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# Modeling the effects of polydispersity on the viscosity of noncolloidal hard sphere suspensions

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#### Abstract

The present study develops an extension of the approach pioneered by Farris [Trans. Soc. Rheol. **12**, 281–301 (1968)] to model the viscosity in polydisperse suspensions. Each smaller particle size class is assumed to contribute to the suspension viscosity through a weighting function in two ways: first, indirectly, by altering the background viscosity, and second, directly, by increasing the contribution of the larger particles to the suspension viscosity. The weighting functions are developed in a consistent fashion as a power law with the exponent, h, a function of the relative volume fraction ratio and the base, g, a function of the solid particle size ratio. The model is fit to available theoretical and experimental results for the viscosity of several binary suspensions and shows good to excellent agreement depending on the functions g and h chosen. Once parameterized using binary suspension viscosity data, the predictive capability to model the viscosity of arbitrary continuous size distributions is realized by representing such distributions with equivalent ternary approximations selected to match the first six moments of the actual size distribution. Model predictions of the viscosity of polydisperse suspensions are presented and compared against experimental data. © 2016 The Society of Rheology. [http://dx.doi.org/10.1122/1.4938048]

#### **I. INTRODUCTION**

The theoretical study of the rheology of suspensions has a long history. It dates back to the seminal work by Einstein who first described theoretically the relationship between viscosity and the solids volume fraction in dilute suspensions of solid spheres [1,2]. Subsequent works on understanding higher order effects in more concentrated systems include the work of Batchelor [3] and Happel and Brenner [4]. It is clear from experimental evidence that the total solids' fraction is not the only factor affecting the rheological properties of suspensions [5]. Particle size polydispersity is also an important factor with immediate consequences in numerous industrial processes including the handling of slurries and in the food industry. In many applications, it is important to determine the particle size distribution (PSD) that minimizes the viscosity of a given particulate formulation. Therefore, it is not surprising that attempts to model the limit of no-flow (maximum packing) in particulate systems [6,7] and more generally polydispersity effects on rheology [8–10] comprise a longstanding area of inquiry. More recently, alternative models have been proposed to describe the effects of polydispersity on viscosity, including works by Qi and Tanner [11], Dörr et al. [12], and Farr [13].

Experimental measurements [10,14–16] and simulation results [17] show that polydispersity induces significant changes in suspension rheology, when compared to monodisperse systems. For example, computer simulations by Chang and Powell [17] starting from initially random configurations indicate that the formation of clusters of large and small particles in a mixed suspension under flow is a plausible microstructural explanation for the reduction in suspension viscosity upon mixing two particles of different size. At the moment, no first principles theory is available to predict the effects of polydispersity except in certain limiting cases. More specifically, Wagner and Woutersen [18] presented exact calculations for the effects of polydispersity on the viscosity of Brownian suspensions in the dilute regime. However, the development of first principles theories for concentrated suspensions remains an open question despite being of great practical relevance. In the absence of such theories, there are three main phenomenological approaches that have been used to understand and model the effects of polydispersity on suspension rheology. These are the maximum packing fraction approach, the Mooney approach [8], and the Farris approach [9]. A common feature of the most successful of these approaches is the use of multiplicative calculations to account for the effect of size separation on viscosity. The main difference between these approaches arises from the treatment of the maximum packing fraction either as a constant or as a variable that depends on the PSD.

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The use of a variable maximum packing fraction represents the simplest methodology toward accounting for the effects of particle size polydispersity on suspension rheology. From the theoretical point of view, there has always been an interest to evaluate the limit of flowability in dispersed systems [6,7], leading to the development of models to predict the maximum packing fraction of particulate systems. Based on these models, rheologists have used the maximum packing fraction to model the viscosity of binary suspensions [10,15,16]. In the first variant of this approach, the viscosity is assumed to obey any one of the empirical or semiempirical viscosity correlations for monodisperse hard sphere suspensions [19–21]. A review of these and other

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viscosity correlations is presented by Faroughi and Huber [22]. The auxiliary information on the PSD only enters into the viscosity calculation via a modification of the maximum packing fraction based on various models [6,7,23]. Despite some early successes, shortcomings have been identified with some of these maximum packing models. Qi and Tanner [11] identified shortcomings in the maximum packing model by Ouchiyama and Tanaka [7]. In particular, this model yields unphysical predictions in the limit of vanishing values of the small particle volume fraction in a binary suspension. On the other hand, the model by Furnas [6] is based on geometrical arguments and is inherently limited to suspensions with large differences between consecutive particle sizes. In the case of binary suspensions, this model predicts a single maximum packing fraction that corresponds to the theoretical maximum attainable packing.

Qi and Tanner [11,24] developed a model that provides a method to directly calculate the suspension viscosity in binary and multimodal suspensions by consecutively accounting for the effects of the different size classes on the overall viscosity in a multiplicative fashion. Starting from the larger size particles, where the maximum packing fraction is assumed to be random close packing, each subsequent smaller particle size is assumed to have an adjusted maximum packing fraction that depends on the volume fractions and the particle sizes present in the system. The suspension viscosity is then calculated as a multiplicative product of the contributions of each individual size class to the relative viscosity of the suspension. Related to the Qi and Tanner approach is the work of Dörr et al. [12] who have developed an effective medium approach that considers the contribution of each size class to suspension viscosity explicitly. In their model, the suspension viscosity is computed recursively based on the addition of particles of a larger size class to an effective suspension of smaller size particles. This approach is different from that of Qi and Tanner [11,24], who use a multiplicative rule. Their model also uses a modified maximum packing fraction that is associated with the stepwise addition of each size class and is computed based on excluded volume arguments. However, like the Furnas maximum packing model [6], this model is currently limited to suspensions with large size differences between successive classes. A unique additional contribution of this work is the matched asymptotic expansion to a generalized viscosity correlation that allows one to arbitrarily choose the second order Taylor coefficient (Huggins coefficient), in addition to satisfying the Einstein limit. This provides an additional flexibility to account for different interparticle interactions present in real systems and introduces an interesting paradigm to systematize the analysis of viscosity measurements across a wide variety of systems.

Mooney [8] presented an alternative to the maximum packing fraction models by using a "crowding factor" to describe the effect of adding particles to a Newtonian medium. Using symmetry arguments as constraints, he derived an expression to describe the suspension viscosity taking into account explicitly the contributions of each size class. This was essentially a renormalization of the Einstein dilute limit result to describe the relative viscosity in a monodisperse suspension through an exponential function of the volume fraction. However, instead of the  $2.5\phi$  dependence [2], the effective volume fraction is increased up to  $2.5\phi/(1-k\phi)$ , where k is a crowding factor that is chosen to represent concentration effects in monodisperse suspensions. For polydisperse suspensions, Mooney postulated a dependence of the crowding factor on the relative particle sizes. Finally, the total suspension viscosity is calculated from multiplicative contributions from each size class. Even though Mooney alluded to the extension of his approach to polydisperse suspensions, he never completely addressed this aspect in the original publication. Following Mooney's work, Farr [13] extended the original approach with two main contributions. First, he proposed a model for how the crowding factor depends on size ratios for arbitrary size distributions, completing an important aspect of Mooney's original idea. Second, Farr allowed for additional complexity in the modeling of the suspension viscosity by including a "dispersity effect" to account for the heterogeneity of particle interactions in a polydisperse suspension, therefore introducing more flexibility to allow for better fits to experimental data. Faroughi and Huber [25] have also recently described a theoretical argument for a crowdingbased rheological model for binary suspensions. They establish the crowding effect as the reduction in the "dead fluid volume" that is associated with a given level of packing, and are able to show good agreement with experimental data.

Farris [9] described another alternative theoretical approach toward calculating the effect of polydispersity on the suspension viscosity. His model was motivated by previous work on sedimentation in binary suspensions [26] where the large particles, in the presence of much smaller particles, are observed to behave in a manner that suggests that they are interacting with an effective Newtonian viscosity corresponding to a suspension of the smaller particles. The total suspension viscosity is computed as a product of the relative viscosity of the large particles multiplied by an effective viscosity of the renormalized medium. The attractive feature of this approach is that it provides a methodology toward constructing the viscosity of a polydisperse suspension of particles by explicitly considering the effect of each particle size class during the viscosity calculation. However, it is currently limited to suspensions with large size differences between successive particle size classes. Although Farris demonstrated the possibility of introducing crowding factors to extend his model applicability to systems with arbitrary size distributions, no systematic methodology was provided to achieve this, leaving this modeling approach incomplete.

