

A simple semiempirical model for the effective viscosity of multicomponent suspensions

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Abstract We propose a methodology to approximate the viscosity of multicomponent suspensions. The procedure consists of successive applications of expressions for the viscosity of binary mixtures, originally written as the product of monomodal stiffening functions. First, the viscosity of a binary mixture made of the two smallest components is calculated. This allows to extract a volume fraction that will be used, together with the volume fraction of the third component, to feed the next iteration of the procedure to calculate the viscosity of a trimodal mixture and so on. The application of this approach to arbitrary mixtures requires the detailed knowledge of the geometry of the system in the form of size ratios and compositions. When this information is unknown, an approximation of the model can still be used as a fitting tool. With that purpose, the final expression for the viscosity is written in terms of an effective volume fraction that is further approximated by the use of a (1,2) Padé approximant. This approximation allows to incorporate the crowding effects due to different species in a volume fraction-dependent crowding factor that can be used as a fitting parameter to match experimental or simulation data. We have applied the model to mixtures of particles with different sizes and tested its accuracy comparing with experimental results obtaining very good agreement.

Keywords Mixture · Quemada's model · Colloids · Shear viscosity · Mooney equation

Introduction

Suspensions of colloidal particles are present in everyday life and plays a mayor role in many technological applications. The study of their rheological properties has received a lot of attention since in many cases its precise control is essential. In particular, there have been many experimental, theoretical, and numerical works studying the viscosity of suspensions. Most of the models describe the viscosity as a function of the concentration for monomodal suspensions of particles of a single kind (Einstein 1906, 1911; Maron and Pierce 1956; Krieger and Dougherty 1959; Quemada 1998). However, in practice, most suspensions are mixtures of particles with different shapes, sizes, porosities, electric charge or other physical and chemical properties that may be important in predicting the viscosity of suspensions (Shewan and Stokes 2015). Thus, the interest to study suspensions consisting of mixtures of such particles. In spite of the large amount of work on this subject (Furnas 1931; Eveson 1959; Hoffman 1992; Sudduth 1993a, b; Chang and Powell 1994; D'Haene and Mewis 1994; Wagner and Woutersen 1994; Greenwood et al. 1997; Dames et al. 2001; Lionberger 2002; Núñez et al. 2002; Servais et al. 2002; Mwasame et al. 2016a), the problem to predict the structure and flow properties of general mixtures is still an open problem.

The addition of particles to a homogeneous isotropic fluid increases the viscosity of the resulting suspension. In the case of a dilute suspension of identical particles, the viscosity $\eta(\phi)$ as a function of the volume fraction ϕ of the particles was first derived by Einstein (1906, 1911) and is given by the expression

$$\eta(\phi) = \eta_0 (1 + [\eta]\phi), \quad (1)$$

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where η_0 is the viscosity of the original fluid and $[\eta]$ is the intrinsic viscosity, which is a single particle property that depends on factors such as shape, porosity, and electric charge ($[\eta] = 5/2$ for hard spheres).

Several models have been proposed in order to extend Einstein's expression to larger volume fractions. Due to the formidable difficulty to incorporate the many body nature of non-dilute systems in the calculation of rheological quantities such as the shear viscosity of the system, simplifying strategies have been devised to include in an approximate way all these contributions. A very successful approach consists in treating the hydrodynamic interactions by means of a recursive differential procedure in which particles are progressively incorporated to the suspension while the crowding effect are contained in an *effective* volume fraction ϕ_{eff} . This procedure leads to an universal representation of all experimental results in a master curve for η vs. ϕ_{eff} indicating that ϕ_{eff} is a natural variable for these systems (Mendoza and Santamaría-Holek 2009). This differential effective medium technique (DEMT) has been applied to suspensions of hard spheres (Mendoza and Santamaría-Holek 2009), emulsions of spherical droplets (Mendoza and Santamaría-Holek 2010), suspensions of arbitrarily shaped hard particles (Santamaría-Holek and Mendoza 2010), suspensions of permeable particles (Mendoza 2011), suspensions of soft (inter-penetrable) particles (Mendoza 2013), and suspensions with power-law matrices (Tanner et al. 2010), with excellent results. This model has been extended to consider multimodal suspensions with a dominant large particle composition (Qi and Tanner 2011, 2012). Other recent advances include the development of a simple analytic approximation for the viscosity of any size distribution of hard spheres (Farr 2014), a crowding-based model for the case of bimodal-sized particles with interfering size ratios (Faroughi and Huber 2014), and models for the case of polydisperse non-colloidal hard sphere suspensions (Dörr et al. 2013; Mwasame et al. 2016b).

The purpose of the present work consists in extending previous models (Mendoza and Santamaría-Holek 2009; Santamaría-Holek and Mendoza 2010; Faroughi and Huber 2014) to treat the case of mixtures of particles with a diversity of intrinsic viscosities including mixtures of particles with different shapes, sizes, or porosities. We compare the resulting expressions with experimental data for the low shear viscosity of bimodal mixtures of non-colloidal hard spheres, with experimental results for the Bingham viscosity of a coal slurry, and with the high shear viscosity of polydisperse colloidal dispersions, finding an excellent agreement in all cases.

The paper is organized as follows. “Effective volume fraction and recursive procedure for monomodal suspensions” describes the model and introduces the basic equations for the calculation of $\eta(\phi)$ (an alternative derivation

of the basic equations using space-crowding ideas originally due to Mooney (1951) is presented in Appendix A). In “Mixtures of particles with the same intrinsic viscosity but different sizes” we extend the formalism to treat mixtures of particles with the same intrinsic viscosity and “Mixtures of particles with different intrinsic viscosities” considers mixtures of particles with different intrinsic viscosities. Finally, “Conclusions” is devoted to conclusions.

Effective volume fraction and recursive procedure for monomodal suspensions

The viscosity of a suspension η can be expanded in a virial series as

$$\eta(\phi) = \eta_0 \left(1 + [\eta]\phi + k_H [\eta]^2 \phi^2 + \dots \right). \quad (2)$$

where the Huggins coefficient, $k_H(x)$ accounts for two-body interactions including excluded volume but also hydrodynamic. These interactions become increasingly important when increasing the filling fraction. For dilute suspensions, expression (2) can be approximated by

$$\eta(\phi) \simeq \eta_0 (1 + [\eta]\phi_{eff}) \quad (3)$$

where we have defined the effective volume fraction ϕ_{eff} as

$$\phi_{eff} = \frac{\phi}{1 - c\phi}, \quad (4)$$

with c a fitting constant related to crowding effects. For this approximation the virial series reads

$$\eta(\phi) = \eta_0 \left(1 + [\eta]\phi + c[\eta]\phi^2 + \dots \right). \quad (5)$$

Thus, if one approximates Eq. 2 using Eq. 3 one possibility is to choose c so that $c = k_H[\eta]$, assuming k_H is known. In this way, both expressions are identical up to order ϕ^2 . This strategy could be useful for low concentrations only since no correlations between higher order terms in Eqs. 2 and 5 exists.

In order to obtain an expression for $\eta(\phi)$ useful for larger concentrations we follow the method proposed in (Mendoza and Santamaría-Holek 2009, 2010; Santamaría-Holek and Mendoza 2010). In this approach, further corrections arising from hydrodynamic interactions are incorporated by means of a recursive procedure. This theoretical method is based on a progressive addition of particles to the sample in which the new particles interact in an effective way with those added in previous stages (Bullard et al. 2009). Using Eq. 3 as starting point for the recursive procedure we obtain (Mendoza and Santamaría-Holek 2009, 2010; Santamaría-Holek and Mendoza 2010)

$$\eta(\phi) = \eta_0 (1 - \phi_{eff})^{-[\eta]}, \quad (6)$$

or, using the definition of ϕ_{eff}

$$\eta(\phi) = \eta_0 \left(1 - \frac{\phi}{1 - c\phi}\right)^{-[\eta]} \tag{7}$$

The viscosity as given by Eq. 6 diverges when $\phi_{eff} = 1$, in other words, c depends on the critical volume fraction ϕ_c which is the concentration at which the suspension loses its fluidity and is given by

$$c = \frac{1 - \phi_c}{\phi_c} \tag{8}$$

Note that $\phi_{eff} \simeq \phi$ at low volume fractions and $\phi_{eff} = 1$ at the critical packing $\phi = \phi_c$. A series expansion of Eq. 7 gives

$$\eta(\phi) = \eta_0 \left\{ 1 + [\eta]\phi + \left[c[\eta] + \frac{1}{2}[\eta](1 + [\eta]) \right] \phi^2 + \dots \right\} \tag{9}$$

Comparing Eqs. 5 and 9, we see that the recursive procedure has introduced additional contributions starting from the quadratic term. Such contributions are hydrodynamic in origin as will be explained below.

