Submitted to the Journal of Rheology

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

Paul M. Mwasame, Norman J. Wagner, Antony N. Beris^{a)}

Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

Corresponding Author. Tel. 1- 302- 831-8018, E-mail address: beris@udel.edu

Synopsis

The present study develops an extension of the approach pioneered by Farris [T. 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 ratios 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.

Keywords: Viscosity model, Polydispersity, Noncolloidal suspension, Huggins coefficient, Moment approximation

^{a)} Author to whom correspondence should be addressed; email: <u>beris@udel.edu</u>

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 [Einstein (1906)]. Subsequent works on understanding higher order effects in more concentrated systems include the work of Batchelor (1970) and Happel and Brenner (1983). It is clear from experimental evidence that the total solids fraction is not the only factor affecting the rheological properties of suspensions [Jeffrey and Acrivos (1976)]. One key factor is particle size polydispersity which has immediate consequences in numerous industrial processes including the processing of slurries and in the food industry. In many applications it is important to determine the particle size distribution that minimize 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 [Furnas (1931), Ouchiyama and Tanaka (1984)] and more generally polydispersity effects on rheology [Mooney (1951), Farris (1968), Chong et al. (1971)] comprise a longstanding area of inquiry. Over the past few years, there has been renewed interest in modeling the effects of the particle size distribution on suspension viscosity. In particular, there have been a number of recent publications that have proposed alternative models to describe the effects of polydispersity on viscosity, including works by Qi and Tanner (2011), Dorr and Sadiki (2013) and Farr (2014).

Experimental measurements [Chong *et al.* (1971), Sweeny (1959), Poslinski *et al.* (1988), Chang and Powell (1994)] and simulation results [Chang and Powell (1993)] show that polydispersity induces significant changes in suspension rheology, when compared to monodisperse systems. For example, computer simulations by Chang and Powell (1993) starting from initially random configurations indicate that clusters of large and small particles are a plausible microstructural explanation for the changes in rheology observed in bidisperse systems. At the moment, no first principles theory is available to predict the effects of polydispersity except for certain limiting cases. More specifically, Wagner and Woutersen (1994) 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 [Mooney, (1951)] and the Farris approach [Farris (1968)].

From the theoretical point of view, there has always been an interest to evaluate the limit of flowability in dispersed systems [Furnas (1931), Ouchiyama and Tanaka (1984)] 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 [Chang and Powell (1994), Chong et al. (1971), Poslinski et al. (1988)]. In the first variant of this approach, the viscosity is assumed to obey any one of the empirical or semi-empirical viscosity correlations for monodisperse hard sphere suspensions [Eilers (1941), Maron and Pierce (1956), Krieger and Dougherty (1959)]. A review of these and other viscosity correlations is presented by Faroughi and Huber (2015). The auxiliary information on the particle size distribution (PSD) only enters into the calculation via a modification of the maximum packing fraction based on various models [Furnas (1931), Ouchiyama and Tanaka (1984), Sudduth (1993)]. Qi and Tanner (2011), identified shortcomings in the maximum packing model by Ouchiyama and Tanaka (1984). 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 (1931) is based on geometrical arguments and is inherently limited to large size differences only. 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 (2011, 2012) 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. (2013) who have developed an effective medium approach that considers the contribution of each size class to suspensions 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, unlike Qi and Tanner (2011,2012) 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 [Furnas (1931)], 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 additional flexibility to account for different inter-particle interactions present in real systems and introduces an interesting paradigm to systematize the analysis of viscosity measurements across a wide variety of systems.

Mooney (1951) presented an alternative to the maximum packing theoretical model for viscosity in suspensions by using a 'crowding factor'. 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 ϕ dependence, the effective volume fraction is increased

up to $\phi/1-k\phi$, where *k* is a crowding factor that is selected phenomenologically 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 (2014) 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 further 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 (2014) have also recently described a theoretical argument for a crowding-based 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 (1968) described an alternative theoretical approach towards calculating the effect of polydispersity on the suspension viscosity. His model was motivated by previous work on sedimentation in binary suspensions [Fidleris and Whitmore (1961)], 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. Under such conditions, he assumed there are no interactions between particles of different sizes. 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 towards 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. Next, a systematic methodology is developed to weight contributions from different size classes. On addition of a larger size particle 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 contributing towards increasing the effective background viscosity. A key element of our approach is to use formulae that by construction preserve the consistency of the model for all possible limiting cases. Still these constraints are not enough 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. This is analogous to the approach of Renon and Prausnitz (1968) to predict the excess Gibbs free energy of multicomponent mixtures from binary data alone. The success of such an approach here indicates the power of linking the complex behavior of systems to that of known limiting cases and of systematically interpolating it 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 Section II, we present the relevant theory and model development for binary and ternary suspensions, as well as the details of its implementation to polydisperse suspensions. In Section III we describe the parametrization of the model based on theoretical calculations of the Huggins coefficient by Wagner and Woutersen (1994). In the same section we also show how the model can be parameterized based on either numerical simulations of spherical particles on a monolayer or experimental viscosity data of a binary suspension. In Section IV, we validate the model by comparing its predictions of binary suspension viscosities against those obtained with recent alternative models from the literature. In Section V, we develop predictions of the viscosity of polydisperse suspensions, comparing them against available experimental data, and we demonstrate their insensitivity to the details of the implementation. Finally, our conclusions follow in Section 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, the model is currently limited to noncolloidal suspensions 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 monondisperse suspension. A number of such empirical and semi-empirical relationships exist [Eilers (1941), Maron and Pierce (1956), Morris and Boulay (1999), Zarraga *et al.* (2000)]. For example, Singh and Nott (2003) fit the volume fraction (ϕ) dependence of the shear viscosity (η_r) measurements in noncolloidal suspensions using Eiler's equation

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

with $\phi_{\text{max}} = 0.58$. The model for the viscosity of polydisperse suspensions developed in this work allows for flexibility in the choice of the functional form of η_r as needed for practical applications. The particular relative viscosity model chosen (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 [Farris (1968)] can now be recast using the formalism of hydrodynamic functions.

