinguish their change in structure from their non-sheared isotropic counterparts. Therefore, although the fractal dimension $d_f$ is useful in signaling changes in aggregate structure, in order to address these issues we define more general metrics to characterize aggregate structure and distinguish the effect of shear on them.

C. Compactness-anisotropy analysis

In this section we describe how the characterization of aggregates on a compactness-anisotropy map allows us to distinguish between aggregate structures obtained from sheared and non-sheared systems. We introduce the dimensionless local volumetric potential energy density (LPED) $U/V_{cl}$ as a measure of compactness of an aggregate, where

$$\frac{\tilde{U}}{V_{cl}} = \frac{U}{V_{cl}} \frac{\sigma^3}{\varepsilon} = \frac{1}{kV_m} \sum_{i=1}^{k} \sum_{j>i}^{k} \sigma^3 \varepsilon U^{LJ}(r_{ij}), \quad (7)$$

where $\sigma$ is the solute particle diameter, $\varepsilon$ is the potential well–depth, $V_m$ is the volume of a single particle, $U$ is the interaction potential [in this case taken to be Lennard–Jones potential $U^{LJ}(r_{ij})$ between particles $i$ and $j$ as defined in Eq. (4)], $r_{ij}$ is the separation distance between solute particles $i$ and $j$, $k$ is the number of interior particles in the cluster, and $V_{cl} = kV_m$ is the volume of all the bulk particles in the cluster. Particles that lie on the surface of the cluster are not included in the definition of LPED, thus excluding the effect of cluster size on LPED. Particles that lie on the surface of the cluster are identified using the following procedure. The average absolute potential energy per particle is computed for the cluster. Then each particle in the cluster with absolute value of potential energy less than 90% of this average is identified as a surface particle. We then recalculate the average absolute potential energy of the cluster excluding the identified surface particles and re-examine the remaining particles in the cluster to see which of them satisfy the criterion for being identified as a surface particle. The identification and recalculation steps are performed recursively until no new surface particles are found.

The dimensionless LPED determines the potential energy of interior particles in the system per unit volume, and it describes compactness of the aggregate structure. Compactness of aggregate structures can also be characterized by the average number of nearest neighbors in the aggregate. Thus, for a highly packed structure, where the number of nearest neighbors is high, the LPED is higher than for a porous structure. The LPED is a useful metric to characterize anisotropic aggregates because it is sensitive to the presence of structural anisotropy in aggregate structures that arise from fewer neighbors in the shear–normal direction. Therefore, in this work LPED $\tilde{U}/V_{cl}$ is used in conjunction with an anisotropy factor $A_{\alpha\beta}$ to classify aggregates produced by shear.

The anisotropy parameter was calculated after determining the equivalent inertia ellipsoid with principal axes for each cluster calculated according to Eq. (A1)–(A4) and is defined as

$$A_{\alpha\beta} \equiv \frac{R_{\alpha}}{R_{\beta}}, \quad (8)$$

where the principal axes are rearranged as $R_1 > R_2 > R_3$. With this specification the anisotropy factor value $A_{\alpha\beta}$ is
always greater than unity for $\alpha < \beta$. This specification of anisotropy is different from those proposed [16,28] where the mean shape anisotropy for the ensemble of clusters ($A_{\alpha\beta}$) was calculated. The mean shape anisotropy does not fit the needs of this work where anisotropy for every cluster in the system needs to be defined.

The reference value for isotropic aggregating systems is $\epsilon = 1$ for $A_{\alpha\beta}$ (only clusters with $k > 100$ are shown). By comparing these data for systems with a uniform shear flow with the nonsheared case (Fig. 4), several important features can be distinguished. A significant asymmetry in anisotropy factors $A_{12}$ and $A_{13}$ is observed for all systems with different potential well depths [Figs. 5(a)–5(d)], which is explained by shearing along the $x$ direction (which corresponds to $\alpha = 1$ in $A_{\alpha\beta}$). Moderate shear flow significantly changes the magnitude of anisotropy factors along the shear flow direction ($A_{12}$ and $A_{13}$) from 5 for the nonsheared systems to up to 40 for $\bar{\varepsilon} = 8$, and up to 10 for $\bar{\varepsilon} = 50$, in the sheared cases. At the same time, the magnitude for the anisotropy factor $A_{23}$ is in the same range as for the nonsheared systems [Figs. 4(e) and 4(f) and Figs. 5(e) and 5(f)]. It is possible to conclude that shear flow introduces anisotropy into the aggregating system by changing the statistically isotropic aggregate structure to cigar-like structures.

