

# RHEOLOGY OF CONCENTRATED EMULSIONS OF SPHERICAL DROPLETS

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## ABSTRACT:

We propose a viscosity model accounting for experiments of emulsions of two immiscible liquids at arbitrary volume fractions. The model is based on a recursive-differential method formulated in terms of the appropriate scaling variable which emerges from an analysis of excluded volume effects in the system. This variable, called the effective filling fraction, incorporates the geometrical information of the system which determines the maximum packing and reduces to the bare filling fraction for infinitely diluted emulsions. The agreement of our model for the viscosity with experiments and previous theories is good for all the range of volume fractions and viscosity ratios.

## ZUSAMMENFASSUNG:

Ein Viskositätsmodell wird vorgestellt, das die experimentellen Resultate für Emulsionen zweier unmischbarer Flüssigkeiten bei beliebigen Volumenkonzentrationen beschreibt. Das Modell basiert auf einer rekursiv-differentiellen Methode, in die die entsprechende Skalierungsvariable eingeht, die aus der Analyse des Effekts des ausgeschlossenen Volumens hervorgeht. Diese Variable, die effektiver Füllstoffgehalt genannt wird, berücksichtigt die geometrische Information des Systems, die die maximale Packungsdichte bestimmt, und entspricht dem wahren Füllstoffgehalt bei sehr verdünnten Emulsionen. Die Übereinstimmung unseres Modells mit Experimenten ist für den gesamten Volumenkonzentrations- und Viskositätsverhältnissbereich gut.

## RÉSUMÉ:

Nous proposons un modèle de viscosité qui s'applique à des expériences sur des émulsions de deux liquides immiscibles avec des fractions volumiques arbitraires. Le modèle est basé sur une méthode différentielle-réursive, formulée en fonction de une variable d'échelle appropriée qui vient d'une analyse d'effets de volume exclus dans le système. Cette variable, appelée fraction de remplissage effective, incorpore une information géométrique du système qui détermine le remplissage maximum et se résume à la simple fraction de remplissage pour des émulsions infiniment diluées. L'accord entre notre modèle pour la viscosité et les expériences, ainsi que les théories précédentes, est bon pour toutes les gammes de fractions volumiques et de ratios de viscosité.

**KEY WORDS:** emulsions, viscosity, effective medium theory

## 1 INTRODUCTION

Due to the central role that they play in many technological processes, the rheology of solid-liquid suspensions is a subject for which a large amount of work has been produced [1–8]. However, the rheological properties of emulsions of immiscible liquids have received much less attention, despite the fact that they are also very important in many industrial applications [1, 2, 9–17].

Emulsions present an interesting rheological behavior with characteristics similar to those of the solid-liquid suspensions. In particular, the

relative viscosity  $\eta_r(\phi)$  of emulsions of nearly spherical droplets also diverges at certain critical value of the filling fraction:  $\eta_r(\phi \rightarrow \phi_c) \rightarrow \infty$ . Also similar is the fact that for very dilute emulsions where the interaction between neighboring drops is absent, the relative viscosity follows the Einstein's like relation [10]

$$\eta_r(\phi) = \frac{\eta(\phi)}{\eta_c} = \left( 1 + \frac{1+2.5K}{1+K} \phi \right) \quad (1)$$

where the viscosity ratio  $K = \eta_d/\eta_c$  contains the viscosity  $\eta_d$  of the dispersed phase and the vis-

cosity  $\eta_c$  of the continuous phase. Equation 1 has been originally introduced by Taylor [10] and is called Taylor's equation. The difference between Einstein's and Taylor's expressions lies in the fact that in the later relation the coefficient multiplying the filling fraction  $\phi$  incorporates information about the nature of the dispersed phase through its viscosity  $\eta_d$ . However, when the viscosity of the dispersed phase is much larger than the viscosity of the continuous phase,  $K \rightarrow \infty$ , one recovers Einstein's expression  $\eta(\phi) = \eta_o(1 + 2.5\phi)$ .

