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Crowding-based rheological model for suspensions of rigid bimodal-sized particles with interfering size ratios

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We present a crowding-based model to predict the shear viscosity of suspensions of rigid bimodal-sized particles. In this model, the mutual crowding factor is defined to explicitly account for the change in the amount of fluid trapped in the interstices formed by particles upon mixing particles with two different sizes. Through this factor, we cancel the effect of size interference by mapping the bimodal suspensions to a suspension of noninterfering size ratio. This approach provides a set of decorrelated particle fractions that depend on crowding and size distribution. The shear viscosity of the resultant suspension is then directly estimated based on the viscosity of corrected components using a stiffening function that accounts for the self-crowding in each size class individually. We tested the proposed model against published experiments over a wide range of particle volume fractions, and we observe an excellent agreement.

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I. INTRODUCTION

The majority of rheology studies on suspensions are conducted to quantify the relative viscosity of monodisperse size distributions [1,2]. However, in nature, suspensions generally involve multimodal distributions. The relative viscosity of multimodal suspensions depends not only on the volume fraction of the solid phase, particle deformation, and induced shear rate, but also on the particle size ratio and particle size distribution. The previous multimodal models [3–12] mostly approximate the relative viscosity based on one of the following two approaches. With the first approach, it is assumed that the particle sizes are noninterfering, and hence the smaller sizes are fully crowded in the interstices formed by large particles. Therefore, the viscosity of such systems is directly estimated based on the viscosity of related components. The second approach uses monodisperse stiffening functions [2,13,14], and applies a correction for the associated maximum close packing considering the polydisperse suspension.

A different approach is to define a crowding factor that accounts for the interaction between different particle size classes. This idea, first introduced by Mooney [3], remains poorly constrained. According to Farris [4], for noninterfering particle sizes R_1 and R_2 ($R_1 \gg R_2$), the viscosity of the suspension can be written as the product of two stiffening functions H,

$$\eta(\Psi_1,\Psi_2) = H(\Psi_1)\,H(\Psi_2), \tag{1}$$

where $\Psi_1 = \psi_l$ and $\Psi_2 = \psi_s/(1-\psi_l)$ are the corresponding corrected volume fractions in which ψ_l and ψ_s refer to the actual volume fraction of the large and small particles, respectively.

Farris [4] argued that by introducing a crowding factor, one could extend his model to account for the behavior of all interfering size ratios. However, at present a theoretical argument for the crowding factor and its application to develop a rheological model that is valid for any interfering size ratio is still missing.

We follow the model of Farris [4] and the idea of Mooney [3] and redefine the bimodal viscosity of the suspension as

$$\eta(\psi_l,\psi_s) = H(\psi_l)H(\psi_s) + \underbrace{H_{12}(\psi_l,\psi_s)}_{\text{crowding effect}}, \tag{2}$$

for interfering size ratios. Here we draw a parallel between this definition of bimodal rheology and the field of probability. The crowding factor here plays a role similar to that of a conditional probability to relate the joint (probability) effect of each individual size class to the rheology of a bimodal suspension. The crowding term is therefore a measure of the interaction between particles of different sizes and its effect decreases as the size ratio, denoted by ζ, increases. The objective of the present work is to derive a relationship that includes the effect of crowding to predict the relative viscosity of bimodal suspensions. We first suggest a practical model to estimate the maximum volume fraction for a bidisperse system. Next, by defining an appropriate crowding factor that accounts for the residual pore space in the system that consists of the two sets of particles, we propose a model to compute the shear viscosity in suspensions of two interfering particle sizes ($1 \leqslant \zeta \leqslant 7$).