Moreover, this “stretching” of aggregates due to shear flow changes their local structure, which is nicely captured by the dimensionless LPED. For systems with weaker interparticle interaction ($\bar{\varepsilon} = 8$), shear at $Pe = 2.1$ is strong enough to significantly separate particle pairs inside aggregates, and as a result the average distance between neighbor monomers increases (aggregates become less compact). Consequently the dimensionless LPED decreases to 9.2 from 10.8 (for nonsheared systems) as seen in Figs. 5(a), 5(c), and 5(e). When interparticle interaction is stronger ($\bar{\varepsilon} = 50$), the same shear flow with $Pe = 2.1$ is not able to stretch monomer pairs inside aggregates to the same extent as in the case of $\bar{\varepsilon} = 8$. However, some displacements of particles due to shear force occur that initiates their local rearrangement. This local rearrangement allows particles to occupy more energy stable locations than they could have due to aggregation without shear. As result of these local rearrangements more compact structures were formed that are supported by increasing value of the average dimension LPED to 12.1.
From these results it is possible to conclude that LPED captures the scale-dependent changes in aggregate structure due to shear. When the force due to shear between monomer pairs is significant compared to the force due to interparticle potential interaction, aggregates with cigar-like structures were formed. These cigars are very long along the shear direction with less compact local structure (when compared to nonsheared aggregates). In the cases where force due to shear is relatively small compared to the force due to interparticle potential interaction, aggregates with cigar-like structures are still observed. However, in this case the “cigars” were shorter. Moreover, shear flow allows the local rearrangement of particles, and as result more compact local structures of aggregates are formed. LPED and anisotropy factor $A_\alpha$ enable us to discriminate between these different aggregation structures.

**IV. CLASSIFICATION OF AGGREGATION OUTCOMES UNDER SHEAR**

As discussed in Appendix B, outcomes of sheared aggregation can be classified in a parameter space defined by the dimensionless potential well depth $\hat{\gamma}$ and the Péclet number $Pe$ based on the values of LPED and the anisotropy parameter $A_{\alpha}$ for the aggregates. Competition between interparticle attractive forces (characterized by $\hat{\gamma}$) and shear (characterized by Péclet number $Pe$) determines aggregation outcomes in sheared systems. The relative magnitude of these forces $F_{pot,sh}$ [defined by Eq. (9) later in this section] is used to distinguish between different aggregation outcomes that are classified according to their characteristics: fractal dimension, maximum size of aggregates in the shear normal direction, and LPED.

Shear introduces a new time scale $1/\gamma$ in aggregating systems, and an additional force arises between a pair of particles due to the shear flow. When shear is applied to an aggregating system, particles attain the local flow velocity on a time scale ($\sim 1/\gamma$). Because of the presence of a velocity gradient in a shear flow, a pair of particles at different locations along the velocity gradient will relax to the local fluid velocity and thus attain different velocities. This relaxation to a different local mean fluid velocity for a pair of particles is the source of an additional force due to shear that tends to move particles away from each other. In sheared systems the aggregation outcome does not solely depend on the magnitude of pair-interaction force that arises from interaction potential, but instead it depends on the relative magnitudes of the pair-interaction force and the shear force. Based on this reasoning it is useful to introduce the interparticle force normalized relative to shear $F_{pot,sh}$ that is defined as

$$f_{pot,sh} = \frac{|F_{pot}(r_{min})|^{max}}{F_{sh}(r_{min})},$$

where $|F_{pot}(r_{min})|^{max}$ is the maximum absolute interparticle force between a pair of particles separated by $r_{min}$, and which is calculated as