In our work, a modification and extension of the Farris approach is presented. As in the original approach, we start by requiring the relative viscosity of the monodisperse suspension to be a function of volume fraction represented by one of the many empirical formulae available, depending on the nature of the suspension. In a monodisperse suspension, the relative viscosity incorporates the additional effect of the particles on the suspending medium. With two differently sized particles, i.e., a bimodal suspension, the definition of the relative viscosity may be extended by renormalizing the effect of the smaller particles as contributing toward changing the medium as well as the larger particles through appropriate weighting functions. More specifically, upon addition of larger particles to a suspension, the weighting functions relegate a fraction of the already present smaller particles to interact directly with the added particle volume fraction, with the remaining fraction contributing toward increasing the effective background viscosity. A key element of our approach is the use of formulae that by construction preserve the consistency of the model for all possible limiting cases. Still these constraints are not sufficient to uniquely define the weighting function. Thus, by necessity, the weighting function involves fitting parameters that need to be determined empirically. This can be achieved using theoretical results as well as experimental and/or simulation data on binary suspensions. Once parameterized based on binary viscosity data, our model can predict the viscosity of suspensions containing particles with multiple sizes, e.g., ternary suspensions. The success of such an approach here indicates the power of linking the complex behavior of systems to that of known limiting cases and then systematically interpolating in a consistent fashion based on a limited set of empirical parameters. This is an especially useful first approach when faced with complex systems for which there is little guidance from first principles theory on how to develop a comprehensive model of the phenomena to be described.

The rest of the paper is organized as follows: in Sec. II, we present the relevant theory (model development) for binary and ternary suspensions, as well as the details of its implementation to polydisperse suspensions. In Sec. III, we describe the parametrization of the model based on theoretical calculations of the Huggins coefficient by Wagner and Woutersen [18]. In the same section, we also show how the model can be parameterized based on experimental viscosity data of a binary suspension. In Sec. IV, we validate the model by comparing its predictions for binary suspension viscosities against those obtained with recent alternative models from the literature. In Sec. V, we develop predictions of the viscosity of polydisperse suspensions, we compare them against available experimental data, and we demonstrate their insensitivity to the details of the implementation. Finally, our conclusions follow in Sec. VI.

#### II. MODEL DEVELOPMENT

#### A. Proposed approach and underlying physical picture

The general framework within which we have developed our viscosity model assumes the presence within the suspension of multiple particle size classes, with the viscous effects attributable to hydrodynamic interactions only. Therefore, strictly speaking, the model is currently limited to ideal noncolloidal as well as colloidal suspensions in the plateau viscosity region at high shear rates (or Peclet numbers). Similar to the maximum packing fraction models, the starting point of the proposed constitutive equation is provided by the relative viscosity relationship of a monodisperse suspension. A number of such empirical and semiempirical relationships exist [19,20,27,28]. For example, Singh and Nott [29] fit the volume fraction  $\phi$  dependence of the shear viscosity  $\eta_r$  from measurements on noncolloidal suspensions using Eilers' equation

$$\eta_r = \left[1 + 1.5\phi \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^{-1}\right]^2, \tag{1}$$

with  $\phi_{\text{max}} = 0.58$ . Owing to differences seen in the monodisperse viscosities of real noncolloidal suspensions in experiments, one must admit some flexibility in the choice of the functional form of  $\eta_r$  as needed for practical applications. Once selected, the particular relative viscosity model, e.g., Eq. (1), can then be used to define a hydrodynamic function for a single-size particle suspension,  $f_u$ , as

$$\eta_r \equiv \exp(f_u). \tag{2}$$

Through this definition, the Farris model [9] can now be recast using the formalism of hydrodynamic functions.

The original approach used by Farris [9] to calculate binary suspension viscosity assumed that the smallest particles act to change the effective suspending medium in which the larger particles exist. Mathematically, we can define a binary hydrodynamic function,  $f_{bi,Farris}$ , to represent Farris' approach as

$$f_{bi,Farris} \equiv f_u(\phi_L) + f_u(\phi_S), \tag{3}$$

where

$$\phi_{S} = \frac{(1-w)\phi_{d}}{(1-\phi_{D}-w\phi_{d})}, \quad \phi_{L} = w\phi_{d} + \phi_{D}.$$
 (4)

The subscripts d and D denote the small and large particle diameters, respectively, in the suspension and w is a suitable weight function that depends on the relative size ratio, d/D. In Eq. (3),  $\phi_L$  and  $\phi_S$  are intermediate variables that represent adjusted volume fractions of the large and small particles, respectively. They are calculated from the true volume fractions,  $\phi_d$  and  $\phi_D$ , of the small and large particles, respectively, as described in Eq. (4). The total volume fraction  $\phi$  is computed from the sum of  $\phi_d$  and  $\phi_D$ . In Eq. (3),  $f_{bi,Farris}$  describes the effective hydrodynamic effect in a binary suspension. Farris [9] primarily discussed the case where w = 0. This represents the limit of large differences between the two particle size classes, i.e.,  $d/D \ll 1$ . The separation of length scales in such a suspension implies a sizeindependent interaction where the larger particles simply feel an increased apparent viscosity due to the smaller particles. Therefore, the viscosity in such a suspension can be described based on excluded volume arguments alone [9]. The equivalent calculation of the viscosity of a binary suspension as described by Farris [9] in terms of the binary hydrodynamic function is given by

$$\eta_{r,Farris} = \exp(f_{bi,Farris}). \tag{5}$$

Although Farris [9] postulated that the weighting function w appearing in Eq. (4) could be generalized to represent

suspensions in which the separation of length scales is not very large, he did not provide a methodology to do so. In this work, we present an alternative formulation and systematically develop a viscosity model that is applicable to suspensions with arbitrary separation of scales, as well as polydisperse and continuous PSDs. The starting point of this approach is to define a binary hydrodynamic function,  $f_{bi}$ , to be generalized in Sec. II C, which we propose is given by

$$f_{bi} = \underbrace{f_u(\beta\phi_d + \phi_D)}_A + \underbrace{f_u(\phi_d)(1-\beta)}_B,\tag{6}$$

where  $\beta$  is a weighting function that is assumed to depend on both the relative size ratio (d/D) and composition  $(\phi_d/\phi_D)$  of the binary suspension. The splitting in Eq. (6) takes into account the dual role of adding small particles to a suspension of larger particles and is justified as follows. The weighting function, defined by  $0 \le \beta \le 1$ , recognizes the fact that we can add smaller particles to a suspension of larger particles such that they take up the remaining free volume available to the larger particles,  $\phi_{max} - \phi_D$ , as well as some of the excluded volume of the larger particles,  $1 - \phi_{max}$ . This is the physical origin of the A term  $f(\phi_D + \beta \phi_d)$ . On the other hand, the B term,  $f(\phi_d)(1-\beta)$ , accounts for the enhanced local dissipation arising from the inclusion of smaller particles into the excluded volume of the larger particles. The essence of this approach is summarized in Fig. 1 for the case of a binary suspension. The viscosity of the binary suspension is then calculated from

$$\eta_{r,bi} = \exp(f_{bi}). \tag{7}$$

This exponential multiplicative formula is reminiscent of the multiplicative rule suggested by Qi and Tanner [11] in their model.

At the heart of this model is the weighting function,  $\beta$ , that accounts for the twofold effect of the smaller particles in (a) increasing the effective volume fraction of the larger particles [term A in Eq. (6)] and in (b) enhancing the overall



**FIG. 1.** Schematic to help visualize the modeling approach followed to describe the effects of polydispersity on the viscosity of a suspension illustrated here in the particular application to a binary suspension. The real binary suspension (far left) is mapped to a renormalized monodisperse suspension (far right) involving a medium with an effective relative viscosity exp  $(f_u(\phi_d)(1 - \beta))$  (shaded background) and solid particles of an effective volume fraction of  $\beta \phi_d + \phi_D$  (shaded large circles).

background viscosity [term B in Eq. (6)]. Therefore, the development of an appropriate form of the weighting function is the focus of Sec. II B.