Although of fundamental importance, Taylor's equation does not reproduce the behavior of concentrated emulsions. The reason for this is that Equation 1 does not contain any information on the interactions between droplets that are present in the concentrated case. These interactions may induce micro or mesostructures controlling the response of the system to a given external perturbation, and may depend on the perturbation imposed on the system, as it is well known from their non-Newtonian rheological properties [18].

Due to the complexity inherent to the rheology of emulsions and solid particle suspensions, computer simulations emerged as a powerful instrument to propose new models and to understand and predict many features of their behavior in terms of the mentioned micro and mesostructures [6, 18–21]. The quantitative description of drop deformation is an excellent example to illustrate the power of combining numerical methods with experiments that allows the determination of capillary numbers and other physical quantities [22] essential for the correct description and prediction of the rheological properties of dilute and concentrated emulsions.

From the theoretical viewpoint, several efforts have been done in order to incorporate these interactions and account for system's properties [11, 12]. Recent advances in obtaining analytical expressions for the volume fraction dependence of the viscosity of emulsions were developed [17]. Due to the complex nature of the system and the difficulty inherent to include hydrodynamic interactions in explicit way [23], these recent analytical expressions were derived within the frame of differential effective medium theories which avoid the many-body problem by adopting the effective medium hypothe-

sis. Alternative approaches based on critical phenomena have also been developed [24]. Although these theories do not give an understanding of the microstructure of the system, as simulations do, they may provide us with simple powerful formulas that can be directly compared with experiments and used to test simulation results. One of these recent theories is presented in [14], where a formula for the viscosity is obtained based on the mentioned differential effective medium procedure

$$\eta_r(\phi) \left( \frac{2\eta_r(\phi) + 5K}{2 + 5K} \right)^{3/2} = (1 - \phi)^{-5/2} \quad (2)$$

that takes into account the effect of the viscosity ratio  $K$ . Although this formula gives a reasonable description of experimental results, it fails to adequately describe experimental data at large concentrations. Pal improved this model by incorporating "crowding effects" through a critical filling fraction  $\phi_c$  [17]:

$$\eta_r(\phi) \left( \frac{2\eta_r(\phi) + 5K}{2 + 5K} \right)^{3/2} = \left( 1 - \frac{\phi}{\phi_c} \right)^{-(5/2)\phi_c} \quad (3)$$

This model (called model 2) improves considerably the quantification of the rheological properties of emulsions of two immiscible liquids even at high filling fractions. However, comparison with experiments shows that it underestimates the value of the viscosity at intermediate volume fractions [17]. Pal also proposed the following model giving excellent agreement with experimental data at large volume fractions [16]

$$\eta_r(\phi) \left( \frac{2\eta_r(\phi) + 5K}{2 + 5K} \right)^{3/2} = \left( 1 - \frac{\phi}{\phi_c} \right)^{-5/2} \quad (4)$$

however, it does not reduce to the correct Taylor's expression at low concentrations. Having in mind all these considerations, in this article we propose an improvement to the differential effective-medium model that gives the correct divergence at the critical concentration, produces a better description of experiments and reduces to the right Taylor's expression at low concentrations.

## 2 ALTERNATIVE DIFFERENTIAL VISCOSITY MODEL: SCALING AND EXCLUDED VOLUME EFFECTS

In his original article, Taylor calculated the viscosity of a dilute suspension of fluid drops under three main assumptions: i) The drops are small enough to maintain a spherical shape due to surface tension, ii) no slipping exists at the interface between the drops and the host fluid, and iii) tangential stresses are continuous at the surface of the drop. Then, using hydrodynamic results for the velocity field out and inside of the sphere, he obtained the corresponding expressions for the components of the stress acting across unit area of the spherical surface and imposed on the tangential components through the continuity condition. The normal stress is not continuous at the surface, fact which is ultimately related to the surface tension. As a result of these impositions, Taylor obtained the explicit expressions for the four constants appearing in the formulas giving the components of the stress tensor. Then, following Einstein's arguments, Taylor showed that in the case of liquid droplets, the factor 2.5 that multiplies the volume fraction  $\phi$  in Einstein's relation  $\eta_r(\phi) = [1 + 2.5\phi]$  must be replaced by  $F = -2.5[\eta_d + 2.5\eta_c]/[\eta_d + \eta_c]$ . This replacement leads to Equation 1.

