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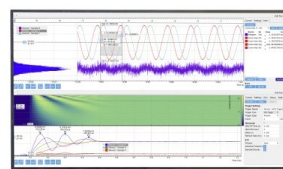
# Viscosity of bimodal suspensions with hard spherical particles

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We analyze two equations for their ability to predict the viscosity of bimodal suspensions with hard spherical particles. The equations express the viscosity as a function of the particle loading and the packing (or, volume) fraction at which the viscosity diverges (viscosity threshold). The latter is found from previously published experimental studies for a variety of sphere diameter ratios and fractions of small particles in total solids. A comparison between the viscosity thresholds and the maximally random jammed packing verifies their interconnection and permits accurate viscosity prediction of bimodal suspensions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901463]

## I. INTRODUCTION

Predicting the viscosity of suspensions is a problem of importance in fields including civil engineering (flow of cement and concrete), soil mechanics (flow of sediments), oil well engineering (flow of cement and fracking fluids), paint design (flow of pigments), and medicine (flow of blood). This has been an active area of research for at least a century, and major advances continue to be made with respect to factors such as the role of interparticle friction,[1] the onset of shear thickening,[2] and the effect of particle shape.[3] Nevertheless, for the important case of Newtonian suspensions of polydisperse particles, there is still no reliable way to predict the dependence of viscosity on the concentration or size distribution of particles. A variety of semi-empirical equations have been developed that relate the viscosity to the packing (or, volume) fraction of particles (packing fraction), $\phi$, but they require knowledge of the critical packing fraction, $\phi_M$, at which the viscosity diverges. However, as noted in an excellent review by Stickel and Powell,[4] the prediction of $\phi_M$ is still an open problem. In this paper, we demonstrate that, for bimodal suspensions, $\phi_M$ is proportional to the packing fraction of particles in the maximally random jammed (MRJ) packing, which is readily determined from simulations. If this correlation extends to other polydisperse suspensions, it will provide a relatively simple method for predicting this important property for materials of practical interest.

The viscosity of suspensions of spherical particles increases exponentially from the dilute to the concentrated regime when evaluated at a fixed shear rate.[5] The exponential behavior is a result of the energy dissipation related to the increasing probability of particle interaction with rising concentration in the system. Even though the physical phenomenon is well known, an exact solution for the evolution of the viscosity is still absent and, as a consequence, a variety of semi-empirical equations have been developed. Common to these relationships is that they reduce to

Einstein's analytical solution[6] for low packing fractions, $\phi$, and that they diverge at a concentration of particles which, in this paper, is called the viscosity threshold, $\phi_M$. As $\phi_M$ is approached, the suspension undergoes a transition between liquid- and solid-like behavior, in the sense that a finite shear deformation generates velocity gradients in the mixture at $\phi < \phi_M$; above the threshold, the suspension is mechanically stable (solid-like) under similar forces. The viscosity threshold is shear-rate dependent, as documented by Krieger[7] for monodisperse suspensions with spherical particles. The present study focuses solely on the (low) shear rate regime where hydrodynamic forces are dominant and the viscosity is shear-rate independent.

The viscosity threshold of a bimodal suspension with rigid, non-colloidal spherical particles exceeds the one for a monodisperse system.[8] By introducing into such a system another component of spheres with a different size, $\phi_M$ becomes a function of the small-to-large sphere diameter ratio, $\alpha$, and the volume fraction of small particles in total solids, $\chi$. The same two parameters are also known to play a vital role when determining the dry packing of bimodal systems. The practical importance of predicting the viscosity of suspensions, $\mu_S$, together with the difficulty of making accurate measurements for various particle size distributions, makes it attractive to identify a connection between $\mu_S$ and the dry packing efficiency of the particles. This motivated Shapiro and Probstein[9] to investigate the connection between the viscosity thresholds of bimodal suspensions and experimentally measured dry packing densities. They concluded that suspensions must develop local ordering when the packing fraction exceeds $\phi \approx 0.524$ in monomodal suspensions, which is about 20% lower than the random close packing obtained when the dry particles are vibrated in a container. They argued that there is no single viscosity threshold, but that $\phi_M$ exhibits a range that depends on the degree of local ordering in the suspension.

We note that $\phi_M$ will exhibit a range that depends on local ordering, where local ordering is history-dependent in

that it depends on the preparation of the suspension. However, for the experimental works discussed here that study the (low) shear rate regime where the viscosity is shear-rate independent, we conclude that suspension preparation and the rheometers used to measure viscosity have introduced, in nearly all cases, a sufficient degree of randomness such that variations in local ordering are not sufficient to cause $\phi_M$ to vary strongly from experiment to experiment. In our work, we provide a stronger and more quantitative correlation than that provided by Shapiro and Probstein,[9] and we find a smaller difference between $\phi_M$ and the random packing density of dry powders. We obtain these results by using the best viscosity data from the literature together with recently developed insight into the MRJ states of binary sphere systems.