$$|F_{pot}(r_{min})|^{max} = \left| 24 \frac{\hat{\gamma}^2}{\sigma} \left( \frac{\sigma}{r_{min}} \right)^{13} - \left( \frac{\sigma}{r_{min}} \right)^{7} \right|,$$

where $r_{min}$ is the pair separation that satisfies the maximum attraction force between pair of particles. The force due to shear between a pair of particles separated by $r_{min}$, $F_{sh}(r_{min})$ is calculated as

$$F_{sh}(r_{min}) = m \gamma G r_{min} = m \gamma 4 Pe D_{\infty} \frac{r_{min}}{\sigma}.$$

By substituting Eq. (10) and Eq. (11) into Eq. (9) and representing values in dimensionless form, a final expression for the interparticle force normalized relative to shear is

$$f_{pot,sh} = \frac{6\hat{\gamma}}{Pe} \left[ 2 \left( \frac{\sigma}{r_{min}} \right)^{14} - \left( \frac{\sigma}{r_{min}} \right)^{8} \right],$$

where dimensionless units are computed as $\hat{\gamma} = \gamma \sigma / \sigma_v$, $D_{\infty} = D_{\infty} / \sigma_v^2$, and $\sigma_v^2 = k_B T / m$, and by taking into account the fact that $\hat{\gamma} D_{\infty} = 1$.

By analyzing Eqs. (9) and (12) it is possible to conclude that when $f_{pot,sh} < 1$ the shear force is stronger than the
interparticle interaction force, and in such a system the breakage of aggregates is expected. When $f_{\text{pot,sh}}>1$ the formation of aggregates in a system is expected [this can be achieved by increasing dimensionless potential well depth $\hat{\varepsilon}$ or by decreasing shear flow intensity $\text{Pe}$ as can be seen from Eq. (12)]. It should be noted that the nondimensional interparticle force is defined based on particle-particle interaction force, which may not be an appropriate one when cluster-cluster aggregation occurs. However, this criterion for classification of aggregation outcomes should still be useful, but it may change the magnitude of the normalized interparticle force $f_{\text{pot,sh}}$ at which this transition occurs.

LD simulations of aggregation in the presence of shear at different Péclet numbers $\text{Pe}$ and with different potential well depths $\hat{\varepsilon}$ are performed and aggregates are characterized in terms of the fractal dimension $d_f$, the most probable aggregate size in the direction perpendicular to the shear flow $R_{\perp}^{\text{mp}}$, and the local volumetric potential energy density LPED, as shown in Table II. The most probable aggregate size in the direction perpendicular to the shear flow $R_{\perp}^{\text{mp}}$ is computed by first determining the equivalent inertia ellipsoid with principal axes $R_1$, $R_2$, $R_3$ for each aggregate. Then, $R_{\perp}^{\text{mp}}$ is the mode of the $R_2$ distribution (if more than one mode exists, the highest value of $R_2$ is chosen). The aggregates are then classified according to the value of the normalized interparticle force $f_{\text{pot,sh}}$, as shown in Fig. 6.

![Figure 6](image_url)

**FIG. 6.** (Color online) Normalized interparticle force relative to shear $f_{\text{pot,sh}}$ (color legend) as a function of the dimensionless interparticle potential well depth $\hat{\varepsilon}$, and Péclet number $\text{Pe}$. The dashed line represents the boundary between nonaggregating and aggregating systems, and the dotted line identifies the region where compactness of local structure is observed. Values in brackets for selected systems represent $d_f$, $R_{\perp}^{\text{mp}}$, and LPED, respectively.