#### B. Model development for binary suspensions

The success of the proposed model depends on careful selection of the weighting function. This selection is guided by observations from experimental measurements of the viscosity in binary suspensions from literature [10,15,30]. The only constraints explicitly considered in the selection of the weighting function are those originating from the ability to recover characteristic limiting behaviors. More specifically, a binary suspension behaves like a monodisperse suspension under certain limiting conditions of relative size and composition of the constituent particles. Therefore, the binary hydrodynamic function  $f_{bi}$ , described in Eq. (6) must fulfill the four key limits outlined below:

$$\lim_{d/D \to 0} f_{bi} = f_u(\phi_D) + f_u(\phi_d) \quad \lim_{d/D \to 1} f_{bi} = f_u(\phi_d + \phi_D),$$
$$\lim_{\phi_D \to 0} f_{bi} = f_u(\phi_d) \qquad \lim_{\phi_d \to 0} f_{bi} = f_u(\phi_D).$$
(8)

Consequently, from the definition of  $f_{bi}$  in Eq. (6), the weighting function,  $\beta \equiv \beta(d/D, \phi_d/\phi_D)$ , for a binary suspension consisting of small particles  $(d, \phi_d)$  and large particles  $(D, \phi_D)$  must obey the following limits:

$$\lim_{d/D\to 0} \beta\left(d/D, \frac{\phi_d}{\phi_D}\right) = 0 \qquad \lim_{d/D\to 1} \beta\left(d/D, \frac{\phi_d}{\phi_D}\right) = 1,$$
$$\lim_{\phi_d/\phi_D\to\infty} \beta\left(d/D, \frac{\phi_d}{\phi_D}\right) = 1 \quad \lim_{\phi_d/\phi_D\to0} \beta\left(d/D, \frac{\phi_d}{\phi_D}\right) = \text{constant.}$$
(9)

A versatile and useful form of the weighting function  $\beta$  that satisfies the above limits is given by a power law

$$\beta \equiv [g(d/D)]^{h(\phi_d/\phi_D)} = g^{h(\phi_d/\phi_D)},$$
(10)

where the exponent, *h*, is assumed to depend only on the particle volume fraction ratio,  $\phi_d/\phi_D$ , and the base, *g*, on the particle size ratio, d/D. These can therefore be interpreted to represent an effective volume fraction ratio and an effective size ratio, respectively. For consistency with the limiting behavior of the weighting function given in Eq. (9), the functional forms of g(d/D) and  $h(\phi_d/\phi_D)$  must, at a minimum, obey the following limiting behaviors:

$$\lim_{d/D \to 0} g(d/D) = 0,$$

$$\lim_{d/D \to 1} g(d/D) = 1,$$

$$\lim_{\phi_d/\phi_D \to 0} h\left(\frac{\phi_d}{\phi_D}\right) = 1,$$

$$\lim_{\phi_d/\phi_D \to \infty} h\left(\frac{\phi_d}{\phi_D}\right) = 0.$$
(11)

It should be noted that the third limit in Eq. (11) can be any constant, but by selecting it to be a specific fixed value (1 is chosen for simplicity), we can uniquely define the g and h functions.

The particular functional form of the weighting function in Eq. (10) is chosen for convenience, in order to facilitate the extension of the model to multimodal and polydisperse suspensions (see Secs. II C and II D). In addition, the form of Eq. (10) allows us to separate the effects of relative size (d/D) and composition  $(\phi_d/\phi_D)$  on the viscosity of a binary suspension. This assertion will be justified later on in this section. For the effective volume fraction ratio, we shall assume

$$h\left(\frac{\phi_d}{\phi_D}\right) = \left(1 - \frac{\kappa\phi_d}{\kappa\phi_d + \phi_D}\right),\tag{12}$$

where the parameter  $\kappa$  plays a similar role to the crowding factor in Mooney's [8] viscosity expression. More sophisticated mixing rules are possible by allowing additional complexity (more parameters) in the functional form of  $h(\phi_d/\phi_D)$ . On the other hand, the yet to be determined effective particle size ratio, g, accounts for all the dependence of the viscosity on the relative size ratio, d/D. Various approaches to determine the relationship between g and d/Dwill be discussed in Sec. III.

A key implied property in the form of the weighting function in Eq. (10) is the decoupling of the effects of relative size and composition on the overall viscosity of a binary suspension. Therefore, it is important to show that the parameter  $\kappa$ appearing in Eq. (12) primarily controls the occurrence of the viscosity minimum. This is demonstrated by using the Krieger–Dougherty viscosity relationship [21] given by

$$\eta_r = \left(1 - \frac{\phi}{\phi_{\max}}\right)^{-2.5\phi_{\max}},\tag{13}$$

where the maximum packing fraction,  $\phi_{\text{max}}$ , is assumed to be random close the packing limit (0.64). This expression is used to define the monodisperse hydrodynamic function in Eq. (2). The occurrence of the viscosity minimum in a binary suspension can be calculated from the first derivative of the binary hydrodynamic function in Eq. (6) with respect to the fraction (by volume) of small particles in the suspension,  $\chi = \phi_d/(\phi_d + \phi_D)$ . This is expressed as

$$\left. \frac{\partial f_{bi}}{\partial \chi} \right|_{\chi_{\min}} = 0, \tag{14}$$

where  $\chi_{\min}$  represents the solid volume fraction of small particles in the total solids loading at which the viscosity minimum is observed. Using Eqs. (2), (10), (12), and (13) to define  $f_{bi}$  in Eq. (6), the extremum condition represented by Eq. (14) can be written explicitly as

$$\phi\left(\frac{(\theta-1) + \alpha\chi_{\min}}{\phi\left(\chi_{\min}(\theta-1) + 1\right)} + \frac{1-\theta}{\phi\chi_{\min}-\phi_{\max}}\right) - \alpha\ln\left(1 - \frac{\chi_{\min}\phi}{\phi_{\max}}\right) = 0,$$
(15)

where

$$\alpha = \frac{d\beta}{d\chi}\Big|_{\chi_{\min}} = \frac{-\kappa \ln(g)\theta}{\left((\kappa - 1)\chi_{\min} + 1\right)^2}$$
(16)

and

$$\theta = g^{(1 - (\kappa \chi_{\min})/[\kappa \chi_{\min} + (1 - \chi_{\min})])}.$$
(17)

The behavior of Eq. (15) is now studied parametrically for two scenarios. In the first scenario, we consider the relationship between  $\chi_{\min}$  and g for various values of  $\kappa$  while holding the total volume fraction ( $\phi$ ) fixed. The results in Fig. 2 suggest that the position of the viscosity minimum is a strong function of  $\kappa$  and depends only weakly on the relative size ratio d/D. In the second scenario, the relationship between  $\chi_{\min}$  and g at fixed values of  $\kappa$  for various values of  $\phi$  is examined. The calculations, summarized in Fig. 2, also suggest that the occurrence of the viscosity minimum is only a weak function of  $\phi$ . Furthermore, for  $\kappa = 6$ , we observe that the value of  $\chi_{min}$  at which the viscosity minimum is seen lies between 0.25 and 0.35. This choice of  $\kappa$  is consistent with empirical observations where, for a fixed size ratio (d/D) and total solids loading  $(\phi)$ , the viscosity minimum is seen to occur when 25–35% of the total solid particles by volume are small [31]. This viscosity minimum is also observed in maximum packing fraction models for binary suspensions [32] as well as numerical experiments on sphere packing [33] where the largest attainable packing fraction, indicative of the viscosity minimum, is seen when approximately 30% of the spheres by volume are small.

The ability of the model to decouple the effects of size and composition in a binary suspension is demonstrated. This means that two pieces of information are needed to parametrize the model. The parameter  $\kappa$  may be chosen such that the viscosity minimum predicted by a specific viscosity model, e.g., Eq. (13) occurs over the desired composition range. On the other hand, the functional form of the effective size ratio, g, can be determined from measurements of binary



**FIG. 2.** A parametric study of the relationship between the minimum viscosity solid particle volume fraction,  $\chi_{min}$ , and the effective size ratio, *g*, defined by Eq. (15), at two different values of the parameter  $\kappa$  and at various total solids volume fractions,  $\phi$ .