The MRJ packing is defined as the least ordered strictly jammed packing that remains mechanically stable under a finite shear deformation.[10,11] This structure is obtained by a packing algorithm that minimizes a set of ordering parameters in the mechanically stable solution space.[10] As indicated in Figure 1, there is a range of packing fractions that are strictly jammed, which means that they are macroscopically stable against shear and compression. For monodisperse spheres, the densest and most perfectly ordered of these is the face-centered cubic crystal (FCC), and the least ordered (maximally random) is MRJ with $\phi_{MRJ} \approx 0.64$. It is perhaps counter-intuitive that the strictly jammed packings with $\phi < \phi_{MRJ}$ are *more* ordered. The phase diagram in Figure 2 schematically illustrates the approach to jammed packings.[12] As the density of the system is raised under equilibrium conditions, there is a transition to a two-phase region of coexistence of fluid and ordered (crystalline) packings, followed by complete crystallization. However, there are also nonequilibrium paths that lead to noncrystalline jammed packings; the final density depends on the rate of compression of the packing. We suggest that concentrated suspensions effectively fall near to the MRJ point reached by nonequilibrium paths



FIG. 2. Phase diagram for frictionless hard spheres, showing the equilibrium path with increasing pressure or density, varying from liquid through a range of coexistence of liquid and crystal, into a crystalline range that ends at the maximum packing fraction ($\pi/3\sqrt{2} \approx 0.74$) corresponding to a face-centered cubic (FCC) crystal. (After Rintoul and Torquato.[11,12])

when ordering and crystallization are suppressed by suspension preparation (mixing) and the agitation provided during the viscosity measurement process. The viscosity diverges when the packing fraction approaches the boundary of the strictly jammed region in Figure 1. We will show that $\phi_M$ falls remarkably close to $\phi_{MRJ}$.

While it is true that there are non-equilibrium paths that lead to non-crystalline jammed packings that have packing fractions substantially different from $\phi_{MRJ}$, these paths are apparently negligible in number compared to those that reach a jammed fraction very near to $\phi_{MRJ}$, for packings prepared without explicit or implicit ordering mechanisms. A very large body of work, including simulation and experiment, supports this conclusion.[10,11,13–16] Those studies show that the MRJ packing fraction $\phi_{MRJ}$ for frictionless monodisperse spheres varies somewhat, but it is always near to ~0.64; for example, it is found computationally to be 0.634 by Hopkins, Stillinger, and Torquato in Ref. 16. The packing fraction of ~0.64 is also the random close packed (RCP) packing fraction of frictionless monodisperse spheres that is often found;[17,18] though the terms MRJ and RCP could be used to describe the same packings, the maximally random jammed state is precisely defined, whereas in the past, the term RCP has been more loosely applied.[10]

Based on a large body of literature and detailed studies such as described in Refs. 13,15, and 16, we conjecture that in the infinite volume limit, non-equilibrium packings of frictionless objects (such as spheres) prepared without explicit ordering, such as tailoring of interparticle forces, external forces or directed sphere placement, and without implicit ordering such as equilibration, will become mechanically stable (jammed) at a value of $\phi_{MRJ}$ dependent only on the shapes and relative sizes of the constituent particles. In the case of binary spheres, this conjecture implies that $\phi_{MRJ}$ will depend only on the sphere diameter ratio, $\alpha$, and the
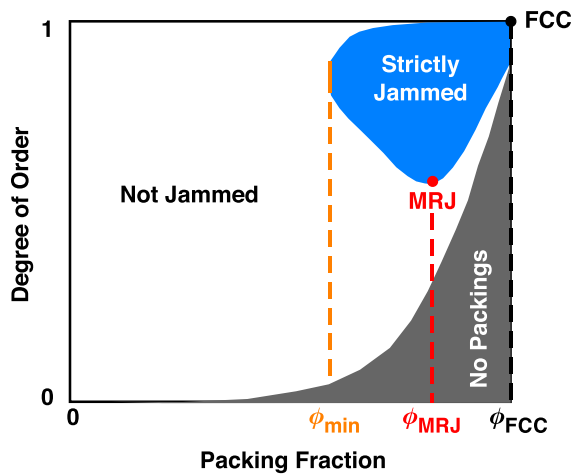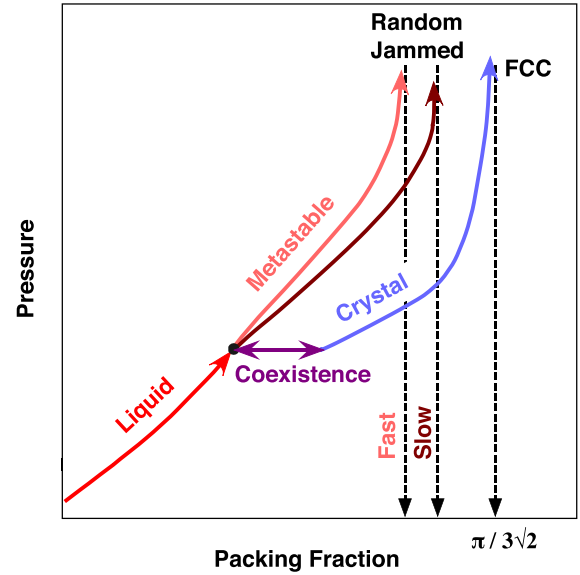