The original approach used by Farris (1968) to calculate binary suspension viscosity assumed that the smallest particles act to change the effective suspension medium in which the larger particles exist. Mathematically, we can define a binary hydrodynamic function, $f_{bi,Farris}$, to represent Farris' approach as

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

where

$$\phi_{S} = \frac{(1-w)\phi_{d}}{(1-\phi_{D}-w\phi_{d})} ,$$

$$\phi_{L} = w\phi_{d} + \phi_{D} .$$
(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*. The renormalized volume fractions of the respective particle sizes appearing in the arguments of the hydrodynamic functions are labelled as ϕ_d and ϕ_D for small and large particles respectively. The total volume fraction ϕ is computed

as the sum of these two quantities. ϕ_L and ϕ_S are intermediate variables that represent adjusted volume fractions of large (L) and small (S) particle contributions to the effective viscosity of the suspension. In Eq. (3), $f_{bi,Farris}$ describes the combined effective hydrodynamic effect in a binary suspension. Farris (1968) primarily discussed the case where *w*=0. This represents the limit of large differences between the two particle size classes i.e. d/D <<1. The separation of length scales in such a suspension implies that the large and small particles are non-interacting. Therefore, the viscosity in such a suspension can be described based on excluded volume arguments alone [Farris (1968)]. The equivalent calculation of the viscosity of a binary suspension as described by Farris (1968), in terms of the binary hydrodynamic function is given by

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

Although Farris (1968) 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 to systematically develop a viscosity model that is applicable to suspensions with arbitrary separation of scales, as well as polydisperse and continuous particle size distributions. The viscosity in such suspensions may be calculated in a recursive fashion. We start from the consideration of the smallest particle fraction, which is assumed to obey one of the monodisperse suspension viscosity rules such as provided by Eq. (1). The effect of the next larger in size particle fraction is then considered. During this construction step, a fraction (β) of the already existing small particles is assumed to interact with the added volume fraction of larger particles, resulting in an effective volume fraction of larger particles ($\beta\phi_d + \phi_D$). These are then assumed to exist in an effective medium whose hydrodynamic function is a fraction ($1-\beta$) of the hydrodynamic function evaluated considering only the smaller particles. This construction can be carried out repeatedly, adding larger and larger particle fractions to the suspension,

while renormalizing the volume fractions at each construction step with appropriate weighting function. The essence of this approach is summarized in Fig. 1 for a binary suspension, and can be represented quantitatively by a binary hydrodynamic function given by

$$f_{bi} = \underbrace{f_u\left(\beta\phi_d + \phi_D\right)}_{A} + \underbrace{f_u\left(\phi_d\right)\left(1 - \beta\right)}_{B},\tag{6}$$

where, β is a weighting function that is assumed to depend on both the relative size ratio (d/D) and composition (ϕ_d / ϕ_D) of the binary suspension. The viscosity of the binary suspension is then calculated from

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

At the heart of this model is the weighting function, β , that accounts for the two fold 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 background viscosity (term B in Eq. (6)). Therefore, the development of an appropriate form of the weighting function is the focus of the following section.



FIG. 1: An illustration of the construction steps to renormalize a binary suspension allowing for the calculation of the viscosity. The goal is to express the viscosity of the real binary suspension (far left) in terms of an effective renormalized suspension (far right) consisting of an effective medium (shaded background) and effective volume fraction (large circles).

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 [Chong *et al.* (1971), Poslinksi *et al.* (1988), Gondret and Petit (1997)]. 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 4 key limits outlined below

$$\lim_{\substack{d \\ D \to 0}} f_{bi} = f_u \left(\phi_D \right) \qquad \lim_{\substack{d \\ D \to 1}} f_{bi} = f_u \left(\phi_d \right) \qquad \lim_{\substack{d \\ D \to 1}} f_{bi} = f_u \left(\phi_D \right) \qquad (8)$$

$$\lim_{\phi_D \to 0} f_{bi} = f_u \left(\phi_D \right)$$

Consequently, from the definition of f_{bi} in Eq. (6), the weighting function, $\beta \equiv \beta \left(\frac{d}{D}, \frac{\phi_d}{\phi_D}\right)$, for a

binary suspension consisting of small particles (d, ϕ_d) and large particles (D, ϕ_D) must obey the following limits

$$\lim_{d/D \to 1} \beta \left(\frac{d}{D}, \frac{\phi_d}{\phi_D} \right) = 1 \qquad \qquad \lim_{d/D \to 0} \beta \left(\frac{d}{D}, \frac{\phi_d}{\phi_D} \right) = 0$$

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

A robust and useful form of the weighting function eta that satisfies the above limits, is given by a power law

$$\beta = \left[g\left(\frac{d}{D}\right)\right]^{h\left(\frac{\phi_d}{\phi_D}\right)} = g^{h\left(\frac{\phi_d}{\phi_D}\right)},\tag{10}$$

where the exponent, h, is assumed to depend only on the particle volume fraction ratio, ϕ_d / ϕ_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:

$$\lim_{\substack{d \\ D \to 0}} g\left(\frac{d}{D}\right) = 0$$

$$\lim_{\substack{d \\ D \to 1}} g\left(\frac{d}{D}\right) = 1$$

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

$$\lim_{\substack{d \\ \phi_D \to \infty}} h\left(\frac{\phi_d}{\phi_D}\right) = 0$$
(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, β , in Eq. (10) is chosen for convenience, in order to facilitate the extension of the model to multimodal and polydisperse suspensions (see Section II C and D). In addition, the form of Eq. (10) allows us to separate the effects of relative size (d/D) and composition (ϕ_d/ϕ_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 further 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 κ plays a similar role to the crowding factor in Mooney's (1951) 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, and is an increasing function of it. A parametric study of the weighting function β described by Eqs. (10) and (12), as a function of the effective particle size ratio, g, $0 \le g \le 1$, is presented in Fig. 2 for various values of ϕ_d / ϕ_D and κ . This result verifies that the limiting behaviors of the weighting function outlined in Eq. (11) are preserved for the choice of h described by Eq. (12).



FIG 2: A parametric study showing the dependence of the weighting function β , defined in Eq. (10), on the effective size ratio, g, for different values of the parameter κ and the volume fraction ratio, ϕ_d / ϕ_D . All the limits of Eq. (9) are fulfilled for the functional form of the weighting function in Eqs. (10) and (12) irrespective of the values of the parameter κ .

A key, implied property, of 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 κ appearing in Eq. (12) primarily controls the occurrence of the

viscosity minimum. This is demonstrated by assuming using a Krieger-Doherty viscosity relationship for a monodisperse suspension given by

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

where the maximum particle volume for flow, ϕ_{max} , is typically assumed to be random close packing limit (0.64). This expression is used to define the monodisperse hydrodynamic function defined by 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, $\chi = \frac{\phi_d}{\phi_d + \phi_D}$. This is expressed as

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

where χ_{\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,

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

where,

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

and

$$\theta = g^{\left(1 - \frac{\kappa \chi_{\min}}{\kappa \chi_{\min} + (1 - \chi_{\min})}\right)}.$$
(17)

The behavior of Eq. (15) is now studied parametrically for two scenarios. In the first scenario, we consider the relationship between χ_{min} and g for various values of κ while holding the total volume fraction (ϕ) fixed. The results in Fig. 3 suggest that the position of the viscosity minimum is a strong function of the choice of κ and depends only weakly on the relative size ratio (d/D), which is implicit in the g function. In the second scenario the relationship between χ_{min} and g at fixed values of κ for various values of ϕ is examined. The calculations, summarized in Fig. 3, suggest that the occurrence of the viscosity minimum is only weakly dependent on ϕ . Furthermore, for $\kappa = 6$ we observe that the value of χ_{min} at which the viscosity minimum is seen lies between 0.25 and 0.35. This choice of κ is consistent with empirical observations where, for a fixed size ratio (d/D) and total solids loading (ϕ), the viscosity minimum is seen to occur when 25-35% of the total solid particles by volume are small [Mewis and Wagner (2012)].