II. RANDOM CLOSE PACKING

Providing a theoretical value for the random close packing of bimodal systems is one of the major challenges to quantify the rheological properties of bimodal suspensions. The mechanical stability condition for monosized sphere packings starts from the random loose packing (with the volume fraction around $\psi = 0.56$) to the face-centered-cubic structure ($\psi = 0.74$), which is the most efficient way to pack equal-sized spheres [15]. However, in practice, the maximum density of packing depends on the protocol followed to produce it, and lies between these two bounds, $0.56 < \psi < 0.74$. It is called the maximum random close packing ψ^M [16–18], which, for jamming of monodisperse frictionless rigid spheres, mostly

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lies between $0.63 < \psi_{\textcircled{1}}^{M} < 0.64$ [18–20]. In bimodal systems, the maximum packing limit depends on the particle size ratio and individual size fractions, and, therefore, the macroscopic rheological behavior of these systems is very sensitive to these two parameters.

To quantify the effect of bidispersity on the maximum packing limit, we set up a semitheoretical argument that will form the basis of the definition of the crowding factor later on. The key aspect of the model starts with finding suitable bounds for the maximum packing limits for a bimodal suspension where the particle size ratio approaches infinity [21],

$$\psi_{\infty}^{M} = \min\left[\frac{\psi_{\textcircled{1}}^{M}}{1-k_s}, \frac{\psi_{\textcircled{1}}^{M}}{\psi_{\textcircled{1}}^{M} + (1-k_l)\big(1-\psi_{\textcircled{1}}^{M}\big)}\right], \tag{3}$$

where $k_s = \psi_s/\psi$ and $k_l = \psi_l/\psi$ represent the fraction of small and large particles, respectively (note that $\psi = \psi_s + \psi_l$ is the total solid phase volume fraction, and thus $k_s + k_l = 1$). The limits in Eq. (3) respectively correspond to situations where (i) large particles are dominant and they reach the jamming density (small particles are crowded only in interstices), and (ii) small particles dominate the suspension and jam. The two expressions in Eq. (3) match when the fraction of the small spheres is $k_s^M = (1-\psi_{\textcircled{1}}^{M})/(2-\psi_{\textcircled{1}}^{M})$, where both sizes produce jamming conditions. We can predict this singular point and its associated threshold packing for any finite size ratio by replacing k_s and k_l respectively by $k_s f_s$ and $k_l f_l$ in Eq. (3). We refer to f_s and f_l as *contracting factors*, and assume they depend only on the particle size ratio. These contracting factors account for the bed (solid plus interstices) volume contraction that occurs upon mixing different particle sizes with a fixed overall volume of solid particles. Contracting factors approach zero when the size ratio approaches unity, and approach unity when the size ratio approaches infinity. Therefore, we may assume empirically that $f_s(\zeta) = (1-\zeta^{-1})^{\alpha}$ and $f_l(\zeta) = (1-\zeta^{-1})^{\beta}$, where ζ denotes the particle size ratio (large to small). The exponents α and β are constants that are estimated by fitting

$$k_s^M(\zeta) = 1 - \frac{f_s}{f_s + f_l\big(1-\psi_{\textcircled{1}}^{M}\big)}, \quad 1 < \zeta \leqslant \infty, \tag{4}$$

and its corresponding threshold packing fraction to published experimental and simulation data [19,21–24]. Using these mapping procedures, we obtain $\alpha = 2.1 \pm 0.1$ and $\beta = 1.9 \pm 0.1$. In Eq. (4), $k_s^M(\zeta)$ expresses the fraction of the small particles at which the threshold random close packing (where the two limits converge to each other and form a cusp) occurs for a mixture of hard spheres of size ratio ζ. These points are depicted in Fig. 1 with black circles for different size ratios.