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suspensions viscosity as a function of size ratio (see Sec. III). While the analysis presented in Eqs. (14)–(17) can be applied to any choice of the monodisperse viscosity correlation, the final closed forms solution may be more complex depending on the particular choices of  $\eta_r$  and  $h(\phi_d/\phi_D)$ . Therefore, in Sec. III,  $\kappa$  will be treated as an additional fitting parameter except when a Krieger–Dougherty viscosity relationship is used for  $\eta_r$  and/or data on the viscosity minimum are available.

#### C. Model extension to ternary suspensions

The ability to calculate the viscosity of a ternary suspension requires the development of an appropriate hydrodynamic function,  $f_{tri}$ , such that the viscosity of the ternary suspension is given by

$$\eta_{r,tri} = \exp(f_{tri}). \tag{18}$$

We achieve this by considering the effect of adding another larger size particle  $(DD \ge D)$  at volume fraction  $\phi_{DD}$ to an existing binary suspension of particle sizes d and  $D \ge d$ with corresponding volume fractions  $\phi_d$  and  $\phi_D$ . To be consistent,  $f_{tri}$  must reduce to the proper binary and monodisperse limits. The trimodal hydrodynamic function must therefore obey the following limits:

$$\lim_{d/D \to 1} f_{tri} = f_{bi} \qquad \lim_{d/DD \to 1} f_{tri} = f_{bi} \qquad \lim_{d/D, d/DD \to 1} f_{tri} = f_{u},$$

$$\lim_{\phi_{d} \to 0} f_{tri} = f_{bi} \qquad \lim_{\phi_{D} \to 0} f_{tri} = f_{bi} \qquad \lim_{\phi_{DD} \to 0} f_{tri} = f_{bi},$$

$$\lim_{\phi_{d}, \phi_{D} \to 0} f_{tri} = f_{u} \qquad \lim_{\phi_{D}, \phi_{DD} \to 0} f_{tri} = f_{u} \qquad \lim_{\phi_{d}, \phi_{DD} \to 0} f_{tri} = f_{u}.$$
(19)

Considering these limits, the binary hydrodynamic function from Eq. (6) is extended to develop an analogous expression for a ternary suspension of successive particle diameters d < D < DD and respective volume fractions  $\phi_d$ ,  $\phi_D$ , and  $\phi_{DD}$  given by

$$f_{tri} = f_u(\beta_2(\beta_1\phi_d + \phi_D) + \phi_{DD}) + f_u(\beta_1\phi_d + \phi_D) \\ \times (1 - \beta_2) + f_u(\phi_d)(1 - \beta_1).$$
(20)

The corresponding extended weighting functions,  $\beta_i$ , are given by

$$\beta_1 \equiv \beta \left( \frac{d}{\alpha^*}, \frac{\phi_d}{\phi_D + \phi_{DD}} \right) = \left[ g \left( \frac{d}{\alpha^*} \right) \right]^{h_1 \left( \phi_d / (\phi_D + \phi_{DD}) \right)}$$
(21)

and

$$\beta_2 \equiv \beta \left( \frac{\alpha^*}{DD}, \frac{\phi^*}{\phi_{DD}} \right) = \left[ g \left( \frac{\alpha^*}{DD} \right) \right]^{h_2(\phi^*/\phi_{DD})}$$
(22)

where

$$\alpha^{*} = \frac{\beta\left(\frac{d}{DD}, \frac{\phi_{d}}{\phi_{DD}}\right)\phi_{D}D + \left(1 - \beta\left(\frac{d}{DD}, \frac{\phi_{d}}{\phi_{DD}}\right)\right)(\phi_{d})d}{\beta\left(\frac{d}{DD}, \frac{\phi_{d}}{\phi_{DD}}\right)\phi_{D} + \left(1 - \beta\left(\frac{d}{DD}, \frac{\phi_{d}}{\phi_{DD}}\right)\right)(\phi_{d})},$$
(23)

$$\phi^* = \beta_1 \phi_d + \phi_D, \tag{24}$$

$$h_1\left(\frac{\phi_d}{\phi_D + \phi_{DD}}\right) = \left(1 - \frac{\kappa\phi_d}{\kappa\phi_d + \phi_D + \phi_{DD}}\right),\tag{25}$$

and

$$h_2\left(\frac{\phi^*}{\phi_{DD}}\right) = \left(1 - \frac{\kappa\phi^*}{\kappa\phi^* + \phi_{DD}}\right). \tag{26}$$

The functional forms of  $\beta_1$  and  $\beta_2$  in Eqs. (21) and (22) are similar to that defined for binary suspensions in Eq. (10). Although the set of expressions in Eqs. (21)–(26) appear to be more complex, they are strictly consistent with all known limits of monodisperse and binary suspensions. For example, by setting  $\phi_{DD}$  equal to 0 in these equations, we recover from Eq. (20) the binary hydrodynamic function in Eq. (6). Note that the formulae above only require information that can be obtained from bimodal data.

The model can be further extended to quaternary suspensions in a straightforward fashion as shown in the Appendix. Similarly, one can proceed in a recursive fashion, to extend the model to arbitrary multi-n-ary suspensions. However, the formulae are complex and, as will be argued shortly, unnecessary. Finally, it is noteworthy that the extended weighting functions described by Eqs. (21)–(26) (as well as Eqs. (A2) and (A3) for quaternary suspensions in the Appendix) incorporate the same parameters appearing in the weighting function defined for binary suspensions in Eqs. (10) and (12). This means that the ternary suspension model only requires binary suspension data to specify the form of the weighting function. This feature gives the model predictive power with respect to estimating the viscosity of ternary and polydisperse suspensions (see Sec. V).

## D. Implementation of the model to polydisperse suspensions

Suspensions of practical relevance such as coal slurries [34] are comprised of continuous size distributions<sup>1</sup> such that it is desirable to be able to predict the viscosity of such suspensions. One approach is to discretize the continuous size distribution and proceed with modeling it as a multi-nary distribution following the method outlined above. However, as we shall show, this is not necessary. Instead, it suffices to simply discretize the continuous PSD with a small but sufficient number of finite size classes in such a way as to fit the first few moments of the actual distribution. Wagner and Woutersen [18] proposed that just three particle size classes (or fitting the first six moments) are adequate to represent the rheological properties of a suspension with a continuous PSD. This means that a continuous size distribution can be described by an equivalent ternary suspension. Therefore, the ternary hydrodynamic function developed in

<sup>&</sup>lt;sup>1</sup>·Continuous size distributions as discussed here refers to single peaked distributions with relatively short tails.

Eq. (20) can be used to predict the viscosity in polydisperse suspensions.

The information to determine the equivalent ternary suspension first needs to be extracted from the volume-weighted continuous size distribution. The moments of the continuous distribution are defined by

$$m_k = \int_0^\infty R^k f_\nu(R) dR, \qquad (27)$$

where  $f_v(R)dR$  represents the normalized volume-weighted number density of noncolloidal particles with radii between sizes *R* and *R* + *dR* and *m<sub>k</sub>* is the *k*th moment of the distribution. The first six moments of the continuous volumeweighted size distribution ( $m_i$ ;  $0 \le i \le 5$ ) are then used to generate an equivalent ternary approximation based on the following equation:

$$m_k = \sum_{i=1}^3 \omega_i L_i^k, \tag{28}$$

where  $\omega_i$  and  $L_i$  are the *i*th weight and sizes of the equivalent ternary system, respectively. The relevant modeling information is then obtained from these weights and sizes using the following relationships:

$$\phi_d = \frac{\omega_1}{\sum\limits_{i=1}^3 \omega_i} \phi \quad \phi_D = \frac{\omega_2}{\sum\limits_{i=1}^3 \omega_i} \phi \quad \phi_{DD} = \frac{\omega_3}{\sum\limits_{i=1}^3 \omega_i} \phi, \quad (29)$$
$$d = L_1 \quad D = L_2 \quad DD = L_3. \quad (30)$$

In Eq. (29),  $\phi$  is the total solids volume fraction and *d*, *D*, and *DD* represent the small, medium, and large particles, respectively, in the system with  $\phi_d$ ,  $\phi_D$ , and  $\phi_{DD}$  being the respective volume fractions. Using the equivalent, but approximate, ternary representation of a continuous size distribution, all the variables appearing in Eqs. (20)–(26) can be defined based on Eqs. (27)–(30). The sensitivity of the model to the number of discrete size classes is examined in Sec. V to justify the six-moment approximation proposed for continuous size distributions in the context of the model developed in this work.