FIG 3: A parametric study of the relationship between the minimum viscosity solid particle volume fraction, χ_{\min} , and the effective size ratio, g, defined by Eq. (15), at two different values of the parameter κ and at various total solids volume fractions, ϕ .

The ability of the model to decouple the size and composition effects in a binary suspension is demonstrated. This means that two pieces of information are needed to parametrize the model. The parameter κ may be chosen such that the viscosity minimum predicted by the model occurs over the desired composition range that is observed experimentally. On the other hand, to determine the functional form of the effective size ratio, g, one needs measurements of binary suspensions viscosity as a function of size ratio (see Section 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 η_r and $h(\phi_d / \phi_D)$. Therefore, in subsequent sections, κ will be treated as an additional fitting parameter whenever a Krieger-Dougherty viscosity relationship is not used for η_r and/or no 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 ϕ_{DD} to an existing binary suspension of particle sizes d and $D \ge d$ and corresponding volume fractions ϕ_d and ϕ_D . To be consistent, f_{tri} must reduce to the relevant binary and monodisperse limits, as the ternary suspension degenerates into either a binary and monodisperse one. The trimodal hydrodynamic function must therefore obey the following limits

$$\lim_{\substack{d \\ D \to 1}} f_{Tri} = f_{bi} \qquad \lim_{\substack{D \\ DD \to 1}} f_{Tri} = f_{bi} \qquad \lim_{\substack{d \\ D \to 0}} f_{Tri} = f_{u}$$

$$\lim_{\substack{d \\ D \to 0}} f_{Tri} = f_{bi} \qquad \lim_{\substack{d \\ \phi_D \to 0}} f_{Tri} = f_{bi} \qquad \lim_{\substack{d \\ \phi_D \to 0}} f_{Tri} = f_{bi}$$

$$\lim_{\substack{d \\ \phi_D \to 0}} f_{Tri} = f_{u} \qquad \lim_{\substack{d \\ \phi_D \to 0}} f_{Tri} = f_{u}$$

$$\lim_{\substack{d \\ \phi_D \to 0}} f_{Tri} = f_{u}$$

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 ϕ_d , ϕ_D and ϕ_{DD} given by

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

The corresponding extended weighting functions, β_i , are given by

$$\beta_{1} \equiv \beta \left(\frac{d}{\alpha^{*}}, \frac{\phi_{d}}{\phi_{D} + \phi_{DD}} \right) = \left[g \left(\frac{d}{\alpha^{*}} \right) \right]^{h_{1} \left(\frac{\phi_{d}}{\phi_{D} + \phi_{DD}} \right)} , \qquad (21)$$

and

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

where

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

$$\phi^* = \beta_1 \phi_d + \phi_D , \qquad (24)$$

$$h_{1}\left(\frac{\phi_{d}}{\phi_{D}+\phi_{DD}}\right) = \left(1 - \frac{\kappa\phi_{d}}{\kappa\phi_{d}+\phi_{D}+\phi_{DD}}\right),\tag{25}$$

and

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

The functional form for β_1 and β_2 appearing in Eqs. (21) and (22) is similar to that defined for binary suspensions in Eq. (10). The set of expressions in Eqs. (21)-(26) appear to be more complex, but are strictly consistent with all known limits of the monodisperse and binary suspensions. For example, by setting ϕ_{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 Appendix A. 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. (49)-(51) for quaternary suspensions in Appendix A) 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 Section V).

D. Implementation of the model to polydisperse suspensions

Suspensions of practical relevance such as coal slurries [Rosin and Rammler (1933)] are comprised of continuous size distributions¹ such that 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-n-ary distribution following the method outlined above. However, as we shall show, this is not necessary. Instead, it suffices to simply discretize the continuous particle size distribution 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 (1994) proposed that just three particle size classes (or fitting the first 6 moments) are adequate to represent the rheological properties of a suspension with a continuous particle size distribution. This means that a continuous size distribution can be described by an equivalent ternary suspension. Therefore, the ternary hydrodynamic function developed in 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

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

where $f_{\nu}(R)dR$ represents the normalized volume-weighted number density of non-colloidal particles with radii between sizes R and R + dR and m_k is the k^{th} moment of the distribution. The first 6

¹ Continuous size distributions as discussed here refers to single peaked distributions with relatively short tails.

moments of the continuous volume-weighted size distribution (m_i ; $0 \le i \le 5$) are then used to generate an equivalent ternary approximation based on the following equation

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

where ω_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:

$$\phi_d = \frac{\omega_1}{\sum_{i=1}^3 \omega_i} \phi \qquad \phi_D = \frac{\omega_2}{\sum_{i=1}^3 \omega_i} \phi \qquad \phi_{DD} = \frac{\omega_3}{\sum_{i=1}^3 \omega_i} \phi , \qquad (29)$$

$$d = L_1 \qquad D = L_2 \qquad DD = L_3. \tag{30}$$

In Eq. (29), ϕ is the total solids volume fraction and d, D and DD represent the small, medium and large particles respectively in the system with ϕ_d , ϕ_D and ϕ_{DD} 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 Section V to justify the 6-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 κ needs to be determined. 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 simulation or experimental data of the viscosity of binary suspensions.

A. Determining model parameters from the Huggins coefficient in dilute limit

In dilute hard sphere colloidal suspensions, the Huggins coefficient, k_H , accounts for pair interactions and therefore provides information on colloidal interactions [Russel (1984)]. In practice, the Huggins coefficient is related to the ϕ^2 coefficient in a Taylor expansion of the viscosity with respect to the volume fraction

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

For the Krieger-Doherty relationship in Eq. (13), c_{ϕ^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 (1994) 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 [Wagner and Woutersen (1994)] as

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

where χ_1 and χ_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 [Jeffrey (1992), Wagner and Woutersen (1994)] and is defined to be equivalent upon $\lambda_{ij} \rightarrow 1/\lambda_{ij}$ substitution. The calculations of c_{a^2} from Eq. (32) are presented schematically in Fig. 4, for different compositions and size ratios.