It is interesting to note that Eq. (4) reduces to $(1-\psi_{\textcircled{1}}^{M})/(2-\psi_{\textcircled{1}}^{M})$ as the size ratio approaches infinity, while it approaches unity as $\zeta \to 1$. Bournonville *et al.* [26,27] developed a model where $k_s^M(\zeta)$ approaches zero as the bidispersity vanishes, $\zeta \to 1$. More recently, Brouwers [22] showed that for small size ratios $\zeta \downarrow 1$ the value of $k_s^M(\zeta)$ approaches the limit of 0.5, because of the parabolic nature of random close packing in bimodal systems. The choice of this limit has a small impact on the fitting parameters α and β, but it is important to note that the relationship between the maximum packing and k_s becomes flat when $\zeta \to 1$. As a side note, we report that we tested our rheology model for bimodal suspensions (discussed later) using our packing model [Eqs. (4) and (5)] and compared it to the results obtained similarly but with the packing model of Brouwers [22] at small size ratios $\zeta \downarrow 1$. We found that the discrepancy in the predicted relative viscosity remains less than a percent at small size ratios even at a high volume fraction. The model of Brouwers [22] is more accurate to predict the optimal packing of bimodal suspensions with a size ratio close to unity. However, because of the limited sensitivity of the viscosity prediction to the location of the cusps at small size ratios, $\zeta \downarrow 1$, and the better performance of Eq. (4) over larger size ratios, we decided to proceed with Eq. (4) to estimate the power-law exponents α and β and establish a maximum close packing model for bimodal systems.

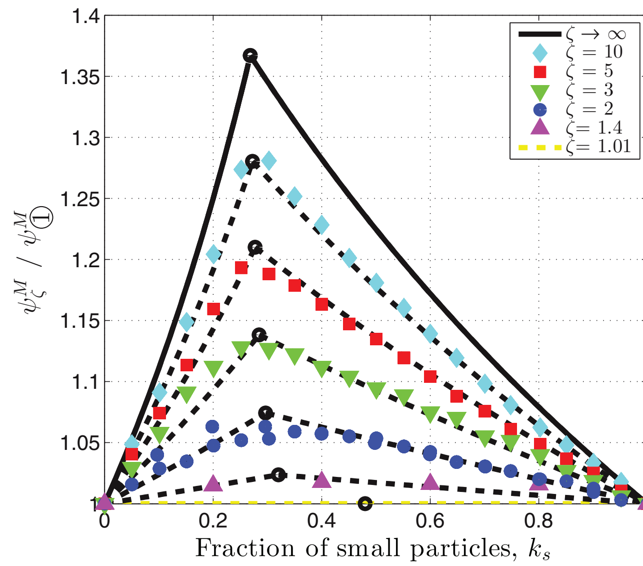

FIG. 1. (Color online) Comparison between our theory stated in Eq. (5) and published experimental and numerical data [19,22,25] for different values of the size ratio (ζ), as indicated. The solid line shows the theoretical value of a packing fraction for the infinite size ratio given by Eq. (3), and the dashed lines represent the value predicted by our model [Eq. (5)] using $\psi_{\textcircled{1}}^{M} = 0.633$. The block circles show the required fraction of the small particles for each size ratio in order to have both sizes separately in a jammed condition.

Consequently, one can approximate the maximum packing limit for binary systems of different ζ and k_s using

$$\psi_{\zeta}^{M} = \min\left[\frac{\psi_{\textcircled{1}}^{M}}{1-f_s k_s}, \frac{\psi_{\textcircled{1}}^{M}}{\psi_{\textcircled{1}}^{M} + (1-f_l k_l)\big(1-\psi_{\textcircled{1}}^{M}\big)}\right], \tag{5}$$

which is plotted against some simulation and experimental data reproduced from Refs. [19,22,25] in Fig. 1. For normalization purposes, we used the reported values of monomodal packing of $\psi_{\textcircled{1}}^{M} = 0.633$ and $\psi_{\textcircled{1}}^{M} = 0.641 \pm 0.4\%$ that are reported in Refs. [19,22] and [25], respectively.