FIG. 1. Illustration of the possible types of packings as a function of packing fraction and degree of order. The blue shaded region in the upper right consists of strictly jammed packings, the most disordered of these are maximally random jammed, with $\phi_{MRJ} \approx 0.64$. The densest possible packing is face-centered cubic (FCC) with $\phi_{FCC} = \pi/3\sqrt{2} \approx 0.74$, and the least dense strictly jammed packing has $\phi_{min} \approx \pi/2\sqrt{2} \approx 0.49$. (After Torquato *et al.*[10,11])

fraction of small particles in total solids, $\chi$. Additionally, should ordering mechanisms be present but frustrated by mixing or other means, in accordance with past findings, we state that the packing fraction at which jamming occurs should be equal to or very nearly equal to $\phi_{MRJ}$.

## II. ANALYSIS

We take advantage of the highly accurate values of $\phi_{MRJ}$ provided in Ref. 16 to investigate the correlation between $\phi_{MRJ}$ and the viscosity threshold from the most consistent viscosity studies on bimodal suspensions with rigid, non-colloidal spherical particles.[8,19–21] These studies were carried out at shear rates high enough so that hydrodynamic, rather than Brownian, forces are dominant, but low enough to avoid artifacts (e.g., lubricating layers separating the suspension from the wall of the vessel). The particles in each of the two modes in the experimental studies show some distribution, ranging from arithmetic particle volume standard deviations of 10%–30% in many cases to as much as 75% in the work of Polinski et al.,[21] whereas the simulations use strictly binary packings. However, some additional simulations of the MRJ packing fraction of bimodal (rather than strictly binary) packings of spheres have been performed, for modes with lognormal size distributions and arithmetic volume standard deviations ranging from 20% to 500%. These simulations suggest that the relatively small arithmetic standard deviations of the

individual modes in the experimental work do not contribute significantly to a difference in packing fraction between the bimodal and strictly binary cases. For example, a bimodal MRJ packing of spheres where the average diameters of the modes have a 5:1 ratio, where 75% of the volume of spheres lies in the large mode and 25% in the small mode, and where the volume standard deviations are 20% for the small mode and 100% for the large mode, exhibit a packing fraction that is only about 1.2% higher than for the strictly binary case with the same diameter ratio and relative composition fractions. Further simulations of the MRJ packing fractions of bimodal sphere distributions are in progress, and the results of this study will be presented in a future work.

To relate $\phi_M$ to $\phi_{MRJ}$, we need an expression for the relative viscosity, $\mu_r = \mu_S/\mu_L$, where $\mu_S$ is the viscosity of the suspension and $\mu_L$ is the viscosity of the liquid in which the particles are suspended. In the absence of an exact analytical theory for $\mu_r$, we utilized the following semi-empirical relationships. The first was chosen because it is widely used, and the second because it performs exceptionally well

$$\mu_r = \left(1 - \left(\frac{\phi}{\phi_M}\right)\right)^{-[\eta]\phi_M}, \tag{1}$$