FIG 4: Calculated values of c_{ϕ^2} using Eq. (32) and the values of $I_H(d/D)$ provided by Wagner and Woutersen (1994) of as a function of the solids fraction of small particles for different size ratios (d/D).

Using our modeling approach, we calculate the binary suspension viscosity ($\eta_{r,bi}$), as described in Section II, by assuming the Krieger-Doherty relationship in Eq. (13) as the model for the monodisperse suspension viscosity. The Taylor expansion of $\eta_{r,bi}$ defined by Eq. (7), is then given by

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

where

$$\beta(g,\chi_1) = g^{\left(1 - \frac{\kappa\chi_1}{\kappa\chi_1 + \chi_2}\right)}, \qquad (34)$$

and ϕ_{max} is assumed to be 0.67 to preserve the consistency with the Wagner and Woutersen (1994) relation in the monodisperse limit. By equating the expression for c_{ϕ^2} provided by Eq. (32) and the ϕ^2 coefficient in Eq. (33), the relationship between the relative size ratio (g) and the size ratio (d/D) can be determined once the parameter κ is determined. Following the procedure described in Section II B, κ is computed independently using Eqs. (15)-(17) together with the observation that the minimum in c_{ϕ^2} always occurs at $\chi_{1,\min}$ equal to 0.5 (see Fig 4). From this procedure, the value of κ is determined to be 0.54. Next, by enforcing equality of Eq. (32) and the ϕ^2 coefficient in Eq. (33), the effective size ratio values (g) that best parametrize the results of Wagner and Woutersen (1994) (see Fig. 4) are extracted and are presented in Fig. 5. These can be fit to a power law given by

$$g = \left(\frac{d}{D}\right)^{0.18} . \tag{35}$$



FIG. 5: The empirically determined g function values and their dependence on (d/D) obtained by enforcing equality of Eq. (32) and the ϕ^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. 5. The solid line is a parameterization of the g function values obtained by fitting to a power law.

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

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

The corresponding comparison for c_{ϕ^2} of the model predictions based on this weighting function and the theoretical results from the calculations by Wagner and Woutersen (1994) using Eq. (32) is then shown in Fig. 6.



FIG. 6. Comparison of calculations of the ϕ^2 coefficient following the theoretical results from Wagner and Woutersen (1994) (symbols) and the calculations from the model (lines) using Eqs. (33) and (36).

The approach outlined in this section represents one way to determine the components of the weighting function, g and κ , that appear in the definition of the binary hydrodynamic function. The ability of the model to capture the semi-dilute behavior (the ϕ^2 coefficient) as provided by an alternative, first-principles, approach, provides some justification for the form of the weighting function used, as well as the definition of the bimodal hydrodynamic function. However, it should be noted that the theoretical results from Wagner and Woutersen (1994) assume that the particle configurations are random. This is not necessarily true for suspensions under flow, even if one starts from a random configuration [Batchelor and Green (1972), Chang and Powell (1993), Mewis and Wagner (2012)]. For example Chang and Powell (1993) 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. Therefore, alternative, necessarily empirical, weighting functions must be developed to reflect the actual microstructure that develops under flow, especially for non-colloidal suspensions. In the

following section, we discuss how to develop such empirical weighting functions by comparison against either numerical simulations or experimental data on the viscosity of binary suspensions.

B. Estimating weighting function using concentrated binary suspensions data

The evaluation of the weighting function defined by Eq. (10) can proceed in two ways depending on the available data. Like the previous section, if the relative viscosity as a function of the composition of small particles (χ_1) is known and displays a viscosity minimum at $\chi_{1,\min}$, then an approach analogous to that described in Eqs. (13)-(17) (Section II B) may be used to independently determine κ . 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 is not available, κ should be considered as a fitting parameter, together with g, to be determined from the binary suspension viscosity data. Therefore at a minimum, one must have binary suspension viscosity data taken over multiple d/D ratios to parametrize the model. 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 K (see Eq. (12)). As such, for a selected K 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 κ value. Finally, a parametrization for g vs. d/D is developed, allowing us to interpolate for all possible effective size ratios. This parametrization must fulfil the limits outlined in Eq. (11) for d/D equal to 0 and 1. This approach to develop the weighting function in Eq. (10) is now demonstrated using simulation data as well as experimental measurements on binary suspension viscosity.

1. Simulations of monolayers of non-colloidal suspensions

The various components of the weighting function, g and K, can be determined by fitting the bimodal suspension viscosity model to the Stokesian Dynamics simulation results by Chang and Powell (1993). These simulations emulate binary suspensions of spherical particles in a monolayer. Owing to their two-dimensional nature, these simulations do not incorporate all the features of a real suspension. Nevertheless they provide a good test bed to develop insights on the form of the weighting function. The monodisperse viscosity relation for the simulation data used is given by

$$\eta_r = \left(1 + \frac{0.22\phi}{(1 - \phi/0.78)}\right)^{7.13} \qquad 0 < \phi < 0.6 ,$$
(37)

where ϕ is the areal fraction with a maximum packing of 0.78. Using Eqs. (6) and (7) to define the binary hydrodynamic function, the simulated binary suspension viscosity results are fit to the viscosity model. The best fit value of κ is 3.13 and the best representation of the relationship between effective size ratio (g) and the true size ratio (d / D), shown in Fig. 7, is given by

$$g = 1 - \left(1 - \frac{d}{D}\right)^{1.67} .$$
 (38)

The corresponding weighting function is given by

$$\beta = \left[g\left(\frac{d}{D}\right)\right]^{h\left(\frac{\phi_d}{\phi_D}\right)} = \left[1 - \left(1 - \frac{d}{D}\right)^{1.67}\right]^{\left(1 - \frac{3.13\phi_d}{3.13\phi_d + \phi_D}\right)},\tag{39}$$

and the resulting model fits are compared to the simulated binary viscosity data in Figs. 8 and 9.

Chang and Powell (1993) reported formation of clusters in their 2-D simulations. This departure of the 2-D suspension from ideal binary suspension behavior can be quantified by comparing the effective size ratio, g, in Eq. (38) to that in Eq. (35) (which is assumed to represent an ideal random binary suspension). This comparison is summarized in Fig. 7. The effective size ratio from Eq. (38) is consistently smaller than that of Eq. (35) as well as the monodisperse value of g = 1. This suggests that the effect of polydispersity in mitigating hydrodynamic interactions is far larger in the non-random binary suspensions simulated by Chang and Powell (1993), when compared against the calculations by Wagner and Woutersen (1994) on random binary suspensions.