If we make $\phi_{eff} = \phi$ then we are neglecting excluded volume interactions. In this case, one recovers the Brinkman-Roscoe’s result (Brinkman 1952; Roscoe 1952) $\eta(\phi) = \eta_0(1 - \phi)^{-[\eta]}$, which contains higher-order corrections to the Einstein-like expression, (1). Since excluded volume interactions have been completely ignored, then these corrections should be attributed to hydrodynamic interactions, and are implicitly incorporated through the differential procedure.

Note that our model, (7), is different from the popular Krieger-Dougherty expression (Krieger and Dougherty 1959),

$$\eta_{KD}(\phi) = \eta_0 \left(1 - \frac{\phi}{\phi_{max}}\right)^{-[\eta]\phi_{max}} \tag{10}$$

where ϕ_{max} is the volume fraction at maximum packing. This expression underestimates the viscosity of the suspension at large volume fractions as explained thoroughly in Santamaría-Holek and Mendoza (2010).

An alternative derivation of Eq. 3 (which serves as a basis for the recursive procedure) based on Mooney’s space-crowding ideas (Mooney 1951) is given in Appendix A.

Illustrative calculations for monomodal suspensions

The model given by Eqs. 7 and 8, has been tested for different systems, in particular, for a suspension of identical hard spheres as shown in Fig. 1. Here, we plot the viscosity as a function of the concentration ϕ for a homogeneous hard-sphere suspension as obtained from experiments (red symbols), and as given by our model (Mendoza and

Santamaría-Holek 2009) with $[\eta] = 2.5$ and $\phi_c = \phi_{RCP} \simeq 0.637$ (random close packing). As a second illustrative example, we use our model to fit the viscosity of a suspension of aligned prolate ellipsoids (see Fig. 1). The interest in ellipsoidal particles arises among other reasons because they have been used as models of globular proteins and their hydrodynamic properties can be expressed analytically. In particular, the orientationally averaged intrinsic viscosity can be calculated for arbitrary aspect ratios $p = b/a$, where b is the polar radius and a is the equatorial radius is given by Landau et al. (1984)

$$[\eta] = \frac{2}{5} (p^2 - 1)^2 \left\{ \frac{-(4p^2 - 1)B + 2p^2 + 1}{3p^2(3B + 2p^2 - 5)[(2p^2 + 1)B - 3]} + \frac{14}{3p^2(3B + 2p^2 - 5)} + \frac{2}{(p^2 + 1)(-3p^2B + p^2 + 2)} + \frac{p^2 - 1}{p^2(p^2 + 1)[(2p^2 - 1)B - 1]} \right\} \tag{11}$$

where

$$B = \begin{cases} p^{-1} (p^2 - 1)^{-1/2} \cosh^{-1} p, & \text{when } p > 1, \\ 1, & \text{when } p = 1, \\ p^{-1} (1 - p^2)^{-1/2} \cos^{-1} p, & \text{when } p < 1. \end{cases} \tag{12}$$

The value of $[\eta]$ is then used in Eq. 7 to compute the viscosity of the suspension.

In the inset of Fig. 1, we show the behavior of the orientationally averaged intrinsic viscosity as a function of the aspect ratio p . As can be seen, the lower value of the intrinsic viscosity occurs for spherical particles and increases slightly more sharply for prolate ellipsoids than for oblate ones. In Fig. 1, we plot the viscosity of a pure suspension of aligned prolate hard ellipsoids with $p = 4$ and we compare the result with the data obtained from an empirical equation for the effective viscosity of concentrated suspensions of aligned rigid prolate spheroids due to Brodnyan (1959), given by

$$\eta(\phi) = \eta_0 \exp \left[\frac{2.5\phi + 0.399\phi(p-1)^{1.48}}{1 - 1.35\phi} \right] \quad \text{for } p \geq 1. \tag{13}$$

Comparison of our model with the empirical Eq. 13 (symbols) represents an indirect comparison of our model with experimental results because the empirical equation was obtained by fitting to experimental data. Using both $[\eta]$ and ϕ_c as fitting parameters we obtain for $p = 2$, $[\eta] \simeq 3.2$, a bit larger than the value obtained for an isotropic distribution, Eq. 11, and $\phi_c \simeq 0.6$. For $p = 4$, we obtain $[\eta] \simeq 4.78$,

and $\phi_c \simeq 0.58$. Notice the excellent agreement between our model and the experimental data for both, hard spheres and aligned prolate ellipsoids.

Mixtures

Here, we extend the previous results to mixtures, first for a suspension of particles with identical intrinsic viscosity but a distribution of sizes and subsequently to mixtures of particles with different intrinsic viscosities.

Mixtures of particles with the same intrinsic viscosity but different sizes

Most suspensions are in practice polydisperse, thus the need to study the effect that the distribution of sizes has on the effective viscosity of a suspension. In this section, we will show explicitly how to obtain approximate expressions for multimodal mixtures and also show that our expression (7) is still useful to calculate the viscosity of a system with distribution of sizes if the crowding parameter c is taken as a ϕ dependent quantity of the form $c = c' + c''\phi$, with c' and c'' constants.

Bimodal suspensions

Firstly, we consider the case of a suspension of particles with two different diameters but with identical intrinsic viscosities. According to Faroughi and Huber (2014), the viscosity of bimodal-sized particles with interfering size ratios can be written as the product of two monomodal viscosities with corrected volume fractions that take into

account crowding between different species. Their resulting expression is

$$\frac{\eta(\phi_1 + \phi_2)}{\eta_0} = \eta(\Psi_1) \eta(\Psi_2), \tag{14}$$

where $\phi_1 = \phi_s = \xi\phi$ and $\phi_2 = \phi_l = (1 - \xi)\phi$, represent the volume fractions of the first (small) and second (large) species, respectively. Note that $\phi_l + \phi_s = \phi$ is the total volume fraction of the mixture. The corrected volume fractions

$$\Psi_1 = \frac{\phi_s + C_f(\xi, \lambda)\phi_l}{1 - (1 - C_f(\xi, \lambda))(\phi_l - C_f(\xi, \lambda)\phi_l)} \tag{15}$$

and

$$\Psi_2 = \frac{\phi_l - C_f(\xi, \lambda)\phi_l}{1 - C_f(\xi, \lambda)(\phi_s + C_f(\xi, \lambda)\phi_l)}, \tag{16}$$

are functions of ϕ_s, ϕ_l , and size ratio of the large to the small spheres $\lambda = D_l/D_s$ (see Faroughi and Huber 2014), and the stiffening functions $\eta(\Psi_i)$ are given by Eq. 7. The crowding factor appearing in the previous equations is Faroughi and Huber (2014)

$$C_f(\xi, \lambda) = \frac{\phi_{RCP}}{\phi_{bm}(\xi, \lambda)} \frac{\phi_{bm}(\xi, \lambda) - \phi'_\infty}{\phi_{RCP} - \phi'_\infty}, \tag{17}$$

$$= \frac{\phi_{bm}(\xi, \lambda) - \phi_{RCP}(2 - \phi_{RCP})}{\phi_{bm}(\xi, \lambda)(\phi_{RCP} - 1)}, \tag{18}$$

with $\phi_{RCP} \simeq 0.637$ the random close packing of a mono-disperse suspension of hard spheres, $\phi'_\infty = \phi_{RCP} + (1 - \phi_{RCP})\phi_{RCP}$ is the maximum packing of any possible random binary mixture of spheres, and $\phi_{bm}(\xi, \lambda)$ represents the maximum packing fraction for a suspension of size ratio λ and small particle proportion ξ and can be approximated by Faroughi and Huber (2014)

$$\phi_{bm}(\xi, \lambda) = \min \left[\frac{\phi_{RCP}}{1 - (1 - 1/\lambda)^{2.1} \xi}, \frac{\phi_{RCP}}{\phi_{RCP} + (1 - (1 - 1/\lambda)^{1.9} (1 - \xi))(1 - \phi_{RCP})} \right]. \tag{19}$$

The crowding factor has the limiting values $C_f(0, \lambda) = C_f(1, \lambda) = 1$. Figure 2 shows the excellent agreement between the model of Faroughi and Huber (solid lines) with the experimental data of Poslinski et al. (1988).