$$\mu_r = \left(1 + 0.75\left(\frac{\phi/\phi_M}{1 - (\phi/\phi_M)}\right)\right)^2. \tag{2}$$
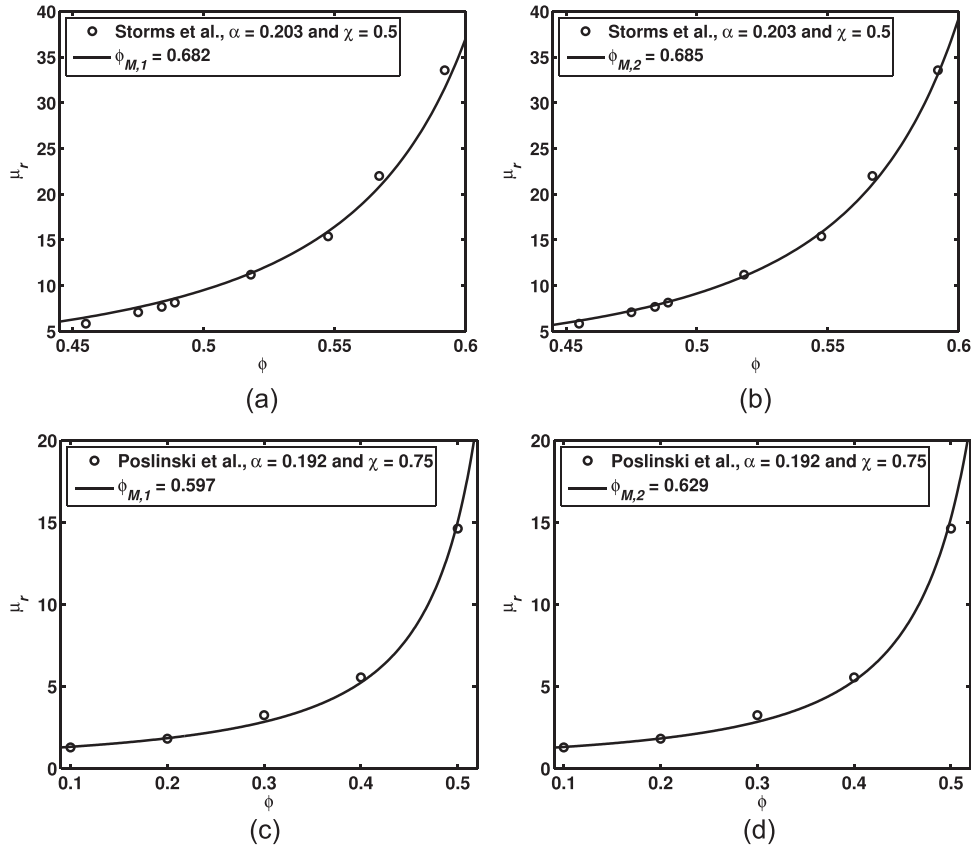


FIG. 3. Experimentally measured viscosities (points) and fits to Eqs. (1) and (2) (curves). Subscripts 1 and 2 refer to Eqs. (1) and (2), respectively. (a) and (b) Data from Storms et al.[20] for $\alpha = 0.203$ and $\chi = 0.5$ fit with $\phi_{M,1} = 0.682$ and $\phi_{M,2} = 0.685$; (c) and (d) measurements from Poslinski et al.,[21] where $\alpha = 0.192$ and $\chi = 0.75$ fit with $\phi_{M,1} = 0.597$ and $\phi_{M,2} = 0.629$.
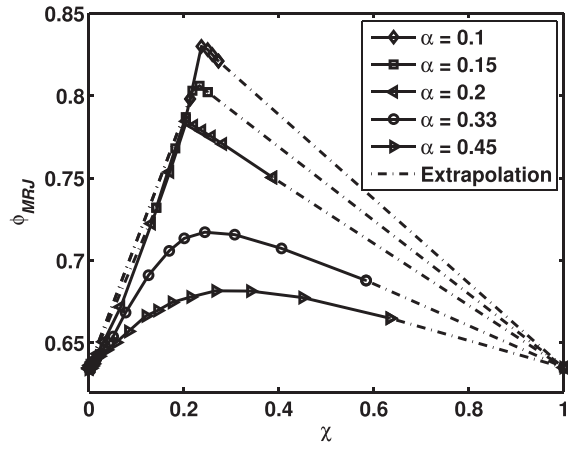
FIG. 4. The MRJ packing fraction for binary systems as a function of $\chi$ for selected $\alpha$ values (data from Hopkins *et al.*[16]).

Equation (1) was proposed for monodisperse suspensions by Krieger and Dougherty;[22] in the present study, the intrinsic viscosity $[\eta]$ is fixed at 5/2, so that the equation reduces to Einstein's expression for dilute solutions, $\mu_r = (1 + 2.5\,\phi)$. Equation (2) was proposed by Chong *et al.*,[8] who showed that it agreed well with the viscosity measurements on a monodisperse suspension and three different bimodal systems. This equation also reduces to Einstein's expression, but only if $\phi_M = 0.6$, which is appropriate for a monodisperse system; therefore, it is not expected to perform well at low concentrations for polydisperse suspensions.

Two examples of the quality of the fit of Eqs. (1) and (2) to experimental data from Refs. 20 and 21 are shown in Figure 3. The viscosity threshold is found by a least-squares fit to log[viscosity], so that the results are not excessively biased by higher viscosities. Each of the equations provides a good approximation to the experimental data, but the two equations predict different viscosity thresholds, especially for the data of Poslinski *et al.*;[21] in the latter case, Eq. (1) predicts a viscosity threshold that is less than for a monodisperse suspension. Both of these

differences are artifacts that originate from the fact that the experimental data points for these studies are not collected close to $\phi_M$.

Comparing the top and bottom charts in Figure 3, it is evident that similar viscosities can be obtained at different packing fractions by altering the $\chi$ value. In this case, $\phi_M$ changes by more than 0.05 regardless of whether Eq. (1) or Eq. (2) is used. An increase in $\phi_M$ can also be obtained by reducing $\alpha$, since this allows the smaller spheres to be located in the interstices of the larger particles.[8] A similar trend is known from the MRJ packings of binary systems[16] (see Figure 4); however, those packings also include small spheres separating large particles, as well as filling the interstices.