FIG. 7: The empirical relative size ratio (g) as a function of the true size ratio (d/D) determined from the 2-D monolayer simulations of Chang and Powell (1994). The solid points represent the empirically determined relative size ratios fit to the simulation data shown in Fig. 8 and 9. The continuous line represents (Eq. (38)) the parameterization that is most consistent with the fit values of the relative size ratios. For comparison, the dotted line (Eq. (35)) corresponds to the parameterization based on the effective Huggins coefficient of random suspensions (see Fig. 5).



FIG. 8. Model fit compared to simulation data from Chang and Powell (1993) showing the dependence of the relative viscosity on the particle size ratio (d/D) with the fraction of small spheres is fixed at 0.27 for binary all cases. The weighting functions for the fits were calculated using the effective size ratio values (g) in Fig. 7 and $\kappa = 3.13$. Monodispersed d/D=1, Binary d/d=0.5 and d/D=0.25.



FIG. 9. Relative viscosity of binary suspensions at different compositions and particle size ratios. Total areal fraction is fixed at 0.5. Model fit (solid lines) compared to simulation data from Chang and Powell (1993) showing the dependence of relative viscosity on fraction of small particles in the suspension for different particle size ratios (d/D). The weighting functions for the fits were calculated using the g function values in Fig. 7 and $\kappa = 3.13$. Monodispersed, d/D=1; Binary d/D=0.5 and d/D=0.25.

In this case, the binary viscosity model shows its ability to represent the behavior of the simulated two-dimensional binary suspensions providing an analytical parameterization of all the simulation data. Nevertheless, for practical applications, it may be necessary to develop an alternative parameterization of the model based on more realistic, three-dimensional binary experimental data. The penalty incurred is that the resulting model lacks full predictive capability regarding the estimation of the viscosity of real binary suspensions. However, it will be shown that this shortcoming is mitigated by the fact that once the model is parametrized, it can be extended to truly multimodal or polydisperse noncolloidal suspensions without the need to add any new parameters as discussed in Section II C.

2. Experimental measurements of concentrated non-colloidal suspensions

The experiments by Chong *et al.* (1971) on binary suspensions of glass spheres are taken as a model system to develop an alternative set of model parameters. Chong *et al.* (1971) 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 the total solids fraction. This suggests that the system is a reasonable representation of an ideal noncolloidal suspension. A viscosity correlation from Morris and Boulay (1999) is adopted to define the monodisperse viscosity of experiments by Chong *et al.* (1971):

$$\eta_r = 1 + 2.5\phi \left(1 - \phi / \phi_{\max}\right)^{-1} + m \left(\phi / \phi_{\max}\right)^2 \left(1 - \phi / \phi_{\max}\right)^{-2}.$$
 (40)

The parameters m = 0.41 and $\phi_{max} = 0.607$ are determined by fitting the monodisperse viscosity data from Chong *et al.* (1971). Subsequently, the binary hydrodynamic function is defined and the parameter κ 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 κ is estimated to be 2.46 and the effective size ratio, g, that best describes the experimental data, shown in Fig. 10, is given by

$$g = \left(1 - \left(1 - \frac{d}{D}\right)^{3.24}\right)^{1.91}.$$
 (41)

The overall weighting function is then given by

$$\beta = \left[g\left(\frac{d}{D}\right)\right]^{h\left(\frac{\phi_d}{\phi_D}\right)} = \left[\left(1 - \left(1 - \frac{d}{D}\right)^{3.24}\right)^{1.91}\right]^{\left(1 - \frac{2.46\phi_d}{2.46\phi_d + \phi_D}\right)},$$
(42)

The associated model fit and comparison to the binary suspension viscosity data of Chong *et al.* (1971) are presented in Fig. 11 for comparison.



FIG 10: The effective size ratio (g) as a function of true relative size ratio (d/D) from fitting the viscosity model to experimental data by Chong et al. (1971). The solid points represent the g values that were used to fit the experimental results in Fig. 11. The solid line represents the parameterization of the g values obtained by fitting to the data in Fig. 11. For comparison, the dotted line is the effective size ratio previously extracted from the 2-D simulations of Chang and Powell (1994) (see Fig 7).



FIG 11. Relative viscosity as a function of total volume fraction. Viscosity model fit (solid lines) are compared to simulation data from Chong et al. (1971) for different particle size ratio (d/D). The fraction of small spheres (χ_1) is fixed at 0.25 for binary all cases. Monodisperse, d/D=1; Binary d/D=0.477, d/D=0.313 and d/D=0.138.

The effective size ratio (g) and parameter (K) determined here are similar to the parametrization of the 2-D simulation data in section III B-1. In Fig. (10), the two different parametrizations of g are seen to be closely related. In addition, the K values from these two parametrizations are 2.46 and 3.13 respectively. At this point, the differences in parameters arising from the fits to the simulation and experimental data sets can be attributed to the different microstructures that govern the rheological behavior of the two systems, reflecting the 2-D and 3-D nature of the two data sets. Therefore, additional flexibility in fitting the weighting function should be allowed in the choice of weight function to reflect such effects as well as the additional complexity that is encountered in real systems, caused by particle interactions and non-universal particle configurations.

IV. COMPARISON TO EXISTING MODELS IN LITERATURE

In this section, the binary suspension viscosity model developed from the parametrization based on experiments by Chong *et al.* (1971) (see Section III B-2) is compared to a model developed by Qi and

Tanner (2011). The latter model is parameterized based on experiments by Chang and Powell (1994) on binary suspensions. Also included is a comparison against the results obtained from a model for binary suspension recently developed by Farr (2014). For consistency with the work of Qi and Tanner (2011), we adopted here the same viscosity expression for the monodisperse suspension that was used in their work

$$\eta_r(\phi) = \left(1 - \frac{\phi}{1 - c\phi}\right),\tag{43}$$

where c is given by

$$c = \frac{1 - 0.639}{0.639} \ . \tag{44}$$

These expressions together with the weighting function developed in Section III B-2 is used to calculate the binary suspension's viscosity. The model developed by Farr (2014) has its own viscosity relationship and is used as-is.

A comparison of these three models is presented in Fig. 12. In the same figure, the three models are also compared against experimental data by Chang and Powell (1994) and Chong *et al.* (1971). Fig. 12 shows that our model predictions capture the experimental trends but lack the asymmetry seen in the experimental data. It should be noted that the model of Tanner and Qi (2011) has a total of 7 parameters and it explicitly enforces a viscosity minimum at a fraction of small particles of 0.27. By admitting extra complexity in the interpolating functions, especially for the form of $h(\phi_d / \phi_D)$, an equally good fit may also be obtained from our model as well (see Appendix B). On the other hand, the model by Farr (2014) that has 2 parameters has the poorest fit to the data seen in Fig. 12. Therefore, our model compares favorably to existing works in the literature, in relation to the desired complexity.