Performing the product in the right-hand side of Eq. 14, we can transform Faroughi and Huber model (Faroughi and Huber 2014) such that it takes the form of Eq. 6 with

$$\phi_{eff} = \Psi_{1,eff} + \Psi_{2,eff} - \Psi_{1,eff}\Psi_{2,eff}, \tag{20}$$

and

$$\Psi_{i,eff} = \frac{\Psi_i}{1 - c\Psi_i}. \tag{21}$$

This way of writing the Faroughi and Huber model will be useful to extend it to multimodal mixtures.

Multimodal suspensions

The original Faroughi and Huber model (Faroughi and Huber 2014) is limited to binary suspensions and hence the need for a generalization to treat the case of multimodal dispersions. Here, we propose an extension of the Faroughi and Huber model to treat multimodal mixtures. If we have a suspension of n groups of particles, each group of a different diameter, we may write, by extension of Eq. 14

$$\frac{\eta(\phi)}{\eta_0} = \eta(\Psi_1) \eta(\Psi_2) \cdots \eta(\Psi_n). \tag{22}$$

If Ψ_i were known, then the viscosity of the mixture would be also known. However, Ψ_i might be difficult if not

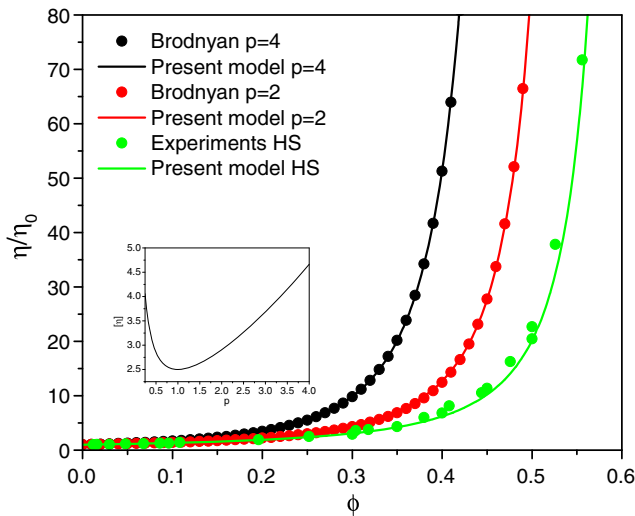


Fig. 1 Relative static low-shear viscosity η/η_0 as function of the volume fraction ϕ for three different cases: A pure suspension of hard spheres (HS). The green symbols represent experimental data given by de Kruif et al. (1985) and the green line is the relative viscosity as obtained by our model with $[\eta] = 2.5$ and $\phi_c = 0.637$. A pure suspension of aligned prolate ellipsoids with $p = 2$ and $p = 4$, as obtained from the empirical equation of Brodnyan (red and black symbols, respectively) and as given by our model with $[\eta] \simeq 3.2$ and $\phi_c \simeq 0.6$ (red line), and $[\eta] \simeq 4.7$ and $\phi_c \simeq 0.58$ (black line). Inset: Orientationally averaged intrinsic viscosity of ellipsoids as a function of the aspect ratio $p = b/a$

impossible to find, and thus, a convenient way to circumvent this difficulty is to obtain the viscosity by applying repeatedly the procedure used in the bimodal case.

As an example, consider a trimodal mixture whose components have volume fractions $\phi_1 = \phi_s$, $\phi_2 = \phi_m$, and

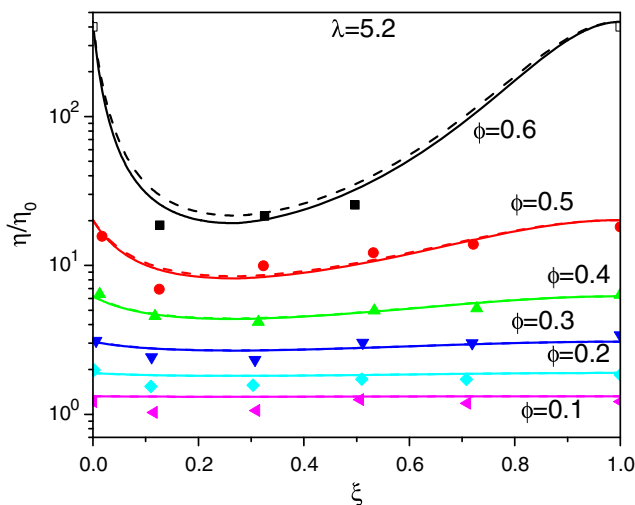


Fig. 2 Relative viscosity $\eta(\phi)/\eta_0$ as function of the volume fraction ϕ for a bimodal suspension. The solid lines are the model of Faroughi and Huber (2014). The dashed lines show the results of the present model with c' and c'' as given by Eqs. 29 and 30, respectively. Symbols: experimental measurements given by Poslinski et al. (1988). The open squares are extracted from Chong et al. (1971)

$\phi_3 = \phi_l$, with s, m , and l referring the small, medium, and large particles, respectively. In a first stage, we take the two species with smaller size and obtain the viscosity of the bimodal mixture as given by Faroughi and Huber model, Eqs. 14 and 15–19. In these expressions, we have to make the following substitutions, $\phi \rightarrow \phi_s + \phi_m$, $\xi \rightarrow \phi_s/(\phi_s + \phi_m)$, and $\lambda \rightarrow D_m/D_s$. In a second stage, we want to use this result together with the viscosity of the third component as if it were a two-component mixture and use Eq. 14 again to obtain the total viscosity. As explained at the end of the previous section, the viscosity of the already calculated binary mixture can be written as Eq. 6 if ϕ_{eff} is given by Eq. 20. In order to use this result to calculate the viscosity of the trimodal mixture, we need to write the obtained viscosity of the components 1 and 2 in exactly the same form as in Eq. 7. With this purpose, we define ϕ_{12} through the relation

$$\phi_{eff} = \frac{\phi_{12}}{1 - c\phi_{12}}, \tag{23}$$

where ϕ_{eff} is given by Eq. 20 and c by Eq. 8. Now, we approximate the viscosity of the trimodal mixture as

$$\frac{\eta(\phi_1 + \phi_2 + \phi_3)}{\eta_0} \simeq \eta(\Psi_{12}) \eta(\Psi_3), \tag{24}$$

where Ψ_{12} and Ψ_3 are the corrected volume fractions for the “second-stage bimodal mixture” with volume fractions ϕ_{12} and ϕ_3 , as prescribed by Eqs. 15 and 16. In this second stage, we make the following substitutions, $\phi \rightarrow \phi_{12} + \phi_3$, $\phi_s \rightarrow \phi_{12}$, and $\phi_l \rightarrow \phi_3$. Analogously, we replace $C_f(\xi, \lambda)$ in Eqs. 15 and 16 by

$$C_f = \frac{\phi_{RCP} \phi_{tm} - \phi'_{tm}}{\phi_{tm} \phi_{RCP} - \phi'_{tm}}, \tag{25}$$

which is the equivalent of Eq. 17 for trimodal mixtures. Here, ϕ_{tm} is the maximum packing of the trimodal mixture and ϕ'_{tm} is the maximum possible packing of any trimodal random mixture of spheres with infinite size ratios $\lambda_i = D_{i+1}/D_i \rightarrow \infty$. A discussion on how to calculate the trimodal maximum packing ϕ_{tm} for a given mixture can be found in Brouwers (2011, 2013). The maximum packing of any trimodal mixture of spheres is $\phi'_{tm} \simeq 0.95$, obtained for $\xi_s = 0.088$, $\xi_m = 0.243$, and $\xi_l = 0.669$, with $\xi_\alpha = \phi_\alpha/(\phi_1 + \phi_2 + \phi_3)$, the particle proportions for small, medium, and large size particles $\alpha = s, m$, and l) (Sudduth 1993c; Genovese 2012). Notice that one recovers the correct monomodal expression when the three components have identical sizes. We will name this approach “iterative model” to distinguish it from the approximation that will be introduced in “Padé approximation for the effective volume fraction”. In Appendix B we collect the necessary equations to calculate the viscosity of a trimodal mixture as described in the previous paragraphs.