We have analyzed 17 different $(\alpha, \chi)$ combinations from four different authors[8,19–21] to compare the viscosity thresholds derived from Eqs. (1) and (2) to the densities of MRJ binary packings. As shown in Table I, the bimodal suspensions cover a good part of the $(\alpha, \chi)$-plane with $\alpha$ ranging from 0.137 to 0.477 and $\chi$ from 0.1 to 0.75. A linear correlation is obtained by plotting $\phi_M$, obtained from fits of the experimentally measured data to both Eqs. (1) and (2), versus $\phi_{MRJ}$ (see Figure 5). The only two data points that stand out are from Sweeny and Geckler[19] for $\alpha = 0.137$ and $\chi = 0.25$ and Poslinski *et al.*[21] for $\alpha = 0.192$ and $\chi = 0.1$. Sweeny and Geckler's data set consists of a single measurement, so a slight variation in that $(\phi, \mu_r)$ point has a great impact when determining $\phi_M$ and that could explain why that point stands out; a viscosity decrease of only 20% would move that point onto the line. In case of Poslinski *et al.* data set, $\phi_M$ exceeds $\phi_{MRJ}$, which is physically impossible according to our conjecture unless the suspension was prepared with explicit or implicit ordering, since it implies that the viscosity would be finite at $\phi_M = \phi_{MRJ}$. These two data points are excluded in the rest of this analysis.

The best linear correlation[26] between $\phi_M$ and $\phi_{MRJ}$ is presented in Figure 5. The plot illustrates that the correlation is slightly weaker for Eq. (1) than for Eq. (2). Most of the studies that are analyzed to generate Figure 5 are limited to

TABLE I. The data from the 17 investigated bimodal systems. Subscripts 1 and 2 refer to Eqs. (1) and (2), respectively.

| Authors | $\alpha$ | $\chi$ | $\phi_{M,1}$ | Error,1 | $\phi_{M,2}$ | Error,2 | $\phi_{MRJ}$ |
|---|---|---|---|---|---|---|---|
| Chong *et al.* [Fig. 7 in Ref. 8, also Tables 21–23 in Ref. 23] | 0.477 | 0.25 | 0.619 | 0.001 | 0.633 | 0.002 | 0.678 |
| | 0.313 | 0.25 | 0.660 | 0.002 | 0.668 | 0.001 | 0.726 |
| | 0.138 | 0.25 | 0.744 | 0.001 | 0.744 | 0.001 | 0.809 |
| Sweeny and Geckler [Table VII in Ref. 19] | 0.371 | 0.25 | 0.622 | … | 0.645 | … | 0.705 |
| | 0.137 | 0.25 | 0.685 | … | 0.687 | … | 0.809 |
| Storms *et al.* [Figs. 4–7 in Ref. 20] | 0.432 | 0.25 | 0.668 | 0.006 | 0.674 | 0.002 | 0.686 |
| | 0.244 | 0.25 | 0.724 | 0.008 | 0.700 | 0.002 | 0.757 |
| | 0.432 | 0.5 | 0.601 | 0.004 | 0.633 | 0.002 | 0.678 |
| | 0.338 | 0.5 | 0.640 | 0.002 | 0.658 | 0.001 | 0.696 |
| | 0.244 | 0.5 | 0.668 | 0.002 | 0.677 | 0.001 | 0.719 |
| | 0.203 | 0.5 | 0.682 | 0.004 | 0.685 | 0.001 | 0.728 |
| | 0.432 | 0.75 | 0.574 | 0.002 | 0.620 | 0.002 | 0.657 |
| | 0.388 | 0.75 | 0.603 | 0.001 | 0.626 | 0.001 | 0.666 |
| Poslinski *et al.* [Fig. 3 in Ref. 21] | 0.192 | 0.1 | 0.768 | 0.023 | 0.729 | 0.010 | 0.698 |
| | 0.192 | 0.3 | 0.733 | 0.020 | 0.714 | 0.011 | 0.771 |
| | 0.192 | 0.5 | 0.698 | 0.018 | 0.694 | 0.013 | 0.732 |
| | 0.192 | 0.75 | 0.597 | 0.009 | 0.629 | 0.006 | 0.683 |

(a)