#### III. BINARY SUSPENSIONS: COMPARISONS AGAINST EXISTING THEORY AND EXPERIMENTS TO DETERMINE MODEL PARAMETERS

To develop the weighting function outlined in Eq. (10), the constituent functions representing the effective size ratio and effective volume ratio, g and h, respectively, must be specified. For the effective volume ratio (h) specified in Eq. (12), only the parameter  $\kappa$  needs to be specified. On the other hand, the effective size ratio (g) is an unknown function whose dependence on the size ratio (d/D) must be determined. In this section, we present a theoretical development of the effective size ratio (g) as well as an alternative empirical development based on experimental data on the viscosity of binary suspensions. To enable quantitative comparison with available experimental data, we further consider the maximum packing fraction as well as the monodisperse viscosity correlation as adjustable parameters to be fit to monodisperse viscosity data.

### A. Independent determination of model parameters

The ability to determine the model parameters from independent data allows for the development of a fully predictive viscosity model. This may be realized by fitting the weighting function to either theoretical results on dilute binary suspensions [18] or alternatively from simulation data like the 2D monolayer simulations [17]. Despite the inherent limitations in using either of these independent results on binary suspensions, for completion, we demonstrate how the model parameters can be developed based on the theory of dilute binary suspension viscosity outlined by Wagner and Woutersen [18]. This approach toward parameterizing the model also demonstrates the limiting behavior of the model in the dilute limit.

In dilute hard sphere colloidal suspensions, the Huggins coefficient accounts for pair interactions [35]. In practice, the Huggins coefficient is related to the  $\phi^2$  coefficient in the Taylor expansion of the viscosity with respect to the volume fraction

$$\eta_r = 1 + 2.5\phi + c_{\phi^2}\phi^2 + \dots \tag{31}$$

For the Krieger–Dougherty relationship in Eq. (13),  $c_{\phi^2}$  turns out to be equal to 5.0 for monodisperse particles if we assume  $\phi_{\text{max}} = 0.67$ . This is exactly the value computed by Wagner and Woutersen [18] for a random configuration of hydrodynamically interacting spheres. The corresponding measure for binary and polydisperse suspensions has also been determined for a random binary suspension of hydrodynamically interacting unequal spheres [18] as

$$c_{\phi^2} = 2.5 + \sum_{j=1}^{2} \sum_{i=1}^{2} \chi_i \chi_j I_H(\lambda_{ij}),$$
 (32)

where  $\chi_1$  and  $\chi_2$  represent the composition of small and large particles in the suspension with  $\chi_1 + \chi_2 = 1$  and  $\lambda_{ij} \equiv d_i/d_j$ .  $I_H(\lambda_{ij})$  accounts for the hydrodynamic pair interactions between spheres computed from previous theoretical results of Jeffrey's resistivities [18,36] and is defined to be equivalent upon  $\lambda_{ij} \rightarrow 1/\lambda_{ij}$  substitution. This symmetry means the viscosity minimum for a binary suspension occurs at equal volume fractions. Using our modeling approach, we calculate the binary suspension viscosity ( $\eta_{r,bi}$ ), as described in Sec. II, by assuming the Krieger–Dougherty relationship as the model for the monodisperse suspension viscosity. The Taylor expansion of  $\eta_{r,bi}$  as defined in Eq. (7) is then given by

$$\eta_{r,bi} = 1 + 2.5\phi + \frac{5}{4} \\ \times \left( \frac{\left(\chi_1(\beta(g,\chi_1) - 1) + 1\right)^2 + \chi_1^2(1 - \beta(g,\chi_1))}{\phi_{\max}} + \frac{5}{2} \right) \phi^2 \\ + O(\phi^3), \tag{33}$$

where

$$\beta(g,\chi_1) = g^{(1 - \kappa \chi_1 / (\kappa \chi_1 + \chi_2))}.$$
(34)

By equating the expression for  $c_{\phi^2}$  provided by Eq. (32) and the  $\phi^2$  coefficient in Eq. (33), the relationship between the effective size ratio (g) and the actual size ratio (d/D) can be established once the parameter  $\kappa$  is determined. Following the procedure described in Sec. II B,  $\kappa$  is computed independently using Eqs. (15)–(17) together with the observation that the minimum in  $c_{\phi^2}$  always occurs at  $\chi_{1,\min}$  equal to 0.5 (see Fig. 4). The value of  $\kappa$  is determined to be 0.54. Subsequently, the effective size ratio values (g) that best parametrize the results of Wagner and Woutersen [18] (see Fig. 4) are extracted and are presented in Fig. 3. These can be fit to a power law given by

$$g = (d/D)^{0.18}.$$
 (35)

The full weighting function defined in Eqs. (10) and (12) corresponding to the effective size ratio provided by Eq. (35) is then given as

$$\beta = [g(d/D)]^{h(\phi_d/\phi_D)} = \left[ (d/D)^{0.18} \right]^{(1 - (0.54\phi_d/0.54\phi_d + \phi_D))}.$$
(36)

The comparison of  $c_{\phi^2}$  from the model based on this weighting function to the theoretical calculations of Wagner and Woutersen [18] is presented in Fig. 4.

The approach outlined in this section represents one way to determine the components of the weighting function, gand  $\kappa$ , that appear in the definition of the binary hydrodynamic function. The ability of the model to capture the semidilute behavior (the  $\phi^2$  coefficient) as provided by an alternative, first-principles, approach, provides some justification for the form of the weighting function used, as well as



**FIG. 3.** The empirically determined *g* function values and their dependence on (d/D) obtained by enforcing equality of Eq. (32) and the  $\phi^2$  coefficient in Eq. (33). Solid points represent *g* function values applied to generate the fits at the different size ratios (d/D) shown in Fig. 4. The solid line is a parameterization of the *g* function values obtained by fitting to a power law.



**FIG. 4.** Comparison of calculations of the  $\phi^2$  coefficient following the theoretical results from Wagner and Woutersen [18] (symbols: d/D = 1 (**I**), d/D = 1/1.6 (**•**), d/D = 1/2 (**•**), d/D = 1/5 (**•**), and d/D = 1/10 (**★**) and the calculations from the model (lines) using Eqs. (33) and (36).

the definition of the bimodal hydrodynamic function. However, it should be noted that the theoretical results from Wagner and Woutersen [18] assume that the particle configurations are determined by Brownian motion with weak shear flow. This is not necessarily true for suspensions under flow, even if one starts from a random configuration [17,31,37]. For example, Chang and Powell [17] reported formation of clusters of large and small particles in simulations of non-Brownian binary sphere suspensions despite starting from a random configuration of particles. Furthermore, these results are rigorously valid only for pair interactions. Therefore, alternative, necessarily empirical, weighting functions must be developed to reflect typical microstructures that develop in real concentrated noncolloidal suspensions. In Sec. III B, we discuss how to develop such empirical weighting functions based on experimental data on the viscosity of binary suspensions.

#### B. Empirical determination of model parameters

The evaluation of the weighting function defined by Eq. (10) can proceed in two ways depending on the available data. Like Sec. III A, if the relative viscosity as a function of the composition of small particles  $(\chi_1)$  is known and displays a viscosity minimum at  $\chi_{1,\min}$ , then an approach analogous to that described in Eqs. (13)-(17) (Sec. IIB) may be used to independently determine  $\kappa$ . Subsequently, the relationship between g and d/D can be estimated by fitting the viscosity model to binary suspension viscosity at different d/D ratios. Otherwise, if such data are not available,  $\kappa$  should be considered as a fitting parameter, together with g, to be determined from the binary suspension viscosity data. Therefore, the minimum required information to independently parameterize the model are binary suspension viscosity data taken over multiple d/D ratios. In this section, the latter approach is used to determine the weighting function.