In Fig. 3, we show the predicted viscosity for a trimodal mixture of spheres with $[\eta] = 2.5$, $\lambda_i = D_{i+1}/D_i \rightarrow \infty$

and the prescribed proportions $\xi_s = 0.088$, $\xi_m = 0.243$, and $\xi_l = 0.669$. For this system, $\phi_{tm} = \phi'_{tm}$ and thus $C_f = 0$. In this case, the present model without fitted parameters (solid line) is very close to the result proposed by Farris (1968) who considers that for non-interfering size ratios, the viscosity can be calculated as the product of the viscosity functions of the individual components, that is, $\eta(\phi_s + \phi_m + \phi_l) = \eta(\phi_l) \eta(\phi_m / (1 - \phi_l)) \eta(\phi_s / (1 - \phi_l - \phi_m))$, or more explicitly,

$$\eta(\phi_s + \phi_l) = \eta_0 \left(1 - \frac{\phi_l}{1 - c\phi_l}\right)^{-[\eta]} \times \left(1 - \frac{\phi_m / (1 - \phi_l)}{1 - c\phi_m / (1 - \phi_l)}\right)^{-[\eta]} \times \left(1 - \frac{\phi_s / (1 - \phi_l - \phi_m)}{1 - c\phi_s / (1 - \phi_l - \phi_m)}\right)^{-[\eta]}. \quad (26)$$

Summarizing, in this section we have obtained the viscosity of a multimodal dispersion by consecutive applications of an expression for the viscosity of a bimodal mixture. Starting from the two smaller components we obtain the corrected volume fractions of this binary system using,

$$c' = \frac{(\phi_{RCP} - 1) \{2(1 - \xi)\xi - 1 - 2C_f(\xi, \lambda) [(1 - \xi)^2 C_f(\xi, \lambda) + \xi(3 - 2\xi) - 1]\}}{\phi_{RCP}}, \quad (29)$$

and

$$c'' = \frac{(1 - \xi) [1 - C_f(\xi, \lambda)] [(1 - \xi) C_f(\xi, \lambda) + \xi]}{\phi_{RCP}^2} \times \{ [2\xi(\phi_{RCP} - 1) - 3\phi_{RCP} + 2] C_f(\xi, \lambda) - 2\xi(\phi_{RCP} - 1) + \phi_{RCP} - 1 \} \times \{ [2\xi(\phi_{RCP} - 1) - 3\phi_{RCP} + 2] C_f(\xi, \lambda) - 2\xi(\phi_{RCP} - 1) + 2\phi_{RCP} - 1 \}. \quad (30)$$

In the case in which $\xi = 0$ or $\xi = 1$, the previous expressions lead to $c' = c = (1 - \phi_{RCP}) / \phi_{RCP}$ and $c'' = 0$. Thus, Eq. 27 reduces to Eq. 4 and we recover the monomodal suspension result. Figure 2 shows the excellent agreement between the Padé-approximated Faroughi and Huber model (dashed lines) with the original Faroughi and Huber model (Faroughi and Huber 2014) (solid lines) and with the experimental data of Poslinski et al. (1988). In the rest of the manuscript, we will refer to the Padé-approximated expression as “present model” to distinguish it from the iterative approach described in “Multimodal suspensions”.

Even if the Faroughi and Huber model (Faroughi and Huber 2014) is preferable over its approximation in the

Faroughi and Huber prescription, Eqs. 15 and 16 (Faroughi and Huber 2014). Then, we obtain the effective volume fraction ϕ_{eff} , given by Eq. 20, and ϕ_{12} as given by Eq. 23 of this binary mixture. Then, we use this result together with the viscosity of the next larger component to calculate the corrected volume fractions and the viscosity of a trimodal mixture. Successive applications of this procedure allows to obtain the viscosity of n -modal mixtures.

Padé approximation for the effective volume fraction

In this section, we propose to approximate Faroughi and Huber model (Faroughi and Huber 2014) in a way that will be useful in the case in which there is not complete geometrical information of the system. The effective volume fraction for this model, (20), can be approximated using a (1,2) Padé approximant¹ to obtain

$$\phi_{eff} \simeq \frac{\phi}{1 - c(\phi)\phi}, \quad (27)$$

where

$$c(\phi) = c' + c''\phi, \quad (28)$$

with

binary mixture case, the (1,2) Padé approximated expression given in the present work can be immediately generalized to multimodal suspensions and to mixtures of particles with different intrinsic viscosities, and even if a closed form for c' and c'' might be difficult to find in the general mixture case, they can still be used as fitting parameters. At this point it is important to stress that Faroughi and Huber

¹A Padé approximant of order (m, n) to an analytic function $f(x)$ at $x = 0$ is defined by the rational function $R(x) = \frac{\sum_{j=0}^m a_j x^j}{1 + \sum_{k=1}^n b_k x^k}$ and gives the “best” approximation of a function by a rational function of given order.

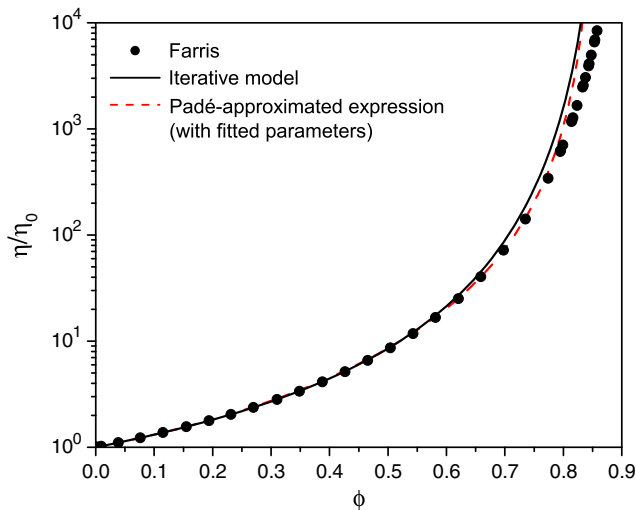


Fig. 3 Relative viscosity $\eta(\phi)/\eta_0$ vs. particle volume fraction ϕ of a trimodal suspension of spheres with infinite size ratios and particle proportions $\xi_s = 0.088$, $\xi_m = 0.243$, and $\xi_l = 0.669$. The symbols correspond to Farris prediction. The solid black line is the prediction of the iterative model obtained from two consecutive applications of the bimodal model as explained in the main text (see also Appendix B). No fitted parameters appear in this model. The dashed red line represents the Padé approximated expression with the fitted parameters $c' = 0.40$ and $c'' = -0.27$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.86$

model (Faroughi and Huber 2014) is restricted to the interval $1 \leq \lambda \leq 7$ and it overestimates the value of the critical packing. Indeed, the original Faroughi and Huber model can be transformed into the form of Eq. 6 if ϕ_{eff} is given by Eqs. 20 and 21 without requiring additional approximations. The divergence of the viscosity occurs when $\phi_{eff} = 1$. For