(b)
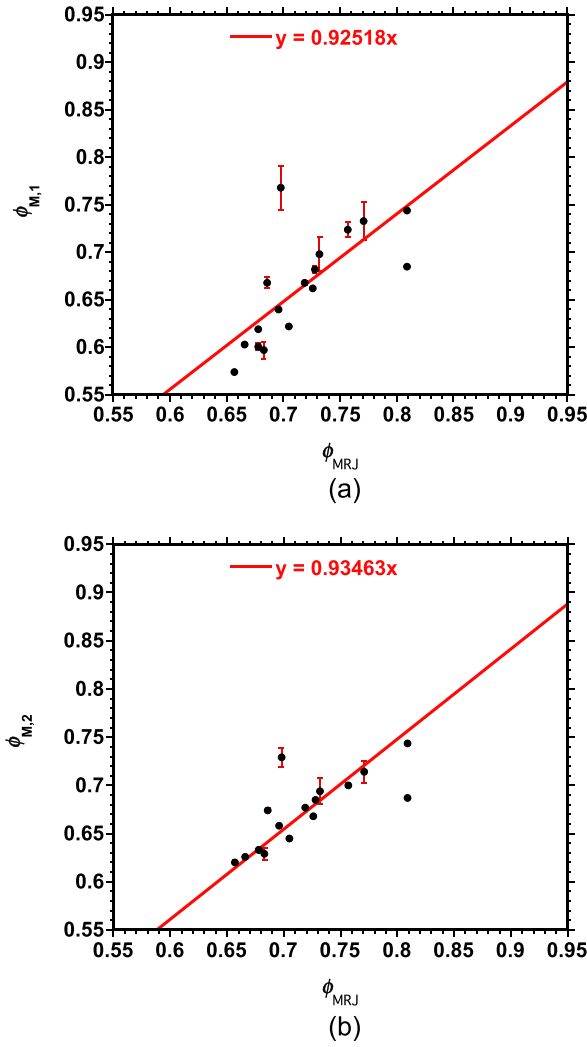
FIG. 5. The viscosity threshold from (a) Eq. (1) and (b) Eq. (2) versus the MRJ packing fraction for 17 binary systems. The slope represents the best constant correlating the two parameters. Subscripts 1 and 2 refer to Eqs. (1) and (2), respectively. The correlation coefficients for the linear fits are (a) $R^2 = 0.828$ (excluding the dubious points from Sweeney and Geckler[19] and Poslinski *et al.*[21]) and (b) $R^2 = 0.894$. The error bars represent the error due to extrapolation to find $\phi_M$ from the data, and do not explicitly include any experimental error in the viscosity measurement.
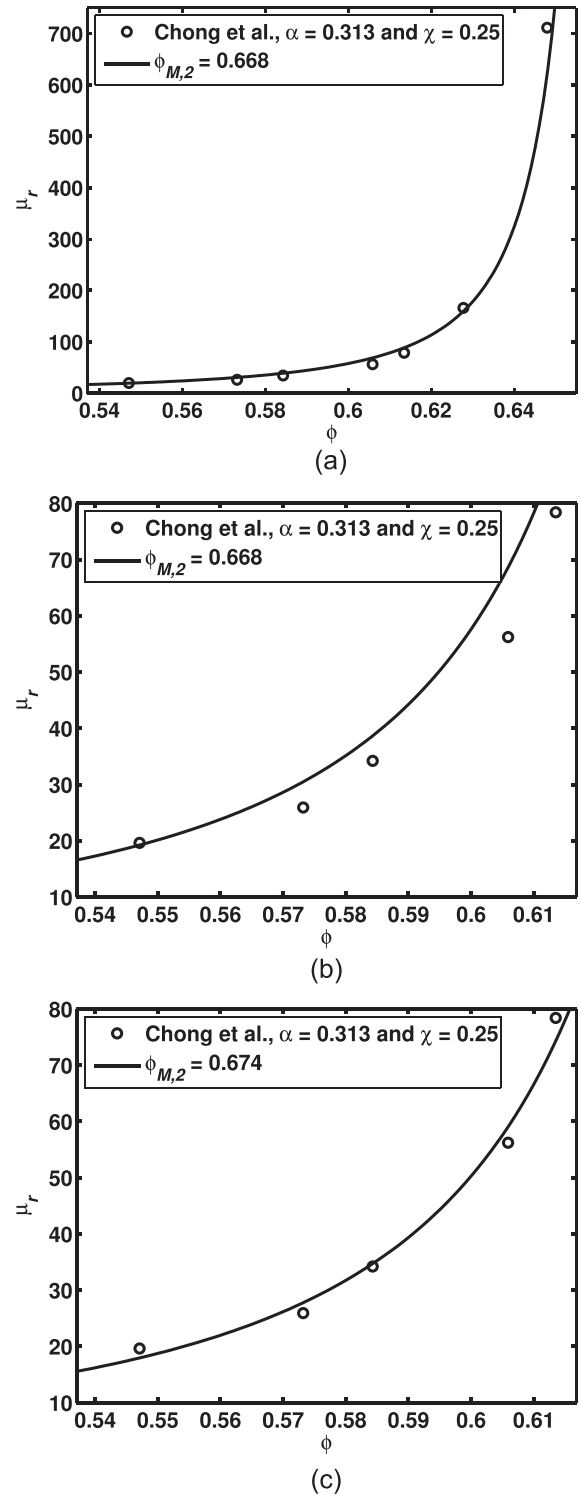