III. RELATIVE VISCOSITY IN BIMODAL SUSPENSIONS

To proceed on the rheological properties of bimodal systems, we need to define a proper stiffening function (see

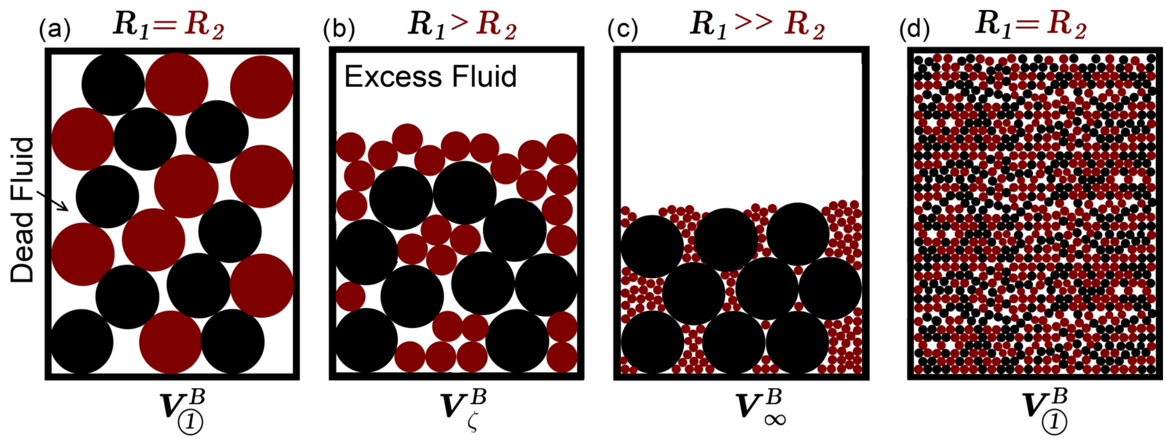

FIG. 2. (Color online) Schematic representation of the excess and dead fluid volume in different binary systems. (a) A packed monomodal system of large particles with a bed volume of $V^B_{①}$, (b) a binary system with a size ratio in the range of $1 < \zeta < 7$ and a bed volume of V^B_{ζ}, (c) a binary packed system of noninteracting particles ($\zeta \to \infty$) with the smallest possible bed volume of V^B_{∞}, and (d) a packed monomodal system of small particles with a bed volume of $V^B_{①}$.

Ref. [2]) which accurately accounts for the crowding and microscopical interactions among the embedded equal-sized particles in concentrated suspensions. For this purpose, one may use the model proposed by Ref. [14],

$$H(\psi) = \left(1 - \frac{\psi}{1 - \Omega\psi}\right)^{-2.5}, \quad (6)$$

where $\Omega = (1 - \psi^M_{①})/\psi^M_{①}$. Ω is a geometrical constant that accounts for the effective volume of particles (particles' volume plus the volume of the trapped matrix inaccessible to other particles). Therefore, Ω is a measure of the *self-crowding effect* [2].

As the size ratio increases, the amount of trapped matrix, the so-called *dead fluid* (see Fig. 2), decreases, and hence more fluid is available to suspend the total particles. Consider a stepwise construction for a system with a total particle volume fraction $\psi = \psi_s + \psi_l$. By introducing the large particles, we note that the viscosity of the suspension increases by a factor $H(\psi_l)$. The viscosity is further increased if we add the small particles. This increment is smaller than if the small particles were large, because of the reduction in the dead fluid volume. The added small particles are homogeneously placed in the available space not occupied by the effective volume of the large particles, and may frustrate the jamming network of the large particles. Therefore, particles with interfering sizes feel each others' effective volume (particle plus associated dead fluid), and they are crowded mutually (the addition of small particles also decreases the available free space for the large particles). When the size ratio between particles increases, the amount of dead fluid trapped between the particles decreases and the effective volume approaches the volume of particles. Following the model in Eq. (1), we aim to find the corrected volume fractions Ψ_1 and Ψ_2 such that Eq. (2) reduces to Eq. (1) in a way that H_{12} is merged into $H(\Psi_1)$ and $H(\Psi_2)$. These corrected volume fractions therefore should depend on the mutual crowding factor C_f, the volume fractions of the small particles ψ_s, and the large particles ψ_l. In the dilute limit, there is no dead fluid, therefore, the bimodal system can be interpreted as a monomodal system of the total solid phase ψ. This highlights that the crowding effect is crucial at high particle concentrations, where crowding among particles becomes important.