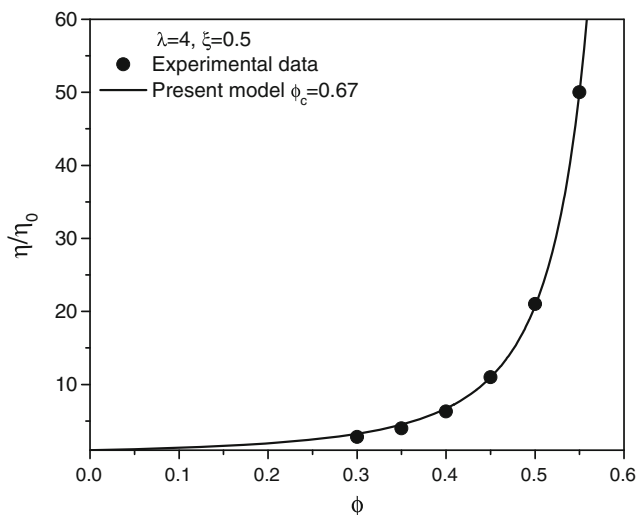


Fig. 4 Relative viscosity $\eta(\phi)/\eta_0$ as function of the volume fraction ϕ for a bidisperse suspension. The solid black line shows the results of the present model with $c' \simeq 0.81$ and $c'' \simeq -0.46$ which according to Eq. (31) corresponds to $\phi_c \simeq 0.67$. Symbols: experimental measurements given by Shapiro and Probstein (1992)

example, for the parameters of Fig. 4, $\lambda = 4$ and $\xi = 0.5$, the condition $\phi_{eff} = 1$ leads to the value $\phi_c(\xi, \lambda) \simeq 0.75$ which is above the maximum packing value obtained from Eq. 19, $\phi_{bm}(\xi, \lambda) \simeq 0.71$. Nonetheless, Faroughi and Huber model (Faroughi and Huber 2014) allowed us to obtain expressions for c' and c'' , (29) and (30). If a model for the binary system, different from that of Faroughi and Huber is used as starting point, different expressions would be obtained for c' and c'' . Alternatively, if we use them as fitting parameters, we can assess what would be the best possible agreement with experimental and simulation data using the (1, 2) Padé approximation, without relying in a specific starting binary model.

Summarizing, in this section we have shown that the viscosity of a binary mixture can be approximately calculated using Eqs. 4 and 6, except that the c in Eq. 4 is replaced by $c(\phi)$ as given by Eq. 28. In the case of spherical particles the parameters c' and c'' are given by Eqs. 29 and 30 but in general can be considered as fitting parameters that are related to the critical packing where the viscosity diverges by the relation

$$\phi_c(\xi, \lambda) = \frac{-(1 + c') + \sqrt{(1 + c')^2 + 4c''}}{2c''}. \tag{31}$$

The last equation has been derived by solving $\phi_{eff} = \frac{\phi_c(\xi, \lambda)}{1 - c(\phi_c(\xi, \lambda))\phi_c(\xi, \lambda)} = 1$, and using Eq. 28. If one makes the requirement that $\phi_c(\xi, \lambda) = \phi_{bm}(\xi, \lambda)$, where $\phi_{bm}(\xi, \lambda)$ is the maximum packing of a bidisperse suspension, then the number of fitting parameters reduces to only one. An additional fitting parameter as compared to the monomodal case is necessary since the maximum packing $\phi_{bm}(\xi, \lambda)$ can not be the only physical parameter in consideration. This is due to the fact that for a given value of $\phi_{bm}(\xi, \lambda)$, there are two different proportions of small spheres ξ_1 and ξ_2 , respectively, which share the same maximum packing, that is, $\phi_{bm}(\xi_1, \lambda) = \phi_{bm}(\xi_2, \lambda)$. In principle, there is no reason to expect exactly the same viscosity curves in both cases. Thus, the additional fitting parameter has the role of distinguishing between them.

From a practical point of view, sometimes it is preferable to use c' and $\phi_c(\xi, \lambda)$ as fitting parameters and then use Eq. 31 to find c'' , especially when the data do not extend to large volume fractions. This avoids the possibility that Eq. 31 gives complex values for $\phi_c(\xi, \lambda)$.

The transition from fluid to solid for mono-disperse and bidisperse suspensions of hard spheres was considered by Shapiro and Probstein (1992). Their experimental data are very well fitted by our model as shown in Fig. 4. The data correspond to a bimodal dispersion with size ratio of the large to the small spheres $\lambda = D_l/D_s = 4$ and the proportion of small spheres $\xi = 0.5$. The two fitting constants were $c' \simeq 0.81$ and $c'' \simeq -0.46$ which according

to Eq. 31 corresponds to $\phi_c(\xi, \lambda) \simeq 0.67$ (solid black curve). The obtained critical volume fraction is larger than the random close packing of a mono-disperse suspension of hard spheres, $\phi_{RCP} \simeq 0.637$. This is to be expected since a polydisperse system of spheres can be packed more closely than a mono-disperse suspension. We can examine how the fitting value for $\phi_c(\xi, \lambda)$ compares with the maximum packing of a bidisperse suspension. According to the approximation given by Eq. 19, for the system of Fig. 4 we get $\phi_{bm}(\xi, \lambda) \simeq 0.71$, a bit larger than the value obtained from the fitting (an alternative approximation for the maximum packing, proposed in Ref. (Qi and Tanner 2011), gives $\phi_{bm}(\xi, \lambda) \simeq 0.686$, closer to the value obtained from the fitting).

In Fig. 5 results for the high shear viscosity of bimodal mixtures (Probstein et al. 1994) where a very fine component is mixed with a coarse component, have been equally well fitted by the present model. For the composition with $\xi = 1$, we used the monomodal version of the model with $\phi_c(\xi, \lambda) \simeq 0.56$. For $\xi = 0.75$, the fitting constants were $c' \simeq 0.79$ and $c'' \simeq -0.38$ which according to Eq. (31) corresponds to $\phi_c(\xi, \lambda) \simeq 0.65$. Finally, for $\xi = 0.25$, the fitting constants were $c' \simeq 0.32$ and $c'' \simeq -0.003$ which corresponds to $\phi_c(\xi, \lambda) \simeq 0.76$.

Previous studies on the viscosity of multimodal dispersions have found that typical models for the viscosity, like the Krieger and Dougherty expression, (10), fail to give good fits to the experimental data unless the intrinsic

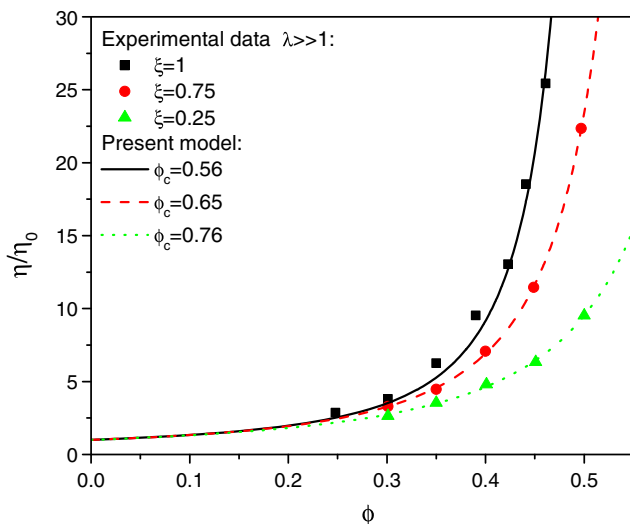


Fig. 5 High shear relative viscosity $\eta(\phi)/\eta_0$ as function of the volume fraction ϕ for three binary mixtures of large and small spheres. *Black solid line*: present model with $\phi_c \simeq 0.56$. *Red dashed line*: present model with $c' \simeq 0.79$ and $c'' \simeq -0.38$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.65$. *Green dotted line*: present model with $c' \simeq 0.32$ and $c'' \simeq -0.003$ which corresponds to $\phi_c \simeq 0.76$. *Symbols*: experimental measurements given by Probstein et al. (1994) for three different compositions as indicated

viscosity $[\eta]$ is replaced by an empirical value that is usually different than its nominal value (Gondret and Petit 1997; He and Ekere 2001; Pishvaei et al. 2006). It is argued that the intrinsic viscosity depends on the absolute size of the particles, particularly for colloidal particles, due to surface chemical forces or electrostatic forces (He and Ekere 2001). If instead of using the appropriate expression for the crowding term for binary suspensions, given by Eq. 28, we use the crowding constant appropriate for the monomodal case, given by Eq. 8, then a good fit to Shapiro and Probstein's data is obtained only if $\phi_c(\xi, \lambda) \simeq 0.67$ and $[\eta] \simeq 2.75$. This suggests that the use of an intrinsic viscosity $[\eta]$ with a value larger than the nominal to fit experiments for bimodal or other polydisperse suspensions could be the result of using expressions designed for monomodal suspensions with a constant crowding factor, and not necessarily the result of additional physical effects.