(a)



(b)



(c)

FIG. 6. (a) The fit of Eq. (2) to Chong *et al.*[8] data for $\alpha = 0.313$ and $\chi = 0.25$. (b) The same fit when zooming in on the measurements below a relative viscosity of 100. (c) The fit of Eq. (2) to the same set of data, but excluding the data points above a relative viscosity of 100. The correlation coefficients for the fits are (b) $R^2 = 0.875$ and (c) $R^2 = 0.987$.

the interval $1 \leq \mu_r \leq 100$. Only the study by Chong *et al.*[8] includes measurements close to $\phi_M$. Equation (2) provides a good fit to those data (e.g., see Figure 6(a)), but the fits are not as good as for the other studies at relative viscosities between 1 and 100 (Figure 6(b)). Nevertheless, running a similar analysis as depicted in Figure 5, now considering Chong *et al.*[8] measurements only in the interval $1 \leq \mu_r \leq 100$, results in good fits (Figure 6(c)) and gives the same strong linear correlation between $\phi_M$ and $\phi_{MRJ}$, as shown in Figure 7. Consequently, replacing $\phi_M$ with $0.935\,\phi_{MRJ}$ in Eq. (2) enables a good estimate of the relative viscosity of a bimodal suspension with hard spherical particles in the low shear rate regime. The quality of the prediction is illustrated in Figure 8.

A similar analysis could be performed on any of the many equations that have been proposed to represent the viscosity of suspensions. For example, Eq. (21) of the paper by Martys[24] was derived to match the Einstein and Huggins coefficients (i.e., the first and second terms in the expansion

of viscosity versus packing fraction) and to diverge with an exponent of 2. Note that the equation contains a typographical error. The term in the definition of $K_2$ that reads $n\,(n-1/2)$ should instead be $n\,(n-1)/2$. Using Martys equation, we find a noisier correlation than that shown in Figure 7. Shapiro and Probstein[9] used a complicated semi-empirical
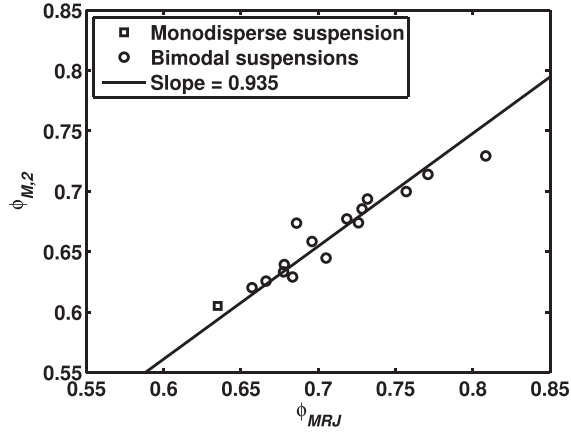
FIG. 7. The viscosity threshold from Eq. (2) versus the MRJ packing for 15 binary systems when evaluating the data sets up to a relative viscosity of approximately 100. The slope represents the best constant correlating the two parameters ($R^2 = 0.849$).

equation that yielded relatively low values for $\phi_M$. None of these empirical equations is expected to be exact as $\phi_M$ is approached, so each will give a slightly different result. However, if the true relationship of $\phi_M$ and $\phi_{MRJ}$ is
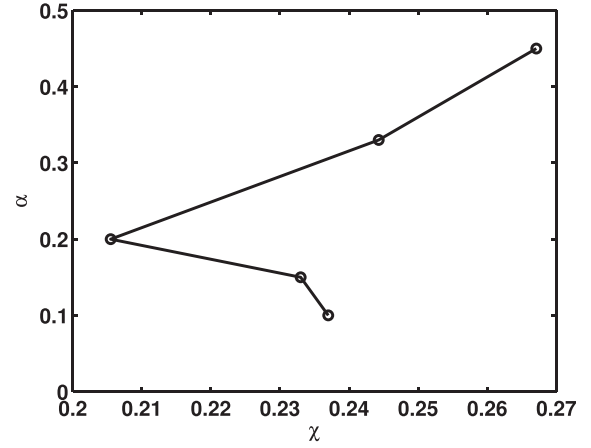


FIG. 9. The $\chi$ value that produces the maximally random jammed packing fraction $\phi_{MRJ}$ (and $\phi_M$) for selected $\alpha$ values (data from Hopkins *et al.*[16]).

approximated through the use of a given viscosity equation, then the viscosity predictions based on that equation should be reasonably accurate.