Although Mooney [3] outlined two different physical trends as functions of size ratio for the crowding factor, we argue that there is a direct relationship between the crowding factor and the dead fluid volume, as shown in Fig. 2. The crowding factor should depend on both size ratio and size distribution. For monosized suspensions of jammed small or large particles, the amount of the dead fluid is the same, i.e., the same bed volume, as shown in Figs. 2(a) and 2(d). At a fixed total volume of particles, as ζ departs from unity, an excess in the available matrix (excess fluid) is observed as shown in Figs. 2(b) and 2(c), i.e., both bed volume and dead fluid decreases. The lowest volume of dead fluid for any packed binary systems is reached when $\zeta \to \infty$ and the small size fraction is $k_s^M(\zeta \to \infty)$, as schematically depicted in Fig. 2(c). Therefore, we establish crowding as the reduction in the dead fluid upon mixing two interfering particle sizes. We define the crowding factor as

$$C_f(\zeta, k_s) = \frac{V^B_{\zeta} - V^B_{\infty}}{V^B_{①} - V^B_{\infty}}, \quad (7)$$

where V^B represents the bed volume, and subscripts refer to different size ratios (see Fig. 2). Equation (7) reduces to

$$C_f(\zeta, k_s) = \frac{\psi^M_{①}}{\psi^M_{\zeta}}\left(\frac{\psi^M_{\zeta} - \psi'^M_{\infty}}{\psi^M_{①} - \psi'^M_{\infty}}\right), \quad (8)$$

when the total solid phase fraction remains constant. In Eq. (8), ψ'^M_{∞} represents the maximum packing fraction for a suspension of noninterfering size ratio $\zeta \to \infty$ at which the cusp is formed [where the fraction of the small particles is such that both sizes produce jamming conditions, $k_s = k_s^M(\infty)$]. This function is plotted in Fig. 3 for an arbitrary system where $\psi^M_{①} = 0.633$. We observe that, for each size ratio, the minimum crowding factor occurs at $k_s = 0.268$, which corresponds to the minimum possible dead fluid. The crowding factor approaches unity when either $k_s \to 0$ or $k_s \to 1$. A

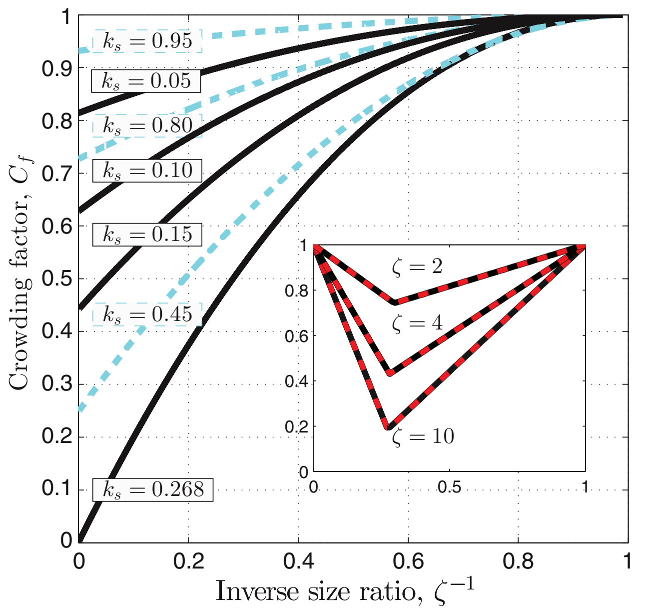

FIG. 3. (Color online) Crowding factor variation with respect to the size ratio and small particle fraction in a binary system computed using Eq. (8) where calculations are performed for $\psi_{①}^M = 0.633$.

zero crowding factor represents a specific situation where each particle size jams without disturbing the monosized packing structure of the other size. It also points to the minimum possible dead fluid (maximum excess fluid), as schematically shown in Fig. 2(c). According to Fig. 3, as the size ratio increases, the effect of k_s on the crowding factor and hence the dead fluid increases.