FIG 12. Relative viscosity as a function of the fraction of small particles in the suspension. Comparison of calculated viscosity from model of Qi and Tanner (2011) (dotted line) to predictions from our model (solid lines) and Farr's model (dashed lines). Circle symbols correspond to data from Chang and Powell (1994). Square symbols correspond to data from Chong et *al.* (1971). (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.

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

In this section, the ternary viscosity model developed in Sections II C and D is applied to predict the viscosity of several suspensions characterized by continuous polydispersity using the framework outlined in Sections II C and D. The model predictions in this section are based on the weighting function developed in Section III B-2 based on the fit to the binary data set by Chong *et al.* (1971). The results in this section are based on the assumption that a continuous size distribution may be represented by an equivalent ternary suspension as explained in Section II D. This assumption is also validated in this section. Finally, Eiler's viscosity correlation in Eq. (1) with $\phi_{max} = 0.58$ [Singh and Nott (2003)] is used to define the monodisperse suspension viscosity for all the predictions shown in this section.

A. Coal slurry application

The first application involves a coal slurry studied by Papachristodoulou and Trass (1984). The volume-weighted cumulative particle size distribution for this system has been characterized and may be approximated by a Rosslin-Rammler distribution (Rosin and Rammler 1933, Vesilind 1980) defined by

$$F(x) = 1 - \exp\left[-0.693 \left(\frac{x}{D_{50}}\right)^{\lambda}\right],\tag{45}$$

with a median size (D_{50}) of 37µm and λ equal to 1.6 as shown in Fig. 13. The volume fractions are calculated using the density of bituminous coal which is 1346 kg m⁻³ and that of the light # 6 oil which was reported to be 978 kg m⁻³ by Papachristodoulou and Trass (1984). Since coal slurries typically behave like Bingham fluids at high solids 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 the Bingham viscosity. Papachristodoulou and Trass (1984) 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. 14 that are compared with the model predictions are the reduced Bingham plastic viscosities. In general, 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.



FIG. 13. Cumulative size distribution of a coal slurry. The experimentally measured particle size distribution for a coal slurry from Papachristodoulou and Trass (1984) is fit to a Rossin-Rammler cumulative size distribution with a median size of 37 μ m. The bar charts in the background represent the three mode approximation of the continuous size distribution Eqs. (22)-(24).



FIG. 14. 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 Rosslin-Rammler distribution from Papachristodoulou and Trass (1984). Monodisperse viscosity calculated from Eiler's viscosity relationship in Eq. (1) (dashed line) is also presented for comparison.

A convergence study is now presented in order to justify the choice of the 6 moment truncation (trimodal appproximation) applied to model the viscosity of polydisperse suspensions as presented in this work. For this, a comparison of various approximations up to the 8 moment approximation (quaternary approximation--see Appendix A) of the coal size distribution is presented in Fig. 13. The results show that by the 6-moment (ternary) approximation the results have essentially converged and indicate that three moment approximation is a sufficient representation for a continuous particle size distribution. 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.



FIG. 15. 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 2-moment (monodisperse), 4-moment (binary), 6 moment (ternary) and 8-moment (quaternary) approximations of the coal slurry particle size distribution in Fig. 13.

B. Distributed particle sizes application

The second application tests the sensitivity of this model to different particle size distributions.

Probstein et al. (1994) performed rheological measurements of the shear viscosity for polydisperse

suspensions of noncolloidal suspensions obeying different particle size distributions. In particular, they examined a log-normal particle size distribution as well as a uniform particle size distribution as shown in Fig. 16. The theoretical cumulative distributions fit to these two experimental particle size distributions are provided by a lognormal distributions with $\mu = 4.58$ and $\sigma = 0.36$ as

$$F(x) = \frac{1}{2} + \frac{1}{2} \operatorname{erf}\left(\frac{\ln(x) - \mu}{\sqrt{2}\sigma}\right),\tag{46}$$

and a uniform distribution with a=36.95µm and b=215.46µm as

$$F(x) = \frac{\ln(x) - \ln(a)}{\ln(b) - \ln(a)}$$
 (47)

These two distributions are illustrated in Fig. 16. Fig. 17 illustrates the equivalent ternary representations of the lognormal distribution.



FIG. 16. Comparison of the lognormal and uniform size distributions of the particles in the suspension fit to theoretical distribution in Eqs. (46) and (47) respectively. Experimental measurements from Probstein *et al.* (1994).



FIG 17: Experimentally measured lognormal particle size distribution (solid line) and its theoretical fit from Eq. (46) compared to the equivalent ternary approximation that is used in the calculation of the weighting function for the prediction of the suspension viscosity shown in Fig. 18.

The experimentally measured viscosities by Probstein *et al.* (1994) from the log-normal distribution are seen to be consistently larger than those derived from the uniform particle size distribution for a given total solids loading. In Fig. 18, the model predictions of the viscosity are seen to follow the experimentally observed trends well. These results provide further validation of the modeling scheme adopted in this work. Furthermore, this also illustrates the sensitivity of the model to closely related but slightly different broad size distributions. This example shows that the model can distinguish between closely related distributions and provides differences in the predictions that closely follow those observed in the experiments.



FIG. 18. Comparison of model predictions and experimental data of polydisperse suspensions based on the ternary representation of the experimental size distributions in Fig. 16. Experimental measurements from Probstein *et al.* (1994).

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 (η_r) and the weighting function (β), describing the effects of the size ratio (d/D) and the volume fraction ratio (ϕ_d / ϕ_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 $\beta \equiv \left[g(d/D)\right]^{h(\phi_d/\phi_D)}$. At a minimum, each of the constituent functions, g and h, contains a single parameter that can be estimated from binary suspension viscosity data. It is demonstrated that through a careful choice of 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, like the Qi and Tanner (2011) model which incorporates a maximum packing fraction and the Farr model [Farr 2014] which is based on the Mooney approach [Mooney (1951)].

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 made possible by first implementing a discretization of the smooth continuous distribution to its ternary equivalent, so that the first 6 moments are preserved, following the suggestion by Wagner and Woutersen (1994). 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 mixed continuous-discrete size distributions or multimodal distributions.