We can also compare the best fit obtained using the model with c' and c'' as fitting parameters with Farris model for the trimodal mixture of Fig. 3. In this case the fitted constants are $c' = 0.40$ and $c'' = -0.27$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.86$. It can be observed that the approximation reproduces accurately Farris' results up to $\phi \simeq 0.8$.

The rheological properties of aqueous polystyrene latex dispersions from three synthetic batches with varying

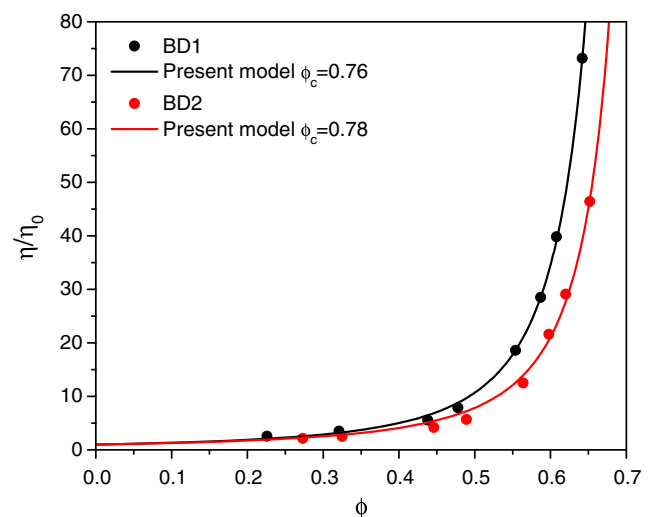


Fig. 6 High shear relative viscosity $\eta(\phi)/\eta_0$ as function of the volume fraction ϕ for two systems with different polydispersity. A moderately broad distribution (BD1) of particles with average size 400 nm and a degree of polydispersity 0.301, and a very broad distribution (BD2) of particles with the same average size but increased polydispersity 0.484, *Black line*: present model with $c' \simeq 0.46$ and $c'' \simeq -0.18$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.76$. *Red line*: present model with $c' \simeq 0.10$ and $c'' \simeq 0.24$ which corresponds to $\phi_c \simeq 0.78$. *Symbols*: experimental measurements given by Luckham and Ukeje (1999)

degrees of polydispersity were experimentally studied by Luckham and Ukeje (1999). In Fig. 6 we show their data for the high shear relative viscosity for two distributions: a moderately broad distribution (BD1) consisting of particles with size 400 nm and with a polydispersity of 0.301, and a very broad distribution (BD2) consisting of particles of the same average size but with a polydispersity of 0.485. The lines correspond to the best fit of the present model given by Eqs. 6, 27, and 28 with $c' \simeq 0.46$ and $c'' \simeq -0.18$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.76$ for BD1, and $c' \simeq 0.10$ and $c'' \simeq 0.24$ which corresponds to $\phi_c \simeq 0.78$ for BD2. Note that the critical volume fraction ϕ_c is larger, due to the polydispersity, than the corresponding high shear value for monomodal suspensions $\phi_c = 0.7405$. Also, notice that in the BD2 case, $c'' > 0$, which contrasts with the fit of all the other cases and with the result given by Eq. 30 for the bimodal case which always evaluates to negative values. Since the value $c'' \simeq 0.24$ originates on a fitting procedure and not on an underlying derivation, it is not clear if this discrepancy is a real consequence of the broadness of the distribution, a possible inaccuracy of the fitted data or a limitation of the model.

Another application of the model considers a coal slurry studied in Papachristodoulou and Trass (1984) with a particle size distribution given by a Rosin-Rammler distribution (Rosin and Rammler 1933; Vesilind 1980). 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 typically present in coal slurries. Therefore, the experimental viscosities reported in Papachristodoulou and Trass (1984) are the relative Bingham plastic viscosities. In Fig. 7, the Bingham viscosity is compared with the best fit of the present model given by Eqs. 6, 27, and 28 with an intrinsic viscosity $[\eta] = 2.5$. The fitting parameters were $c' \simeq 0.98$ and $c'' \simeq -0.81$ which according to Eq. 31 corresponds to $\phi_c \simeq 0.71$. Again, the data are very well fitted by our model.

Mixtures of particles with different intrinsic viscosities

We propose a convenient generalization of the previous section to treat the case of particles with different intrinsic viscosities as in the case of mixtures of particles with different shapes or with different porosities. For simplicity let us consider a binary system and assume that the viscosity can again be written as the product of two monomodal viscosities with corrected volume fractions that take into account crowding between different species

$$\frac{\eta(\phi_1 + \phi_2)}{\eta_0} = \eta(\Psi_1) \eta(\Psi_2). \tag{32}$$

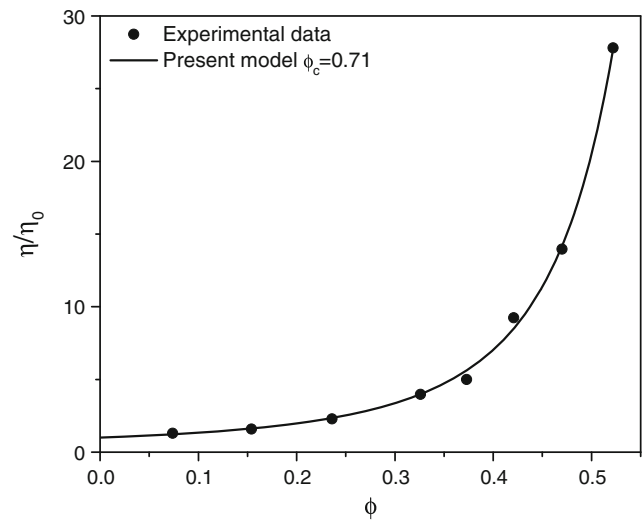


Fig. 7 Relative viscosity $\eta(\phi)/\eta_0$ as a function of the volume fraction ϕ of coal particles in a coal slurry. Comparison of the fitting of our model (solid line) to experimental data for coal slurry with a Rosin-Rammler distribution (Papachristodoulou and Trass 1984). Solid line: present model with $c' \simeq 0.98$ and $c'' \simeq -0.81$, which according to Eq. 31 corresponds to $\phi_c \simeq 0.71$. Symbols: experimental measurements given by (Papachristodoulou and Trass 1984)

This can be expressed as

$$\begin{aligned} \frac{\eta(\phi_1 + \phi_2)}{\eta_0} &= (1 - \Psi_{1,eff})^{-[\eta]_1} (1 - \Psi_{2,eff})^{-[\eta]_2} \\ &= \left[(1 - \Psi_{1,eff})^{[\eta]_1/[\eta]_{eff}} (1 - \Psi_{2,eff})^{[\eta]_2/[\eta]_{eff}} \right]^{-[\eta]_{eff}} \\ &\simeq \left(1 - \frac{[\eta]_1}{[\eta]_{eff}} \Psi_{1,eff} - \frac{[\eta]_2}{[\eta]_{eff}} \Psi_{2,eff} + \dots \right)^{-[\eta]_{eff}}, \tag{33} \end{aligned}$$

where

$$[\eta]_{eff} = [\eta]_1 \xi_1 + [\eta]_2 \xi_2, \tag{34}$$

is the effective or averaged intrinsic viscosity of the mixture. Here, $[\eta]_i$ and $\xi_i = \phi_i/(\phi_1 + \phi_2)$ are the intrinsic viscosity and proportion of component i , respectively, with $\sum \xi_i = 1$, and

$$\Psi_{i,eff} = \frac{\Psi_i}{1 - c_i \Psi_i}, \tag{35}$$

with c_i representing the self crowding of species i .

Now we define

$$\phi_{eff} = \frac{[\eta]_1}{[\eta]_{eff}} \Psi_{1,eff} + \frac{[\eta]_2}{[\eta]_{eff}} \Psi_{2,eff} + \dots, \tag{36}$$

so that the viscosity can be written as

$$\eta(\phi) = \eta_0 (1 - \phi_{eff})^{-[\eta]_{eff}}. \tag{37}$$

Thus, one has the same functional form as for the mono-disperse system except that $[\eta]$ is replaced by $[\eta]_{eff}$, given by Eq. 34. Although the corrected volume fractions, Ψ_i , are

not known in this case, it is reasonable to assume that ϕ_{eff} can be approximated again by a (1, 2) Padé approximant to recover Eq. 27. Note that in this approximation, the definitions (36) and (20) coincide if the intrinsic viscosities are the same. Expressions for c' and c'' will depend not only on the geometrical characteristics of the system under consideration like size ratio, composition, aspect ratio of the particles, but also on $[\eta]_i$. Presumably, a procedure similar to the one proposed in Faroughi and Huber (2014) for spheres, would allow to find such expressions for other mixtures.