To remove the crowding effect H_{12} from Eq. (2), we need to decorrelate the two particle size classes while conserving the volume of dead fluid. First, we map an arbitrary binary system of size ratio ζ with particle volume fractions ψ_s and ψ_l to a binary system of noninterfering size ratio, where the small particles jam. We construct a linear transformation $\Pi_1 : [0,1] \times [0,1] \rightarrow [0,1] \times [0,1]$ such that the set of volume fractions $(\psi_1,\psi_2) = \Pi_1(\psi_l,\psi_s)$ conserve the amount of dead fluid in the suspension (the same crowding factor),

$$\Pi_1 : (\psi_1,\psi_2) = (\psi_l - C_f\psi_l, \psi_s + C_f\psi_l). \qquad (9)$$

This transformation is illustrated in Fig. 4. Through this mapping, the size classes ($\zeta \rightarrow \infty$) and volume fractions change, but it conserves the amount of dead fluid (constant crowding factor) and hence the rheological behavior of the suspension is not modified. One can understand the mapping of ψ_l and ψ_s into ψ_1 and ψ_2 as a linear transformation that decorrelates the two distributions, and removes the effect of the crowding factor arising from the size ratio. The resultant bimodal suspension is located on a coordinate system χ_s (along the curve on the right in Fig. 4) between the two extremes illustrated in Figs. 2(c) and 2(d). Along this coordinate, the excess fluid volume of the real suspension (ψ_l,ψ_s,ζ) can be retrieved by performing a second linear transformation $(\Psi_1,\Psi_2) = \Pi_2(\psi_1,\psi_2)$ that conserves the amount of excess and dead fluid in the suspension, but does not necessarily conserve the total volume fraction. In summary, the transformation

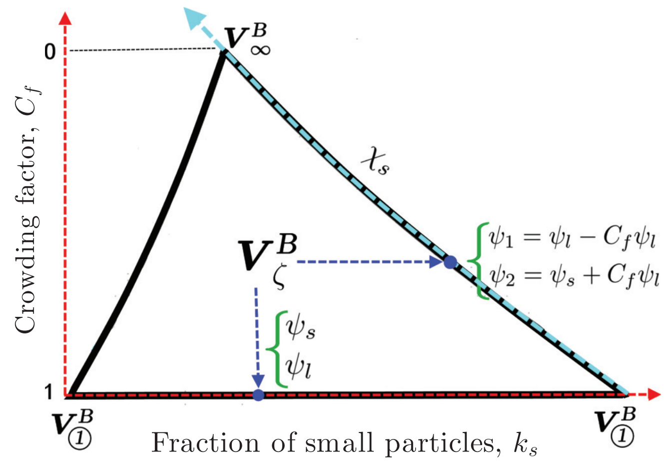

FIG. 4. (Color online) The linear projection of an arbitrary bimodal system of volume particle fractions ψ_s and ψ_l to a configuration where sizes are not interfering and small particles are in a jamming state. This transformation conserves the crowding factor (the same amount of dead fluid) and yields a set of particle volume fractions ψ_1 and ψ_2 projected on a coordinate χ_s.

Π_1 allows us to decouple the two size classes ($\zeta \rightarrow \infty$) while Π_2 corrects the bed volume for each distribution by adjusting the amount of dead fluid that each particle size fraction traps. Finally, we define the transformation $(\Psi_1,\Psi_2) = \Pi_2(\psi_1,\psi_2)$ as

$$\Psi_1 = \frac{\psi_1}{1 - C_f\psi_2}, \quad \Psi_2 = \frac{\psi_2}{1-(1-C_f)\psi_1}. \qquad (10)$$

These totally decorrelated volume fractions for $\zeta \rightarrow \infty$ can be directly used to compute the relative viscosity of suspension of interfering sizes using Eq. (1).