The semi-empirical model to describe the effect of polydispersity on the viscosity of noncolloidal suspensions presented in this work has been developed here 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 [Morris (2015)]. 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. Other potential applications of the proposed model may include the determination of the ideal continuous particle size distribution that results in the minimum viscosity, a problem that is of relevance to industrial processing. Furthermore, the proposed model may also be

applied towards understanding the evolution of viscous stresses in aggregating suspensions that do not display a yield stress. Extensions to account for such aggregation effects can easily be incorporated by coupling the model developed in this work to a population balance equation using the method of moments [Randolph and Larson (1962), Hulburt and Katz (1964)]. In this way, the model has potential applications to an even wider class of problems of engineering relevance.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. CBET 312146. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

REFERENCES

Batchelor, G. K., and J. T. Green, "The determination of the bulk stress in a suspension of spherical particles to order c^2 ," Journal of Fluid Mechanics **56**, 401-427 (1972).

Chang, C., and R. L. Powell, "Dynamic simulation of binary suspensions of hydrodynamically interacting spherical particles," Journal of Fluid Mechanics **253**, 1-25 (1993).

Chang, C., and R. L. Powell, "Effect of particle size distributions on the rheology of concentrated binary suspensions," Journal of Rheology **38**, 85-98 (1994).

Chong, J. S., E. B. Christiansen, and Baer, A. D., "Rheology of concentrated suspensions," Journal of Applied Polymer Science **15**, 2007-2021 (1971).

Dörr, A., A. Sadiki, and A. Mehdizadeh, "A discrete model for the apparent viscosity of polydisperse suspensions including maximum packing fraction," Journal of Rheology **57**, 743-765 (2013).

Eilers, H., "Die Viskosität von Emulsionen hochviskoser Stoffe als Funktion der Konzentration," Kolloid-Zeitschrift **97**, 313-321 (1941).

Einstein, A., "A new determination of molecular dimensions," Ann. Phys **19**, 289-306 (1906).

Farr, R. S., "Simple heuristic for the viscosity of polydisperse hard spheres," The Journal of Chemical Physics **141**, - (2014).

Farris, R. J., "Prediction of the Viscosity of Multimodal Suspensions from MonodisperseViscosity Data," Transactions of The Society of Rheology (1957-1977) **12**, 281-301 (1968).

Faroughi, S., and C. Huber, "A generalized equation for rheology of emulsions and suspensions of deformable particles subjected to simple shear at low Reynolds number," Rheologica Acta **54**, 85-108 (2015).

Faroughi, S. A., and C. Huber, "Crowding-based rheological model for suspensions of rigid binary-sized particles with interfering size ratios," Physical Review E **90**, 052303 (2014).

Fidleris, V., and R. L. Whitmore, "The physical interaction of spherical particles in suspensions," Rheologica Acta **1**, 573-580 (1961).

Furnas, C. C., "Grading Aggregates - I. - Mathematical Relations for Beds of Broken Solids of Maximum Density," Industrial & Engineering Chemistry **23**, 1052-1058 (1931).

G.K. Batchelor, "Slender-body theory for particles of arbitrary cross-section in Stokes flow", Journal of Fluid Mechanics, **44**, 419-440 (1970).

Gondret, P., and L. Petit, "Dynamic viscosity of macroscopic suspensions of binary sized solid spheres," Journal of Rheology **41**, 1261-1274 (1997).

Happel, J., and H. Brenner, *Low Reynolds number hydrodynamics: with special applications to particulate media Vol.* **1** (Springer, 1983).

Jeffrey, D. J., "The calculation of low Reynolds number resistance functions for two unequal spheres," Phys. Fluids A **4**, 16–29 (1992).

Hulburt, H. M., and S. Katz, "Some problems in particle technology: A statistical mechanical formulation," Chemical Engineering Science **19**, 555-574 (1964).

Krieger I.M, T.J. Dougherty, A mechanism for non-Newtonian flow in suspensions of rigid spheres, Transactions of The Society of Rheology (1957-1977), **3**, 137-152 (1959).

Jeffrey, D. J., and A. Acrivos, "The rheological properties of suspensions of rigid particles," AIChE Journal **22**, 417-432 (1976).

Maron, S. H., and P. E. Pierce, "Application of ree-eyring generalized flow theory to suspensions of spherical particles," Journal of Colloid Science **11**, 80-95 (1956).

Mewis, J., and N. J. Wagner, *Colloidal Suspension Rheology*, Cambridge University Press, New York, (2012)

Mooney, M., "The viscosity of a concentrated suspension of spherical particles," Journal of Colloid Science **6**, 162-170 (1951).

Morris, J., "Discontinuous Shear Thickening and Dilatancy: Frictional Effects in Viscous Suspensions," Bulletin of the American Physical Society **60** (2015).

Morris, J. F., and F. Boulay, "Curvilinear flows of noncolloidal suspensions: The role of normal stresses," Journal of Rheology **43**, 1213-1237 (1999).

Ouchiyama, N., and T. Tanaka, "Porosity estimation for random packings of spherical particles," Industrial & Engineering Chemistry Fundamentals **23**, 490-493 (1984).

Papachristodoulou, G., and O. Trass, "Rheological propertis of coal—oil mixture fuels," Powder Technology **40**, 353-362 (1984).

Poslinski, A. J., M. E. Ryan, R. K. Gupta, S. G. Seshadri, and F. J. Frechette, "Rheological Behavior of Filled Polymeric Systems II. The Effect of a Binary Size Distribution of Particulates," Journal of Rheology **32**, 751-771 (1988).

Probstein, R. F., M. Z. Sengun, and T. C. Tseng, "Binary model of concentrated suspension viscosity for distributed particle sizes," Journal of Rheology **38**, 811-829 (1994).

Qi, F., and R. Tanner, "Relative viscosity of binary suspensions," Korea-Australia Rheology Journal **23**, 105-111 (2011).

Qi, F., and R. Tanner, "Random close packing and relative viscosity of multimodal suspensions," Rheologica Acta **51**, 289-302 (2012).

Randolph, A. D., and M. A. Larson, "Transient and steady state size distributions in continuous mixed suspension crystallizers," AIChE Journal **8**, 639-645 (1962).

Renon, H., and J. M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," AIChE Journal **14**, 135-144 (1968).

Rosin, P., and E. Rammler., "The laws governing the fineness of powdered coal," Journal of the Institute of Fuel **7**, 29-36 (1933).

Russel, W. B., "The Huggins coefficient as a means for characterizing suspended particles", J. Chem. Soc., Faraday Trans. 2, **80**, The Royal Society of Chemistry, 31-41 (**1984)**.

Singh, A., and P. R. Nott, "Experimental measurements of the normal stresses in sheared Stokesian suspensions," Journal of Fluid Mechanics **490**, 293-320 (2003).

Sudduth, R. D., "A generalized model to predict the viscosity of solutions with suspended particles. III. Effects of particle interaction and particle size distribution," Journal of Applied Polymer Science **50**, 123-147 (1993).

Vesilind, P. A., "The Rosin-Rammler particle size distribution," Resource Recovery and Conservation **5**, 275-277 (1980).