The following methodology was used to fit the parameters. First, an appropriate monodisperse viscosity relationship, such as Eq. (1), specific to the particular system, needs to be selected such that it best describes the monodisperse suspension viscosity. The next step is to determine the empirical weighting function. For this section, we limit ourselves to the simple expression for *h* that involves a single parameter  $\kappa$  [see Eq. (12)]. As such, for a selected  $\kappa$  value, we fit the corresponding *g* for any given d/D ratio so that the error is minimized. This procedure is repeated iteratively until the overall relative error between the calculated viscosities from Eq. (7) and the experimental binary viscosities is minimized. At the end of the fitting process, there are as many *g* values as there are d/D ratios and a single  $\kappa$  value. Finally, a parametrization for *g* vs d/D is developed, enabling interpolation for arbitrary effective size ratios.

The experiments by Chong *et al.* [10] on binary suspensions of glass spheres are taken as a model system to develop an alternative set of model parameters based on the procedure described above. Chong *et al.* [10] reported that the relative viscosities of the monodisperse systems that were ultimately blended to form the binary suspensions displayed relative viscosities independent of size and temperature, depending only on the total solids fraction. This suggests that the system is a reasonable representation of an ideal, noncolloidal suspension. The viscosity correlation from Morris and Boulay [27] used to define the monodisperse viscosity of the experiments by Chong *et al.* [10] is given by

$$\eta_r = 1 + 2.5\phi(1 - \phi/\phi_{\max})^{-1} + m(\phi/\phi_{\max})^2(1 - \phi/\phi_{\max})^{-2}.$$
(37)

The parameters m = 0.41 and  $\phi_{\text{max}} = 0.607$  are determined by fitting the monodisperse viscosity data from Chong *et al.* [10]. Subsequently, the binary hydrodynamic function is defined and the parameter  $\kappa$  and relative size ratio g are obtained by fitting the model to the experimental data using Eqs. (2), (6), (7), (10), and (12). The resulting fitting parameter  $\kappa$  is estimated to be 2.46 and the effective size ratio, g,



**FIG. 5.** The effective size ratio (g) as a function of relative size ratio (d/D) from fitting the viscosity model to experimental data by Chong *et al.* [10]. The solid points represent the g values that were used to fit the experimental results in Fig. 6. The solid line represents the parameterization of the g values. For comparison, the dotted line [Eq. (35)] is the effective size ratio from the dilute limit parametrization.

that best describes the experimental data, shown in Fig. 5, is given by

$$g = \left(1 - \left(1 - d/D\right)^{3.24}\right)^{1.91}$$
. (38)

The overall weighting function is then given by

$$\beta = [g(d/D)]^{h(\phi_d/\phi_D)}$$
$$= \left[ \left( 1 - (1 - d/D)^{3.24} \right)^{1.91} \right]^{(1 - (2.46\phi_d/2.46\phi_d + \phi_D))}.$$
 (39)

The associated model fit and comparison to the binary suspension viscosity data of Chong *et al.* [10] are presented in Fig. 6.

The effective size ratio (g) and the parameter  $(\kappa)$  determined from the experimental data are different from those determined from the theoretical results in Sec. III A. The observed differences in parameters arising from the two approaches can be attributed to the different microstructures that govern the rheological behavior of the two systems as well as differences in hydrodynamic interactions in the dilute and concentrated regimes. Therefore, for practical application of this model, flexibility should be allowed by choosing the weighting function to reflect such effects as well as the additional complexity that is encountered in real systems caused by particle interactions and inhomogeneous particle configurations.

#### IV. COMPARISON TO EXISTING MODELS IN LITERATURE

In this section, the binary suspension viscosity model developed based on the weighting function in Eq. (39) is compared to a model developed by Qi and Tanner [11]. The latter model is parameterized based on experiments by



**FIG. 6.** Relative viscosity as a function of total volume fraction. Viscosity model fit (solid lines) are compared to simulation data from Chong *et al.* [10] for different particle size ratio (d/D). The fraction of small spheres  $(\chi_1)$  is fixed at 0.25 for binary all cases. Monodisperse, d/D = 1 (**I**); Binary suspensions: d/D = 0.477 (**O**), d/D = 0.313 (**A**), and d/D = 0.138 (**★**).

Chang and Powell [16] on binary suspensions. Also included is a comparison against the results obtained from a model for binary suspension recently developed by Farr [13]. For consistency with the work of Qi and Tanner [11], we also use the same viscosity expression by Mendoza and Santamaria-Holek [38] in Eq. (40) to define the monodisperse hydrodynamic function.

$$\eta_r(\phi) = \left(1 - \frac{\phi}{1 - c\phi}\right)^{-5/2},\tag{40}$$

where c is given by

$$c = \frac{1 - 0.639}{0.639}.\tag{41}$$

These expressions together with the weighting function developed in Eq. (39) are used to calculate the binary suspension viscosity. The model developed by Farr [13] has its own viscosity relationship and is used as-is.

A comparison of these three models is presented in Fig. 7. In the same figure, the three models are also compared against experimental data by Chang and Powell [16] and Chong *et al.* [10]. The best fit to the experimental data is provided by the model of Qi and Tanner [11] the model by Farr [13] has the poorest fit. Therefore, our model compares favorably to existing works in the literature, in relation to the desired complexity. Although our model appears to capture the trends in the data by Chang and Powell [16] and Chong et al. [11] qualitatively, it does not capture all the details such as the asymmetry seen at higher volume fractions. By admitting extra complexity in the interpolating functions used in our model, a much better representation of the experimental data is possible. Indeed, a significant improvement can be obtained by defining the weighting function,  $\beta = g^h$ , using



**FIG. 7.** Relative viscosity as a function of the fraction of small particles in the suspension. Comparison of calculated viscosity from model of Qi and Tanner [11] (dotted line) to predictions from our model (solid lines) and Farr's model (dashed lines). Blue ( $\bullet$ ) and black ( $\bigcirc$ ) symbols correspond to data from Chang and Powell [16]. The red ( $\blacksquare$ ) symbols correspond to data from Chong *et al.* [10]. (1), (2), and (3) represent the viscosities calculated corresponding to the experimental conditions given by the circle, triangle, and square symbols, respectively, for the three models.

$$g = \left(1 - (1 - d/D)^{0.9}\right)^{1.41} \tag{42}$$

and

$$h = \left(1.68 \left(\frac{\phi_d}{\phi_d + \phi_D}\right)^2 - 2.01 \left(\frac{\phi_d}{\phi_d + \phi_D}\right) + 1\right) \times \left(1 - \frac{2.5\phi_d}{2.5\phi_d + \phi_D}\right).$$
(43)

The viscosities calculated using Eqs. (42) and (43) for weighting function together with Eq. (40) are presented in Fig. 8 along with a comparison against the Chang and Powell [16] data as well as the model predictions of Qi and Tanner [11]. The agreement of our model with both is good. Therefore, it is clear that by modifying the weighting function, while still keeping the basic structure of the original equations, a rich variety of suspension viscosity behavior can be obtained. Furthermore, the newly defined weighting function still enjoys all the original properties of the model, i.e., all the limits are fully obeyed.

#### V. PREDICTING THE VISCOSITY OF POLYDISPERSE SUSPENSIONS: RESULTS AND DISCUSSION

In this section, the ternary viscosity model developed in Sec. II C is applied to predict the viscosity of several suspensions characterized by continuous polydispersity using the framework outlined in Sec. II D. As an empirical approach, to obtain quantitative predictions using our model, we allow for flexibility in the choice of the monodisperse viscosity relationship  $\eta_r$  to reflect system specific nonidealities. In the first set of viscosity predictions for coal slurries [39], owing to lack of experimental data on the monodisperse viscosity,  $\eta_r$  is selected based on experimental results on monodisperse



**FIG. 8.** Comparison of calculated viscosity from model of Qi and Tanner [11] (dotted line) and our model using weighting functions defined by Eqs. (42) and (43) (solid line). Blue ( $\bullet$ ) and black ( $\bigcirc$ ) symbols correspond to data from Chang and Powell [16]. The red ( $\blacksquare$ ) symbols correspond to data from Chong *et al.* [10].

noncolloidal suspensions by Singh and Nott [29], which we assume accounts for any shape irregularities. In the second application, we use an alternative expression that is consistent with the experimental results of Probstein *et al.* [40]. In both cases, the weighting function previously developed in Eq. (39) is used. The assumption that a continuous size distribution may be represented by an equivalent ternary suspension, as explained in Sec. II D, is also validated.