This classification uses the normalized interparticle force relative to shear $f_{\text{pot,sh}}$ as a criterion to identify aggregation outcomes in the parameter space defined by the dimensionless interparticle potential well depth $\hat{\varepsilon}$ and the Péclet number $\text{Pe}$. In Fig. 6 the color legend represents values of $f_{\text{pot,sh}}$. Based on the correlation between aggregation metrics and the value of the normalized interparticle force $f_{\text{pot,sh}}$, three different regions are identified: (a) no aggregation ($f_{\text{pot,sh}}<1$); (b) aggregation with less dense local structure ($1 \leq f_{\text{pot,sh}} < 4$) corresponding to LPED values less than that of nonsheared aggregates (10.8 from Fig. 4); and (c) aggregation with compact local structure ($f_{\text{pot,sh}} > 4$) corresponding to LPED values greater than that for nonsheared aggregates. The dashed line represents the border between regions where aggregates do not form ($f_{\text{pot,sh}} < 1$) and the region where formation of aggregates is observed ($f_{\text{pot,sh}} > 1$). The dotted line separates regions when aggregates with compact local structure (when compared to nonsheared aggregates) are formed. Consider two systems that fall in the region characterized by less dense local aggregates (indicated by arrows with aggregation metrics in Fig. 6) that start from significantly different initial conditions: ($\hat{\varepsilon}$; $\text{Pe}$) = (8; 2.1) and (50; 8.0). Since these two systems are in the same region in parameter space as defined by their $f_{\text{pot,sh}}$ values, their aggregation metrics (fractal dimension, size of largest aggregates and LPED) have very similar values even though their initial conditions are significantly different (see Table II and Fig. 6). The LPED value for both systems is less than that for corresponding nonsheared aggregating systems (LPED = 10.8), indicating less dense local aggregates. On the other hand, a system with initial conditions ($\hat{\varepsilon}$; $\text{Pe}$) = (50; 2.1) has $f_{\text{pot,sh}} > 4$ and according to this classification will form compact aggregates. As seen in Fig. 6 (symbol in locally compact aggregate region with arrow pointing to it and values of aggregation metrics), this system has LPED = 12.1, which is consistent with the classification. Systems with $f_{\text{pot,sh}} < 1$ are also found to exhibit aggregation metrics consistent with their classification as nonaggregating. Based on this analysis of metrics for sheared aggregating systems we conclude that the normalized interparticle force $f_{\text{pot,sh}}$ is useful for classifying aggregation outcomes under shear.

V. SUMMARY

Here we summarize our observations on the effect of shear on aggregation as revealed by the Langevin dynamics simulations. For the value of friction coefficient used in these simulations, once shear is applied to an aggregating system all the particles attain the local flow velocity in a very short time that is on the order of the dissipation time scale $\sim 8/\gamma$. In the sheared cases the aggregate structure depends not only on the magnitude of the interparticle force represented by the potential well depth $\hat{\varepsilon}$ but also on the shear intensity characterized by $\text{Pe}$. Therefore, aggregation outcomes under shear are classified on the basis of the ratio of the interparticle force to the shear force, represented by $f_{\text{pot,sh}}$. When shear is dominant ($f_{\text{pot,sh}} < 1$), then energy that is transferred from kinetic energy of mean velocity into fluctuating kinetic energy overcomes the interparticle interaction energy and aggregate breakage is observed. When the shear force is of the same order of magnitude as the interparticle force and $1 \leq f_{\text{pot,sh}} < 4$...
then aggregates that are larger than the most probable size of aggregate $R^\text{mp}_\perp$ break down until their size satisfies $R_g < R^\text{mp}_\perp$. At the same time the local structure of these aggregates becomes less compact since the shear increases the average neighbor distance $R_{nn}$. When shear is weak relative to potential interaction ($f_{\text{pot,sh}} \gg 4$) the local structure of these aggregates is more compact than the nonsheared case because shear allows the rearrangement of particles in aggregates and particles are able to occupy more energetically favorable positions.

Shear also changes the structure of large-scale aggregates by forming cigar-like aggregates for $f_{\text{pot,sh}} > 1$. In this case a reduction in the fractal dimension $d_f$ (which characterizes the large structure of aggregate) is observed. These findings are consistent with experimental results for moderate shear flow [11].