Wagner, N. J., and A. T. J. M. Woutersen, "The viscosity of binary and polydisperse suspensions of hard spheres in the dilute limit," Journal of Fluid Mechanics **278**, 267-287 (1994).

Zarraga, I. E., D. A. Hill, and D. T. Leighton, "The characterization of the total stress of concentrated suspensions of noncolloidal spheres in Newtonian fluids," Journal of Rheology **44**, 185-220 (2000).

APPENDIX A: HYDRODYNAMIC FUNCTION FOR QUATERNARY DISTRIBUTIONS

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

 $\lim_{\phi_D,\phi_{DD},\phi_{DDD}\to 0} f_{tetra} = f_u$

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

$$f_{Tetra} = f_{u} \left(\beta_{3} \left(\beta_{2} \left(\beta_{1} \phi_{d} + \phi_{D} \right) + \phi_{DD} \right) + \phi_{DDD} \right) + f_{u} \left(\beta_{2} \left(\beta_{1} \phi_{d} + \phi_{D} \right) + \phi_{DD} \right) (1 - \beta_{3}) + f_{u} \left(\beta_{1} \phi_{d} + \phi_{D} \right) (1 - \beta_{2}) + f_{u} \left(\phi_{d} \right) (1 - \beta_{1})$$
(49)

(48)

$$\begin{split} \beta_{l} &= \beta \left(\frac{d}{\alpha^{*}}, \frac{\phi_{d}}{\phi_{D} + \phi_{DD} + \phi_{DD}} \right) = \left[g \left(\frac{d}{\alpha^{*}} \right) \right]^{h_{l} \left(\frac{\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_{l} \left(\frac{\phi^{*}}{\phi_{DD} + \phi_{DD}} \right)} \\ \beta_{3} &= \beta \left(\frac{\alpha^{**}}{DDD}, \frac{\phi^{**}}{\phi_{DD}} \right) = c \left(\frac{\phi_{d}}{\phi_{D} + \phi_{DD}} \right) \left(1 - \frac{m\phi_{d}}{m\phi_{d} + \phi_{D} + \phi_{DD}} + \phi_{DD}} \right), \\ h_{l} \left(\frac{\phi_{d}}{\phi_{DD} + \phi_{DD}} \right) = c \left(\frac{\phi^{*}}{\phi_{DD} + \phi_{DD}} \right) \left(1 - \frac{m\phi^{*}}{m\phi^{*} + \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_{DD}} \right) = c \left(\frac{\phi^{**}}{\phi_{DD}} \right) \left(1 - \frac{m\phi^{**}}{m\phi^{**} + \phi_{DDD}} \right), \\ h_{3} \left(\frac{\phi^{**}}{\phi_{DD}} \right) = c \left(\frac{\phi_{DD}}{\phi_{DD}} \right) \left(1 - \frac{m\phi^{**}}{m\phi^{**} + \phi_{DDD}} \right), \\ \beta_{1} \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_{1} \left(\frac{D}{DD}, \frac{\phi_{D}}{\phi_{DD}} \right) = \left[g \left(\frac{D}{DD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D} + \phi_{DD}} \right)}, \\ \alpha^{**} = \frac{\beta_{\frac{DD}{DDD}} \phi_{DD} DD + \left(1 - \beta_{\frac{DD}{DDDD}} \right) (\phi_{D}) D}{\beta_{\frac{DD}{DDD}} \phi_{DD} + \left(1 - \beta_{\frac{DD}{DDDD}} \right) (\phi_{D})} d_{D}, \\ \beta_{1} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D}} + \phi_{DD}} \right), \\ \beta_{1} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D}} + \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D}} + \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D}} + \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{m\phi_{D}} + \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{DD}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{\phi_{DD}} - \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{D}}{\phi_{DD}} \right) = \left[g \left(\frac{DD}{DDD} \right) \right]^{\left(1 - \frac{m\phi_{D}}{\phi_{D}} + \phi_{DD}} \right), \\ \beta_{2} \left(\frac{DD}{DDD}, \frac{\phi_{D}}{\phi_{D}} \right) = \left[g$$

and

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

Finally, the relative viscosity of the suspension is calculated as,

$$\eta_r = \exp(2.5f_{Tetra}) \ . \tag{51}$$

(50)

APPENDIX B: MODIFIED WEIGHT FUNCTION TO FIT COMPLEX EXPERIMENTAL DATA

The viscosity model based on the parameterization in Sec. II (B-2) seems to capture the trends in the data by Chang and Powell (1994) and Chong *et al.* (1971) well, but it does not capture all the details, such as the asymmetry seen at higher volume fractions (see Fig. 12). The good fit seen in the model by Tanner and Qi (2011) is not surprising if we consider the number of parameters in their model (considering constants to be parameters). By admitting extra complexity in the interpolating functions used in our model, we can also achieve this effect. Indeed, a better fit to the experimental data can be obtained by defining the weighting function, $\beta = g^h$, using

$$g\left(\frac{d}{D}\right) = \left(1 - \left(1 - \frac{d}{D}\right)^{0.9}\right)^{1.41} \quad , \tag{52}$$

and

$$h\left(\frac{\phi_d}{\phi_D}\right) = \left(1.68\left(\frac{\phi_d}{\phi_d + \phi_D}\right)^2 - 2.01\left(\frac{\phi_d}{\phi_d + \phi_D}\right) + 1\right)\left(1 - \frac{2.5\phi_d}{2.5\phi_d + \phi_D}\right)$$
(53)

The model now has 6 parameters (counting the constants appearing in Eqs. (52) and (53), excluding those necessary to fulfil the limits in Eq. (10)). The calculated viscosity using this weighting function and the viscosity relationship in Eq. (43) is presented in Fig. 19 along with a comparison against the Chang and Powell (1994) data as well as the model predictions of Tanner and Qi (2011). The agreement of the model with both is excellent. Furthermore, our model better predicts the convergence in the measured viscosities seen at the two largest volume fractions when the system is dominated by large particles ($\chi_1 \approx 0.1$).

It is therefore clear that by modifying the weighting function, while still keeping the basic structure of the original equations, a wide variety of suspension viscosity behavior may be simulated. Furthermore, the newly defined weight function still enjoys all the original properties of the model i.e. all the limits are fully obeyed. Finally, the weighting function can be extended to ternary suspensions without introducing any new parameters.



Figure 19: Comparison of calculated viscosity from model of Tanner and Qi (2011) (dotted line) and our model using weighting functions defined by Eqs. (52) and (53). Blue (•) and black (\circ) symbols correspond to data from Chang and Powell (1994). The red (**•**) symbols correspond to data from Chang *et al.* (1971).