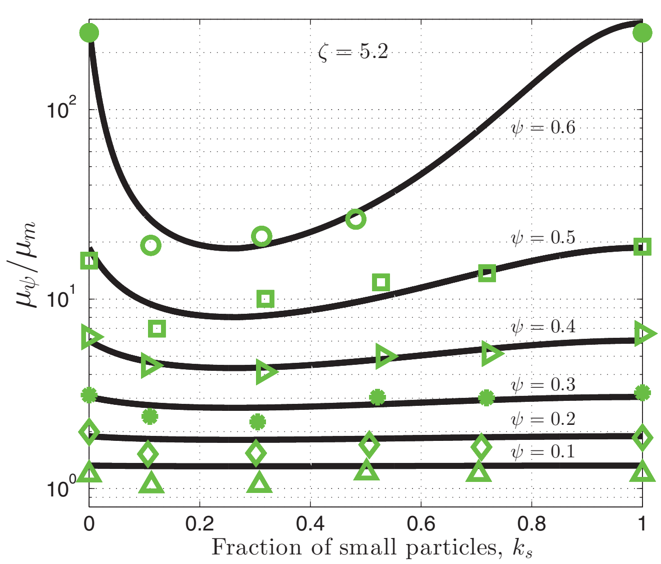

FIG. 5. (Color online) Relative viscosity in bimodal suspensions. Comparison of our crowding-factor-based model results (solid lines) with experimental data sets provided by Poslinski [8] for a binary system with $\zeta = 5.2$ and different total solid phase fractions. The solid circles are extracted from Chong [5] for a relative viscosity of monosized suspensions at a total solid phase fraction of $\psi = 0.6$.

When $\zeta = 1$, we obtain $C_f = 1$, $\Psi_1 = 0$, and $\Psi_2 = \psi_2 = \psi_s + \psi_l$, and the relative viscosity of the bimodal system computed by this model reduces to that of a monomodal system. On the other hand, when $\zeta \to \infty$ and $k_s = k_s^M(\infty)$, we obtain $\Psi_1 = \psi_l$ and $\Psi_2 = \psi_s/(1 - \psi_l)$, which exactly reduces to the formulation proposed by Mooney [3] and Farris [4].

The ability of our model to capture the effect of bidispersity and crowding on the viscosity of bimodal suspensions is tested against experimental data conducted by Poslinski [8] for a system with $\zeta = 5.2$ over a wide range of total solid phase volume fractions ($0.1 \leqslant \psi \leqslant 0.6$). This comparison is depicted in Fig. 5 in which we set $\psi_{①}^M = 0.64 \pm 0.5\%$ following Refs. [8,9,25]. Figure 5 shows the excellent agreement between the proposed theory and the rheology of bimodal-sized suspensions. One can see that the effect of bidispersity is much higher in denser suspensions where the crowding among particles is important, and the excess fluid plays a significant role on the relative viscosity of such systems. Previous models such as those recently proposed by Qi and Tanner [11] and Dorr *et al.* [12] fit these data sets only at the lowest volume fractions (low effect of bidispersity), and their model does not provide a good approximation when the solid phase concentration increases.

IV. CONCLUSION

We present a crowding-based rheological model including self-crowding and mutual crowding for bimodal particle size suspensions. The crowding factor is introduced through a measure of the change in dead fluid volume in the suspension and is therefore related to the maximum packing limit. The model provides a good fit to experimental data for bidisperse suspensions of interfering size ratios ($1 \leqslant \zeta \leqslant 7$). Our model's ability to fit the experimental data over a wide range of volume fractions and size distributions suggests that the proportion of dead to excess fluid in a suspension governs the rheological behavior of bidisperse suspension. This model offers a simple approach to parametrize the effect of bidispheresity on the relative shear viscosity of bimodal suspensions, and can replace complex correlations that are only valid over a limited range of particle volume fraction.

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