VI. CONCLUSIONS

Aggregation of colloidal particles under shear is simulated in model systems using a Langevin dynamics model with an improved potential that has been shown to faithfully reproduce solute pair correlation and cluster size distributions in nonsheared systems. In order to elucidate the effect of shear, a set of reference simulations is performed without shear. In the nonsheared cases the resulting aggregates are multifractal, with a distinct inflection point in the slope of cluster size distributions at small and large scales. Small aggregates correspond to a radius of gyration less than that at the inflection point $R^2_g < R^2_{\text{sh}}$ and have a higher fractal dimension ($d_f \sim 2.4$), whereas large aggregates with $R^2_g > R^2_{\text{sh}}$ have a lower fractal dimension ($d_f \sim 1.5$), indicating a more ramified structure. This is consistent with the aggregation mechanism proposed by Sorensen and coworkers wherein aggregation occurs due to monomer addition at small scales, whereas large aggregates are formed by cluster-cluster aggregation. Shear dramatically changes the aggregates on both length scales and introduces significant anisotropy into aggregate structure (nonsheared aggregates are statistically isotropic although individual aggregates have measurable anisotropy). Anisotropic aggregates are not adequately characterized by the isotropic radius of gyration or the fractal dimension inferred from the variation of cluster size with $R^2_g$. It is found that different types of anisotropic aggregates are clearly distinguished and easily compared to isotropic aggregates by means of a newly introduced compactness-anisotropy map that characterizes aggregates based on their local volumetric potential energy density (LPED) and anisotropy in the radius of gyration tensor. Shear changes the compactness of small aggregates (as characterized by LPED), making them more compact for deeper potential well depths, but less compact for shallower potential well depths. In the case of large aggregates, the intensity of shear flow (characterized by the Péclet number $\text{Pe}$) limits the most probable size $R^\text{mp}_\parallel$ of aggregates in the direction perpendicular to the shear flow, resulting in the formation of cigar-like structures. Outcomes of aggregation under shear are classified in the $\text{Pe} - \hat{\varepsilon}$ space of Péclet number and nondimensional well depth, and it is found that the ratio of interparticle force to shear force $f_{\text{pot,sh}}$ is able to distinguish aggregation outcomes as characterized by $(d_f, R^\text{mp}_\parallel, \text{LPED})$.

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APPENDIX A: RADIUS OF GYRATION FOR ANISOTROPIC SYSTEM

The shape of any aggregate containing $k$ solute particles can be described by its moment of inertia tensor $\mathbf{M}$ with components

\[ M_{\alpha\beta} = \frac{1}{k} \sum_{n=1}^{k} (r_{\alpha,n} - r_{\alpha,\text{cm}})(r_{\beta,n} - r_{\beta,\text{cm}}), \quad \alpha, \beta = 1, 2, 3, \]  

(A1)

where $r_{\alpha,n}$ is the $\alpha$th component of position of $n$th solute particle in the cluster, and $r_{\alpha,\text{cm}}$ is the $\alpha$th component of the cluster center of mass. Then the singular-value decomposition of the inertia tensor $\mathbf{M}$ is performed as

\[ \mathbf{M} = \mathbf{U} \mathbf{S} \mathbf{V}^T, \]  

(A2)

where $\mathbf{U}$ is the unitary matrix, $\mathbf{V}^T$ is the conjugate transpose of the unitary matrix $\mathbf{V}$, and $\mathbf{S}$ is the diagonal matrix corresponding to the principal axes of the inertia ellipsoid with components

\[ S_{\alpha\alpha} = R^2_{\alpha}, \quad \alpha = 1, 2, 3. \]  

(A3)

Then the squares of principal radii of gyration $R^2_{\alpha}$, for $\alpha = 1, 2, 3$, are calculated as

\[ R^2_{\alpha} = \frac{1}{3} (R^2_1 + R^2_2) \]  

(A4)

and the radius of gyration is calculated as [28]

\[ R_g^\parallel = \sqrt{\frac{1}{2} (R^2_1 + R^2_2 + R^2_3)}. \]  

(A5)

Equation (A5) is used for calculating the radius of gyration $R^\parallel$ of anisotropic aggregates in sheared aggregating systems. For anisotropic aggregates that are statistically axisymmetric, the radius of gyration along the major axis is denoted $R_g$, while the radius of gyration in the perpendicular plane is denoted $R_\perp$.