#### A. Coal slurry application

The first application involves a coal slurry studied by Papachristodoulou and Trass [39]. The volume-weighted cumulative PSD for this system has been characterized and may be approximated by a Rosin–Rammler distribution [34,41] defined by

$$F(x) = 1 - \exp\left[-0.693 \left(\frac{x}{D_{50}}\right)^{\lambda}\right],\tag{44}$$

with a median size  $(D_{50})$  of 37  $\mu$ m and  $\lambda$  equal to 1.6, as shown in Fig. 9. The volume fractions are calculated using the density of bituminous coal, which is  $1346 \text{ kg m}^{-3}$ , and that of the light # 6 oil, which was reported to be  $978 \text{ kg m}^{-3}$ by Papachristodoulou and Trass [39]. Because coal slurries typically behave like Bingham fluids at high solid loadings, special care should be taken because of the presence of a yield stress. The yield stress should be subtracted off from the rheological measurements such that we model only the Bingham viscosity. Papachristodoulou and Trass [39] reported the Bingham viscosities, derived by fitting the rheological data to a Bingham equation and therefore, in principle, accounted for the yield stress effect discussed above. Therefore, the experimental viscosities reported in Fig. 10 that are compared with the model predictions are the relative Bingham plastic viscosities. The monodisperse viscosity correlation in Eq. (1) with  $\phi_{\text{max}} = 0.58$  [29] is taken to represent an ideal, noncolloidal coal slurry. Using this information



**FIG. 9.** Cumulative size distribution of a coal slurry. The experimentally measured PSD for a coal slurry from Papachristodoulou and Trass [40] is fit to a Rosin–Rammler cumulative size distribution with a median size of  $37 \,\mu\text{m}$ . The bar charts in the background represent the three mode approximation of the continuous size distribution obtained using Eqs. (27)–(30).



**FIG. 10.** Relative viscosity as a function of the volume fraction of coal particles in a coal slurry. Comparison of predictions from our model (solid line) to experimental data for coal slurry with a Rosin–Rammler distribution from Papachristodoulou and Trass [40].

together with Eq. (39) for the weighting function allows for the prediction of the viscosity of the coal slurry with the PSD given in Fig. 9. The model predictions agree well with the experimental measurements providing validation of the approach taken in deriving the model as well as the size moment truncation of the continuous size distribution.

A convergence study is now presented in order to justify the choice of the six moment truncation (trimodal approximation) applied to model the viscosity of polydisperse suspensions as presented in this work. For this, a comparison of various approximations up to the eight moment approximation (quaternary approximation—see the Appendix) of the coal size distribution in Fig. 9 is presented in Fig. 11. The results show that by the six-moment (ternary) approximation the results have essentially converged and indicate that three moment approximation is a sufficient representation for a continuous PSD. Ultimately, the level of approximation is a matter of choice and any level of approximation can be easily included into the model by systematically extending the hydrodynamic functions to incorporate more size classes.

#### B. Distributed particle sizes application

The second application tests the sensitivity of this model to different PSDs. Probstein *et al.* [40] performed rheological measurements of the shear viscosity for polydisperse suspensions of noncolloidal particles with different size distributions. In particular, they examined a log-normal PSD as well as a uniform PSD, as shown in Fig. 12. The theoretical cumulative distributions fit to these two experimental PSDs are provided by a lognormal distributions with  $\mu = 4.58$  and  $\sigma = 0.36$  as

$$F(x) = \frac{1}{2} + \frac{1}{2} erf\left(\frac{\ln(x) - \mu}{\sqrt{2}\sigma}\right),$$
 (45)

and a uniform distribution with  $a = 36.95 \,\mu\text{m}$  and  $b = 215.46 \,\mu\text{m}$  as

$$F(x) = \frac{\ln(x) - \ln(a)}{\ln(b) - \ln(a)}.$$
(46)



**FIG. 11.** Study of the effect of the various moment approximations on the model predictions of the relative viscosity as a function of total solids loading. The viscosity predictions arising from the two-moment (monodisperse), four-moment (binary), six moment (ternary), and eight-moment (quaternary) approximations of the coal slurry PSD in Eq. (44).

These two distributions are illustrated in Fig. 12. Figure 13 illustrates the equivalent ternary representations of the two distributions.

The experimentally measured viscosities by Probstein *et al.* [40] from a log-normal PSD are seen to be consistently larger than those derived from a uniform PSD for a given total solids loading. The ability of the model to qualitatively and quantitatively reproduce this observation is now examined. Owing to the empirical nature of our viscosity model, an appropriate monodisperse viscosity relationship must be specified. To do this, we use the monodisperse viscosity relationship of Sengun and Probstein [42] with parameters selected such that the viscosity model is able to quantitatively fit the uniform distribution viscosity data (see Fig. 14) while keeping the same weighting function in Eq. (39). The resultant viscosity relationship, applicable for  $\phi > 0.25$  [42], is given by



**FIG. 12.** Comparison of the lognormal and uniform size distributions of the particles in the suspension fit to theoretical distribution in Eqs. (45) and (46), respectively. Experimental measurements from Probstein *et al.* [41].

$$\eta_r = 1 + 1.4 \left(\frac{3\pi}{8}\right) \left(\frac{\beta}{\beta+1}\right) \\ \times \left[\frac{3 + 4.5\beta + \beta^2}{\beta+1} - 3\left(\frac{\beta+1}{\beta}\right) \ln(\beta+1)\right], \quad (47)$$

where

$$\beta = \frac{(\phi/0.55)^{1/3}}{1 - (\phi/0.55)^{1/3}}.$$
(48)

Subsequently, we predict the lognormal distribution viscosity data using Eqs. (39) and (47). The results are summarized in Fig. 14. This example shows that the model quantitatively predicts the lognormal viscosity data and, therefore, can distinguish between closely related distributions. This outcome provides further validation of the modeling scheme adopted in this work and demonstrates its possible use for real engineering applications for which complete information on the system of interest is seldom available. In this specific example, we specify the monodisperse viscosity correlation by requiring that it



FIG. 13. Comparison of the experimentally measured continuous PSDs, lognormal (left) and uniform (right), against their respective equivalent discrete ternary approximations.



**FIG. 14.** Comparison of model predictions of the lognormal distribution viscosity and corresponding experimental data. Predictions are calculated using Eq. (47), which is obtained by fitting the viscosity model to the uniform distribution data with Eq. (39) for the weighting function. Experimental results from Probstein *et al.* [41].

yields accurate fits to the uniform distribution data. However, in general, one may use any of the viscosity correlations for noncolloidal suspensions available in the literature. In such case, the qualitative trends will be certainly preserved, but the quantitative agreement is not guaranteed (see Supplementary Material [43]).

#### **VI. CONCLUSIONS**

In this work, we have presented the development of a new self-consistent model to describe the effects of polydispersity on the viscosity of noncolloidal, hard sphere suspensions. The elements of the model are the viscosity function for the monodisperse noncolloidal suspension  $(\eta_r)$  and the weighting function ( $\beta$ ), describing the effects of the size ratio (d/D) and the volume fraction ratio  $(\phi_d/\phi_D)$  in a binary suspension. The success of the model is in separating these two effects through two different functions g(d/D) and  $h(\phi_d/\phi_D)$  such that  $\beta \equiv [g(d/D)]^{h(\phi_d/\phi_D)}$ . At a minimum, each of the constituent functions, g and h, contains a single parameter that can be estimated from binary suspension viscosity data. We have demonstrated that by carefully selecting these constituent functions, the proposed model can fit a variety of binary suspension data as well as current existing (and more recent) models developed following other alternative approaches, such as the Qi and Tanner [11] model, which incorporates a maximum packing fraction, and the Farr model [13], which is based on the Mooney approach [11]. Finally, we note that the model is limited to polydisperse suspension in which the constituent particles do not exhibit size dependent rheological properties in the monodisperse limit, i.e.,  $\eta_r(\phi_d) = \eta_r(\phi_D) = \eta_r(\phi_{DD})$ .