A consequence of the correlation analysis is that the viscosity threshold from Eq. (2) and $\phi_{MRJ}$ must have similarly shaped surfaces in the $(\alpha, \chi)$-plane. Knowing that makes it possible to plot the $\chi$-value that generates the maximum viscosity threshold, which corresponds to the least viscous suspension, for selected $\alpha$-values (see Figure 9). That optimum is obtained at $0.21 \leq \chi \leq 0.27$ for any $\alpha < 0.45$ (which is the limit of the range for which data are available). This is consistent with the experimental observation that the minimum viscosity of bimodal suspensions can be found in the interval $0.15 \leq \chi \leq 0.35$.[8,21]

As stated previously, the upper bound for $\phi_M$ of a concentrated suspension cannot exceed $\phi_{MRJ}$ if the suspension is prepared without explicit or implicit ordering. Figure 1 indicates that if this is not the case, there is a wide range of strictly jammed structures other than MRJ that might be encountered as the packing fraction in the suspension is increased, and Figure 2 indicates that the nonequilibrium path determines the jamming density. The proximity of $\phi_M$ to $\phi_{MRJ}$ demonstrated here implies that the preparation methods and shear imposed by the rheometer measurement introduces nearly optimal disorder. The diversity of jammed structures could account for some of the scatter in the $\phi_M - \phi_{MRJ}$ correlation, but we cannot exclude the influence of experimental factors including friction, particle size variation, gravitational settling, and interparticle attraction; for example, the ratio of $\phi_M/\phi_{MRJ}$ is expected to be higher for truly frictionless particles.
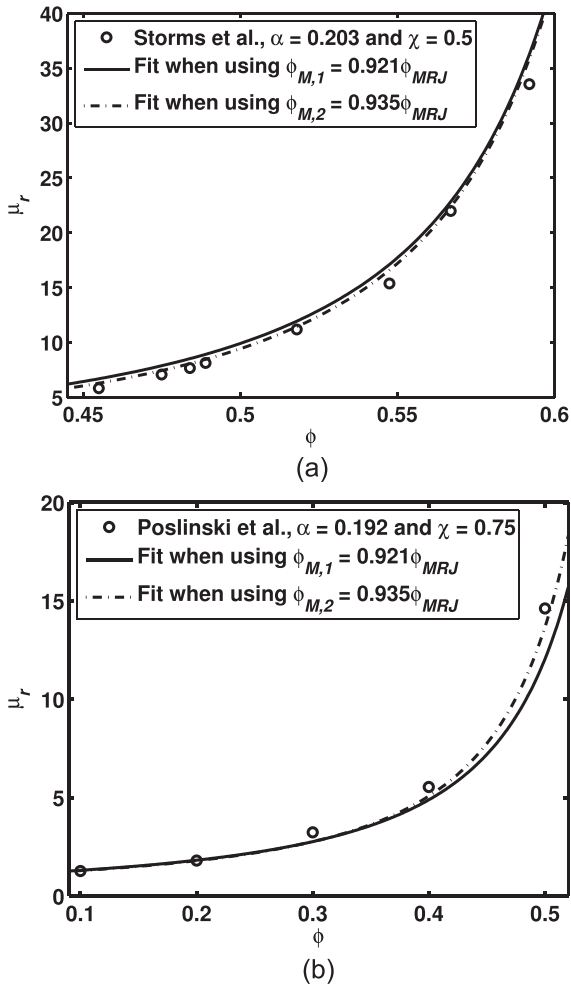


(a)



(b)

FIG. 8. The fit of Eq. (1) with $\phi_{M,1} = 0.927\ \phi_{MRJ}$ and Eq. (2) with $\phi_{M,2} = 0.935\ \phi_{MRJ}$ to measurements from (a) Storms *et al.*[20] for $\alpha = 0.203$ and $\chi = 0.5$ and (b) Poslinski *et al.*,[21] where $\alpha = 0.192$ and $\chi = 0.75$. Subscripts 1 and 2 refer to Eqs. (1) and (2), respectively.

## III. CONCLUSION

A linear correlation was found between the viscosity threshold and MRJ packing fraction, resulting in an equation for accurate viscosity prediction of bimodal suspensions with hard spherical particles. Future research will clarify whether similar correlations exist between the viscosity threshold and MRJ packing of bimodal (rather than strictly binary) systems, more broadly polydisperse particles, and systems with non-spherical particles such as polyhedra.[3,25]

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[26]We have no information regarding the functional form of the relationship between $\phi_M$ and $\phi_{MRJ}$ outside of the range of the experimental data, but we use a straight line because it provides a simple and accurate representation of the observations. The linear fit is arbitrarily forced through zero. Leaving the intercept free would slightly change the slope, but the difference between the curves is smaller than the scatter in the data over the relevant range of packing fractions. The lowest value for $\phi_{MRJ}$ is expected to be no lower than random loose packing for high-friction spheres ($\sim$0.54) and is no higher than 0.87 for binary spheres as $\alpha \rightarrow \infty$.