APPENDIX B: SCALE ANALYSIS OF COLLOIDAL AGGREGATION UNDER SHEAR

The aggregation of colloidal particles under shear in LD simulations introduces a wide range of length scales from monomer diameter (tens of nanometers) to the size of large aggregates (order of micrometers) [29]. There is also a wide range of time scales ranging from Brownian motion of solute particles (order of femtoseconds) and the fluid time scale associated with shear (order of milliseconds).

A system of colloidal particles aggregating in the presence of shear can be characterized by a set of physical parameters $\mathcal{P}$ that includes characteristic scales of length, time, velocity, and interparticle force. At the microscale the characteristic length, time, and velocity scales are those corresponding to
the solute particles arising from the LD dynamical equations [Eqs. (2) and (3)] [13]. However, it is not known a priori which set of dimensionless parameters is most useful for characterizing aggregation outcomes. While metrics such as the radius of gyration $R_g^\perp$, fractal dimension $d_f$, extent of aggregation $\xi$ are used for nonsheared systems, the appropriate metrics for sheared aggregating systems are not yet established. Aggregation introduces clusters characterized by their radius of gyration $R_g^\perp$, which introduces a mesoscale-length scale, and shear flow introduces a macroscale time scale as shown in Table III. A dimensional analysis based on the Buckingham $\Pi$ theorem is used to reduce these physical parameters to a nonunique set of dimensionless parameters $\Pi$. The dimensionless parameters that represent length and time scale ratios of macro- (or meso-) to meso- (or micro-) scales are useful in characterizing scale-separated or scale-overlap regimes.

For sheared aggregating systems, the dimensionless physical parameters were scaled to correspond nondimensional counterparts in a similar manner as for nonsheared aggregating systems in terms of $(\bar{D}_\infty, \bar{\xi})$ as previously described [13], where $\bar{D}_\infty$ is the dimensionless diffusion coefficient and $\bar{\xi}$ is the dimensionless Lennard-Jones potential well depth [see Fig. 7(a)]. The product $\bar{D}_\infty$ can be interpreted as $1/(\gamma \tau_F)$, the ratio of the frictional time scale $\gamma^{-1}$ to the interparticle force time scale $\tau_F$ [13].

When an aggregating system is subjected to shear, an additional dimensionless parameter (Péclet number $Pe$) related to the shear rate $G$ arises [see Eq. (1)]. Therefore, outcomes of sheared aggregation could be classified in a candidate parameter space that is shown in Fig. 7(b). Also, shear limits the size of aggregates that introduces an additional length scale $R_g^\perp$, the most probable size of aggregates in the shear-normal direction. The presence of clusters with a range of sizes in an aggregating system results in as many time scales. On the microscale level, the system is characterized by the velocity autocorrelation time scale for a single particle $\tau_v(1)$, and particle size $\sigma$. On the mesoscale level, when aggregates are formed from a single particles, systems are characterized by the velocity autocorrelation time scale for a cluster containing $k$ monomers $\tau_v(k)$, and a radius of gyration of aggregate $R_g^\perp$. At the macroscale, the system is characterized by the shear time scale (represented by $G^{-1}$) and the most probable size of aggregates $R_g^\perp$ that is limited by shear (see Table III). A sheared aggregating system can be characterized by the ratio of macroscale to microscale timescales $G \tau_v(1)$ that corresponds to the Deborah number $De$ and defines the extent of timescale separation. By analogy, the aggregation outcome can be monitored by the ratio of microscale length scale to macroscale length scale as

$$\sqrt{D_\infty \tau_v(1)} \frac{R_g^\perp}{R_g^\perp},$$

where $\sqrt{D_\infty \tau_v(1)}$ represents the microscale length scale and corresponds to the distance a single particle will travel during time $\tau_v(1)$.