The model developed in this work is also shown to quantitatively predict the viscosity of polydisperse suspensions of noncolloidal particles, based on parameters obtained solely from monodisperse and binary suspensions viscosity data. This is analogous to the approach of Renon and Prausnitz [44] to predict the excess Gibbs free energy of multicomponent mixtures from binary data alone. This useful result is made possible by first implementing a discretization of the smooth continuous distribution to its ternary equivalent, so that the first six moments are preserved, following the suggestion by Wagner and Woutersen [18]. Through a sensitivity analysis study, this approach has been demonstrated to be sufficient to describe the effects of polydispersity on suspension viscosity. Nevertheless, the approach presented in this work is not limited to ternary suspensions and formulae for higher order discrete suspensions can also be developed in a straightforward fashion, albeit there is a significant increase to their complexity. This may be necessary for studying the viscosity of more complex size distributions such as double-peaked size distributions.

The semiempirical model to describe the effect of polydispersity on the viscosity of noncolloidal suspensions presented in this work has been developed on the basis of accounting for purely hydrodynamic effects. However, to describe real suspensions one may also need to include other effects, such as friction [45]. Ultimately, some of these effects may be absorbed in the fitting parameters; however, others may need to be introduced explicitly by suitably modifying the model. For example, in the case of polymer-stabilized suspensions, one may consider improvements to account for the effective volume of the particles in the various size classes due to the presence of adsorbed polymer on the particle surface. In an alternative scenario, one may easily account for shear thinning behavior if the correlation between monodisperse suspension viscosity and shear rate is known. Other potential applications of the proposed model may include the determination of the ideal continuous PSD that results in the minimum viscosity, a problem that is of relevance to industrial processing. Furthermore, the proposed model may also be applied toward understanding the evolution of viscous stresses in aggregating suspensions that do not display a yield stress. Extensions to account for such aggregation effects can be easily incorporated by coupling the model developed in this work to a population balance equation using the method of moments [46,47]. In this way, the model has potential applications to an even wider class of problems of engineering relevance.

Note Added in Proof: The rule described by Eq. (6) for the binary hydrodynamic function is ad-hoc and phenomenological. Its main advantage is its relative simplicity. However, note that, as a result of its simplicity, it does not reduce to the Farris result even in the limit of large D/d particle size ratio when the weight w = 1 is known. Nevertheless, it can be shown that in practice, and therefore for finite D/d particle size ratios, it gives results that are very close provided that the parameter beta that enters Eq. (6) is suitably adjusted, following the rules stipulated by Eq. (9). This is exactly the practice followed here, thus justifying the use of Eq. (6) and explaining its success in all the examples used.

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#### APPENDIX: HYDRODYNAMIC FUNCTION FOR QUATERNARY DISTRIBUTIONS

The tetra-modal hydrodynamic function must fulfill the following limits:

$$\lim_{d/D \to 1} f_{quat} = f_{tri} \qquad \lim_{d/DD \to 1} f_{quat} = f_{tri} \qquad \lim_{DD/DDD \to 1} f_{quat} = f_{tri},$$

$$\lim_{d/DD,DD/DDD \to 1} f_{quat} = f_{bi} \qquad \lim_{d/D,D/DD \to 1} f_{quat} = f_{bi}$$

$$\lim_{d/D,D/DD,DD/DD \to 1} f_{quat} = f_{u}$$

$$\lim_{\phi_{a} \to 0} f_{quat} = f_{tri} \qquad \lim_{\phi_{D} \to 0} f_{quat} = f_{tri},$$

$$\lim_{\phi_{DD} \to 0} f_{quat} = f_{tri} \qquad \lim_{\phi_{D} \to 0} f_{quat} = f_{bi} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{tri},$$

$$\lim_{\phi_{DD} \to 0} f_{quat} = f_{bi} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi},$$

$$\lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi},$$

$$\lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi},$$

$$\lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{bi},$$

$$\lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{u} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{u} \qquad \lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{u}.$$

$$\lim_{\phi_{d,\phi_{DD} \to 0} 0} f_{quat} = f_{u}$$

The following expression, derived by extending the trimodal expression in Eq. (15) is given by

$$\begin{aligned} f_{quat} &= f_u (\beta_3 (\beta_2 (\beta_1 \phi_d + \phi_D) + \phi_{DD}) + \phi_{DDD}) + f_u (\beta_2 (\beta_1 \phi_d + \phi_D) + \phi_{DD}) (1 - \beta_3) \\ &+ f_u (\beta_1 \phi_d + \phi_D) (1 - \beta_2) + f_u (\phi_d) (1 - \beta_1), \end{aligned}$$
(A2)  
$$\beta_1 &= \beta \left( \frac{d}{\alpha^*}, \frac{\phi_d}{\phi_D + \phi_{DD}} \right) = \left[ g \left( \frac{d}{\alpha^*} \right) \right]^{h_1 \left[ \phi_d / (\phi_D + \phi_{DD} + \phi_{DD}) \right]}, \\ \beta_2 &= \beta \left( \frac{\alpha^*}{\alpha^{**}}, \frac{\phi^*}{\phi_{DD} + \phi_{DD}} \right) = \left[ g \left( \frac{\alpha^*}{\alpha^{**}} \right) \right]^{h_2 (\phi^* / \phi_{DD} + \phi_{DDD})}, \\ \beta_3 &= \beta \left( \frac{\alpha^{**}}{DDD}, \frac{\phi^{**}}{\phi_{DDD}} \right) = \left[ g \left( \frac{\alpha^{**}}{DDD} \right) \right]^{h_3 (\phi^{**} / \phi_{DDD})}, \end{aligned}$$

where

$$h_1 \left( \frac{\phi_d}{\phi_D + \phi_{DD} + \phi_{DD}} \right) = c \left( \frac{\phi_d}{\phi_D + \phi_{DD} + \phi_{DD}} \right) \left( 1 - \frac{m\phi_d}{m\phi_d + \phi_D + \phi_{DD} + \phi_{DD}} \right),$$

$$h_2 \left( \frac{\phi^*}{\phi_{DD} + \phi_{DDD}} \right) = c \left( \frac{\phi^*}{\phi_{DD} + \phi_{DDD}} \right) \left( 1 - \frac{m\phi^*}{m\phi^* + \phi_{DD} + \phi_{DDD}} \right),$$

$$h_3 \left( \frac{\phi^{**}}{\phi_{DDD}} \right) = c \left( \frac{\phi^{**}}{\phi_{DDD}} \right) \left( 1 - \frac{m\phi^{**}}{m\phi^{**} + \phi_{DDD}} \right),$$

$$a^* = \frac{\beta \left( \frac{d}{DD}, \frac{\phi_D}{\phi_{DD}} \right) \phi_D + \left( 1 - \beta \left( \frac{d}{DD}, \frac{\phi_D}{\phi_{DD}} \right) \right) (\phi_d) d}{\beta \left( \frac{d}{DD}, \frac{\phi_D}{\phi_{DD}} \right) \phi_D + \left( 1 - \beta \left( \frac{d}{DD}, \frac{\phi_D}{\phi_{DD}} \right) \right) (\phi_d),$$

$$\beta \left( \frac{d}{DD}, \frac{\phi_D}{\phi_{DD}} \right) = \left[ g \left( \frac{d}{DD} \right) \right]^{(1-m\phi_D/m\phi_D + \phi_{DD})},$$

$$a^{**} = \frac{\beta_{DD/DDD}\phi_{DD}DD + (1 - \beta_{DD/DDD}) (\phi_D)D}{\beta_{DD/DDD}\phi_{DD} + (1 - \beta_{DD/DDD}) (\phi_D)},$$

$$\beta \left( \frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DDD}} \right) = \left[ g \left( \frac{DD}{DDD} \right) \right]^{(1-m\phi_{DD}/m\phi_{DD} + \phi_{DDD})},$$

$$and$$

$$\phi^{**} = (\beta_2 (\beta_1 \phi_d + \phi_D) + \phi_{DD}).$$

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(A3)

Finally, the relative viscosity of the suspension is calculated as

$$\eta_r = \exp(f_{quat}). \tag{A4}$$

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