Although in this case we have not found experimental results to compare with and thus it is not possible to obtain the values for c' and c'' from a fit, we can exemplify the application of the model with an idealized system. Consider the case of a mixture of spheres with randomly aligned ellipsoids of aspect ratio $p = 4$ for which $[\eta] \simeq 4.7$. We have chosen ellipsoids with this particular aspect ratio because their maximum random packing closely corresponds to that of the spheres (Donev et al. 2004; Wouterse et al. 2007), i. e., $\phi_{RCP} \simeq 0.637$, thus, $c_i \simeq c = (1 - \phi_{RCP})/\phi_{RCP}$. We define the size ratio of the large to the small species as $\lambda \equiv (V_l/V_s)^{1/3}$, with V_α the volume of species α . Note that we recover $\lambda = D_l/D_s$ in the case of mixtures of spheres. In the left panel of Fig. 8 we plot the viscosity for spheres and ellipsoids with the same volume ($\lambda = 1$), as predicted by Eq. 37. For $\lambda = 1$, the crowding effects of a binary mixture of spheres reduces to that of the monomodal case. We assume that the same occurs for the mixture of ellipsoids and spheres, thus $c' = c = (1 - \phi_{RCP})/\phi_{RCP}$ and $c'' = 0$, but

with the averaged intrinsic viscosity given by Eq. 34. Five cases with ellipsoidal particle proportions $\xi = 0, 0.25, 0.5, 0.75$, and 1 are shown. As expected, the curve for the viscosity gradually transforms from the pure spherical particle case to the pure ellipsoidal particle one. In the right panel of Fig. 8 we consider the opposite situation, that is, a mixture of non interfering size ratio $\lambda \rightarrow \infty$, which corresponds to a mixture of small ellipsoids with large spheres or to a mixture of small spheres with large ellipsoids. Following Farris (1968), in this case, the viscosity can be approximated by the product of the viscosity functions of the individual components, that is, $\eta(\phi_s + \phi_l) = \eta(\phi_l) \eta(\phi_s/(1 - \phi_l))$, with ϕ_s and ϕ_l the volume fractions of the small and large components, respectively. The symbols correspond to the results obtained in this way and the solid lines correspond to the fitting of Eqs. 37, 34, and 27 to the data obtained with the Farris procedure. The fitting constants are $c' = 0.48$ and $c'' = -0.25$ for the case of small ellipsoids and large spheres, and $c' = 0.02$ and $c'' = 0.34$ for the case of small spheres and large ellipsoids. The good agreement shows that the (1, 2) Padé approximation works remarkably well as a fitting tool also in this case. Note that an equimolar mixture of small ellipsoids with large spheres have larger viscosity than a mixture of small spheres and large ellipsoids. This conclusion could not be obtained with a monomodal model since it cannot distinguish between the two situations. The green curve shows the prediction of a monomodal model with the same maximum packing $\phi_{bm}(\xi = 0.5, \lambda \rightarrow \infty) \simeq 0.78$ and average intrinsic viscosity.

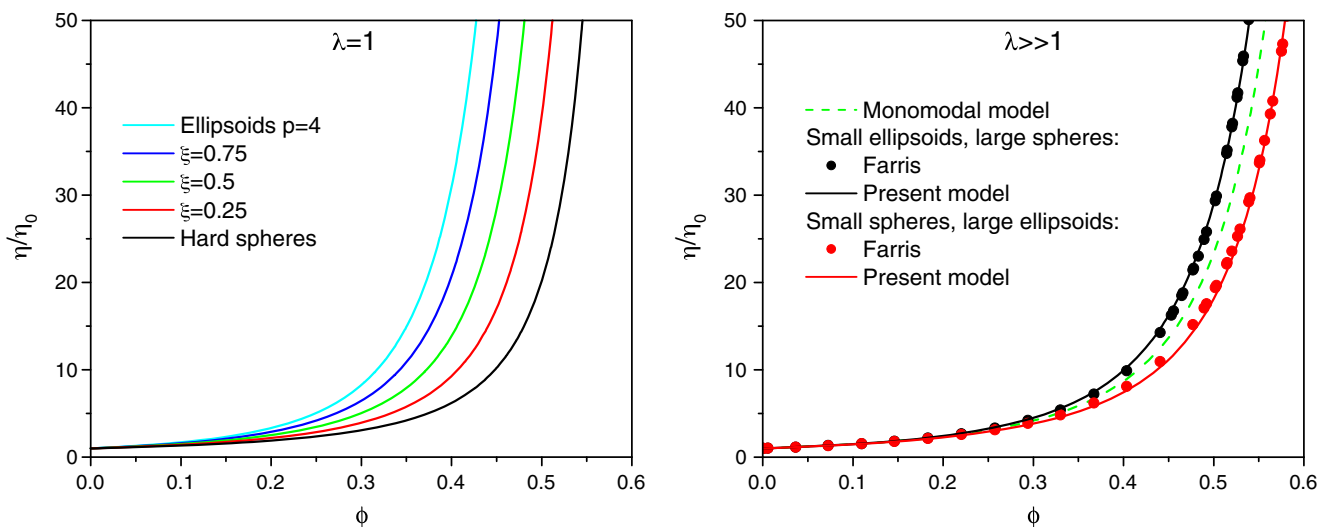


Fig. 8 Relative viscosity $\eta(\phi)/\eta_0$ vs. particle volume fraction ϕ for a mixture of spheres and randomly oriented ellipsoids with aspect ratio $p = 4$, as predicted by Eq. 37. *Left panel*: Spherical particles and ellipsoids of the same volume ($\lambda = 1$) and ellipsoidal particle proportions $\xi = 1, 0.75, 0.5, 0.25$, and 0. *Right panel*: Ellipsoidal particle proportion $\xi = 0.5$ and $\lambda \rightarrow \infty$. The black curve corresponds to small ellipsoids mixed with large spheres as given by Eq. 37 with fitting

constants $c' = 0.48$ and $c'' = -0.25$. The *red curve* corresponds to small spheres mixed with large ellipsoids as given by Eq. 37 with fitting constants $c' = 0.02$ and $c'' = 0.34$. A monomodal model with the same $\phi_{bm}(\xi = 0.5, \lambda \rightarrow \infty) \simeq 0.78$ can not distinguish between the two situations (*green curve*). The *symbols* represent the results obtained from the product of the viscosity functions for each component as specified by Farris (1968)

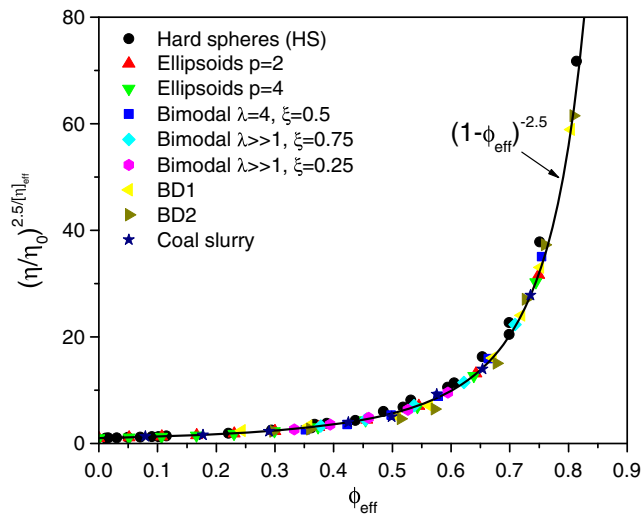


Fig. 9 Master curve for the viscosity. η represents the static low shear viscosity or high shear viscosity depending on the case, as discussed in the text. Symbols are all the data considered in this work

Finally, we would like to stress that a very appealing feature of Eqs. 4 and 37 is that they allow to plot η in a universal curve independent of c' , c'' , and $[\eta]_{eff}$ if we express it as function of ϕ_{eff} instead of ϕ . This is done in Fig. 9 where ϕ_{eff} is calculated using Eq. 4 with the parameters that best fitted the corresponding data for all the systems considered in this work. In all cases, the data collapses very nicely into the master curve.