From these time and length scale ratios, the scale-separated regime can be determined as

$$G \tau_v(1) \ll 1; \quad \frac{D_\infty \tau_v(k)}{R_g^\perp} \ll 1,$$

and the scale-overlap regime is defined as

$$G \tau_v(1) \gg 1; \quad \frac{D_\infty \tau_v(k)}{R_g^\perp} \gg 1.$$

Based on this analysis, different values for the time scale ratio $G \tau_v(1)$ should correspond to scale-separated or scale-overlap regimes in the candidate parameter space shown.

**TABLE III.** Classification of scales encountered in LD simulation of aggregation under shear where $\tau_F$ is the time scale associated with the interparticle force, $\tau_v$ is the characteristic velocity autocorrelation time of a monomer $(\tau_v(1))$ or a cluster $(\tau_v(k))$, $R_g^\perp$ is the aggregate radius of gyration, $R_g^\perp$ is the macroscopic length, and $G$ is the shear rate.

<table>
<thead>
<tr>
<th>Length</th>
<th>Microscale $\sigma$</th>
<th>Mesoscale $R_g^\perp$</th>
<th>Macroscale $R_g^\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>$\gamma^{-1}$</td>
<td>$\tau_F$</td>
<td>$\tau_v$</td>
</tr>
<tr>
<td>Velocity</td>
<td>$\sigma_{mon}$</td>
<td>$R_g^\perp/\tau_v$</td>
<td>$G \times R_g^\perp$</td>
</tr>
</tbody>
</table>
in Fig. 7(b). A proposed aggregation map is constructed by analogy to the aggregation map reported for non-sheared aggregating systems [Fig. 7(c)] [13] with an additional axis for the Péclet number to represent shear.

For all LD simulations of systems described in Table 1, the velocity autocorrelation time scale for a single particle $\tau_v^{(1)}$ is computed, and the values of $G\tau_v^{(1)}$ as a function of the dimensionless potential well depth $\hat{\varepsilon}$ and Péclet number $Pe$ are shown in Fig. 7(c). From the delineation of the parameter space in Fig. 7(b) it is possible to conclude that for all simulated systems reported in Table 1, only the scale-separated regime is observed and shear does not change the Deborah number $De = G\tau_v^{(1)}$ significantly, since decrease in the shear time scale (by increase in the shear rate $G$) decreases the velocity autocorrelation time scale for a single particle $\tau_v^{(1)}$. An explanation for this phenomenon is based on the fact that as intensity of the shear flow (Pe) increases, the most probable size of aggregates $R_m^{(1)}$ decreases [3,6–9]. This decrease in the size of aggregates occurs because particles are leaving the aggregate surface as shear is applied. As result, those particles that leave the aggregate lose their “memory” faster than those left in the aggregate, and overall, the average velocity autocorrelation time calculated for a single particle $\tau_v^{(1)}$ decreases.

Earlier analysis of non-sheared aggregation by the authors led to the following conclusions: (a) aggregation in a system occurs only if the dimensionless potential well depth $\hat{\varepsilon}$ is greater than some critical value $\hat{\varepsilon}_{cr}$ and (b) the dimensionless diffusion coefficient does not control the aggregation outcome, but controls only the rate of aggregation [13]. Based on these findings for non-sheared systems, we conclude that the dimensionless diffusion coefficient is not a relevant parameter for classifying sheared aggregation outcomes, and systems with $\hat{\varepsilon} > \hat{\varepsilon}_{cr}$ are chosen to ensure aggregation in the shear simulations. Therefore, outcomes of sheared aggregation can be classified in a parameter space defined by the dimensionless potential well depth $\hat{\varepsilon}$ and the Péclet number $Pe$, with all outcomes corresponding to the scale-separated regime where the Deborah number is less than unity.

[26] Amit Chakrabarti (private communication).
[29] We do not consider solvent scales because these are not explicitly represented in the LD simulations.