Conclusions

In this paper we have described a methodology to obtain the viscosity of multicomponent suspensions as a function of particle concentration. The procedure consists in successive applications of expressions for the viscosity of binary mixtures, originally written as the product of monomodal stiffening functions. This iterative procedure was explicitly shown in the case of trimodal mixtures. Its application to arbitrary mixtures requires the detailed knowledge of size ratios and compositions. When this information is unknown the model can still be used as a fitting tool. With that purpose, the final expression for the viscosity is written in terms of an effective volume fraction that can be further approximated by the use of a (1,2) Padé approximant. This approach allows to incorporate the crowding effects due to different species in a volume fraction dependent crowding factor that can be used as fitting parameter to match experimental or simulation data. This approximation is summarized in Eqs. 27, 28, 34, and 37 and shows that the same functional form used for a system with a single species is still a useful approximation for the case of mixtures, provided that the

crowding parameter is a volume fraction dependent quantity approximated by Eq. 28. The viscosity of mixtures of particles with different shapes, sizes, porosities, or any other factor that may produce a distribution of intrinsic viscosities can also be considered with this procedure. Note that even if the use of a (1,2) Padé approximation produces accurate results in a large range of volume fractions, a higher order approximation would be required to decrease possible discrepancies at the highest concentrations.

Although we have shown the predictive nature of the model in the case of bimodal and trimodal mixtures, a more convenient way of calculating c' and c'' for the general multicomponent case is still missing.

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Appendix A: Obtention of Eq. 3 based on Mooney’s procedure

Here we give an alternative derivation of our starting equation (3) which is also different from our original derivation in Mendoza and Santamaría-Holek (2009) and is based in a procedure first introduced by Mooney for the case of hard spheres (Mooney 1951). His analysis considers space-crowding effects of the suspended particles on each other and there is no restriction imposed on the concentration. The argument makes use of a functional equation which must be satisfied if the final viscosity is to be independent of the sequence of stepwise additions of partial volume fractions of the particles to the suspension. We repeat his argument here for the reader’s convenience. In extending Einstein’s expression to higher concentrations Mooney describes the first-order interactions as essentially a crowding effect as follows (Mooney 1951): If identical spheres of radius r_1 are added to a suspension in two stepwise additions with volume fractions ϕ_1 and ϕ_2 , the addition of the first fraction will increase the viscosity by a factor $H(\phi_1) = \eta_1/\eta_0$. If the second fraction, ϕ_2 , is added, there will be a further increase in viscosity. This increase can be attributed in part as being due to the increase in viscosity, due to ϕ_2 , of the remaining liquid in the space not occupied by ϕ_1 . This increase will be of the form $H(\varphi_{21})$, where $\varphi_{21} = \frac{\phi_2}{1-c\phi_1}$ is the concentration of ϕ_2 in the remaining liquid and c accounts for the crowding that spheres added in the first step produce in the spheres added in the second step. But the crowding of fractions ϕ_1 and ϕ_2 being mutual, introducing ϕ_2 reduces the free volume accessible to ϕ_1 , and the effective concentration of ϕ_1 in the liquid is then $\varphi_{12} = \frac{\phi_1}{1-c\phi_2}$. To take account of this effect we must now replace $H(\phi_1)$ by $H(\varphi_{12})$. The product $H(\varphi_{12}) \times H(\varphi_{21})$ is the viscosity of a suspension of total concentration,

$\phi_1 + \phi_2$, and hence this product must be equal to $H(\phi_1 + \phi_2)$. This is

$$H(\phi_1 + \phi_2) = \eta_{12}/\eta_0 = H(\varphi_{12}) \times H(\varphi_{21}) \quad (38)$$

$$= H\left(\frac{\phi_1}{1 - c\phi_2}\right) \times H\left(\frac{\phi_2}{1 - c\phi_1}\right). \quad (39)$$

It is found that this functional equation is satisfied if H has the form (Mooney 1951)

$$H(\phi) = \frac{\eta}{\eta_0} = \exp\left(\frac{[\eta]\phi}{1 - c\phi}\right), \quad (40)$$

where $[\eta]$ is chosen to agree with Einsteins's equation for very dilute suspensions ($[\eta] = 2.5$ for spheres). Thus, expanding Eq. 40 we can write

$$\frac{\eta}{\eta_0} = 1 + \frac{[\eta]\phi}{1 - c\phi} + \frac{1}{2} \left(\frac{[\eta]\phi}{1 - c\phi}\right)^2 + \dots, \quad (41)$$

$$\simeq 1 + \frac{[\eta]\phi}{1 - c\phi}, \quad (42)$$

where we have just kept the first two terms, which is valid for dilute systems. Note that this last equation can be written as

$$\eta(\phi) \simeq \eta_0 (1 + [\eta]\phi_{eff}), \quad (43)$$

where ϕ_{eff} is given by Eq. 4. Thus, Eq. 43 is formally identical to Eq. 3, that is used as starting point of the recursive procedure.

Appendix B: Summary of the relations to calculate the viscosity of trimodal suspensions

Here we collect all the relations necessary to calculate the viscosity of trimodal suspensions using the iterative procedure described in “Multimodal suspensions.” In a first stage, we calculate the corrected volume fractions for the two smaller components of the mixture using Faroughi and Huber prescription (Faroughi and Huber 2014)

$$\Psi_s = \frac{\phi_s + C_f(\xi, \lambda)\phi_m}{1 - (1 - C_f(\xi, \lambda))(\phi_m - C_f(\xi, \lambda)\phi_m)} \quad (44)$$

and

$$\Psi_m = \frac{\phi_m - C_f(\xi, \lambda)\phi_m}{1 - C_f(\xi, \lambda)(\phi_s + C_f(\xi, \lambda)\phi_m)}, \quad (45)$$

where $\xi = \phi_s/(\phi_s + \phi_m)$ and the size ratio of the medium to the small spheres is $\lambda = D_m/D_s$. The crowding factor appearing in the previous equations is Faroughi and Huber (2014)

$$C_f(\xi, \lambda) = \frac{\phi_{bm}(\xi, \lambda) - \phi_{RCP}(2 - \phi_{RCP})}{\phi_{bm}(\xi, \lambda)(\phi_{RCP} - 1)}, \quad (46)$$

with $\phi_{RCP} \simeq 0.637$ the random close packing of a mono-disperse suspension of hard spheres and $\phi_{bm}(\xi, \lambda)$ is given by Eq. 19.

We write the effective volume fraction of the bimodal mixture

$$\phi_{eff} = \Psi_{s,eff} + \Psi_{m,eff} - \Psi_{s,eff}\Psi_{m,eff}, \quad (47)$$

where

$$\Psi_{i,eff} = \frac{\Psi_i}{1 - c\Psi_i}, \quad (48)$$

with $i = s, m$, and c is given by Eq. 8. We write

$$\phi_{12} = \frac{\phi_{eff}}{1 + c\phi_{eff}}, \quad (49)$$

and approximate the viscosity of the trimodal mixture as

$$\frac{\eta(\phi_s + \phi_m + \phi_l)}{\eta_0} \simeq \eta(\Psi_{12})\eta(\Psi_l), \quad (50)$$

where the stiffening functions $\eta(\Psi_i)$ are given by Eq. 7. Here,

$$\Psi_{12} = \frac{\phi_{12} + C_f\phi_l}{1 - (1 - C_f)(\phi_l - C_f\phi_l)} \quad (51)$$

and

$$\Psi_l = \frac{\phi_l - C_f\phi_l}{1 - C_f(\phi_{12} + C_f\phi_l)}, \quad (52)$$

where

$$C_f = \frac{\phi_{RCP}}{\phi_{tm}} \frac{\phi_{tm} - \phi'_{tm}}{\phi_{RCP} - \phi'_{tm}}, \quad (53)$$

with ϕ_{tm} the maximum packing of the trimodal mixture and $\phi'_{tm} \simeq 0.95$ the maximum possible packing of any trimodal random mixture of spheres with infinite size ratios $\lambda_i = D_{i+1}/D_i \rightarrow \infty$.

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