The procedure followed by Taylor is very interesting since it emphasizes two different ingredients entering into the suspended phase correction  $\Delta\eta (= \eta_r - 1)$  in Equation 1

$$\Delta\eta(\phi) = \frac{1+2.5K}{1+K} \phi \quad (5)$$

The first ingredient is that the boundary conditions at the surface of the drop determine the stresses applied on it and thus control the contribution due of a single drop to the total stress of the composite system: particle plus continuous phase. The second ingredient comes from the consideration of the contribution of  $N$  droplets to the composite system. Following Landau [25], one may argue that the contribution by the drops  $\Pi_d^V$  to the total stress tensor comes from an average over the volume  $V$  of the system in the form

$$\Pi_d^V \approx \frac{N}{V} \int \Pi_d^{(i)} dV \quad (6)$$

where we represented the single drop contribution to the stress tensor by  $\Pi_d^{(i)}$  which is proportional to the velocity gradient imposed on the system. The upper  $V$  in Equation 6 stands for the volume average and the factor  $N$  accounts for the contribution of the  $N$  independent particles. However, this average is strictly valid only when the system is made of point particles. This restricts the validity of Equation 6 to very diluted systems.

Thus, if one considers that a drop has a volume  $V_d$  then the average must be performed over the free volume accessible to the particles, which is defined by:  $V_{free} = V - cNV_d$ . Here,  $c$  is a constant taking into account the fact that the complete free volume can not be filled with drops. Note that, for different symmetries of the suspended particles, the value of the constant  $c$  will be different. This is specially important in the case of drops which may change their shape when subjected to strong shears. Therefore,  $c$  contains information about the maximum packing of drops the system may allocate.

Therefore, if excluded volume effects are taken into account, the suspended phase contribution to the stress tensor is given by

$$\Pi_d^{V_{free}} \approx \frac{N}{V - cNV_d} \int \Pi_d^{(i)} dV \quad (7)$$

For finite-sized droplets, this relation leads to the result that the Taylor expression scales with the excluded volume factor  $\phi/(1 - c\phi)$  instead of  $\phi$ , and thus gives the following expression for the viscosity of an emulsion

$$\eta_r(\phi) = \left[ 1 + \frac{1+2.5K}{1+K} \left( \frac{\phi}{1-c\phi} \right) \right] \quad (8)$$

Taylor's formula is then recovered in the limit of very small volume fractions ( $\phi \rightarrow 0$ ). Equation 8 explains the experimental fact that the viscosity diverges at volume fractions  $\phi < 1$ , implying that this effect is related to the excluded volume effects. Similar arguments used in the case of solid particles lead to excellent agreement between experiments and theory [8].

The central result of the present analysis is Equation 8, which shows that the scaling variable

incorporating excluded volume effects and describing the dependence of the viscosity of an emulsion of finite-sized droplets on the filling fraction is the effective filling fraction

$$\phi_{\text{eff}} = \frac{\phi}{1 - c\phi} \quad (9)$$

where  $c$  is given by

$$c = \frac{1 - \phi_c}{\phi_c} \quad (10)$$

with  $\phi_c$  the filling fraction at the divergence. As mentioned before, the parameter  $c$  is a structural or crowding factor that takes into account the arrangements of the droplets in the emulsion. Expression 10 is obtained by imposing the condition  $\phi_{\text{eff}} = 1$  at  $\phi_c$ . The importance of  $\phi_{\text{eff}}$  is that it incorporates correlations between particles by taking into account geometrical information having the characteristic that  $\phi_{\text{eff}} \sim \phi$  at low volume fractions and  $\phi_{\text{eff}} = 1$  at maximum packing. In terms of the volume of the sample this simple means that the important quantity is the available volume that the particles can occupy and not the total volume. At low filling fractions the available volume equals the total volume and therefore  $\phi_{\text{eff}} \sim \phi$  while at high filling fractions the particles occupy essentially all the available space and therefore  $\phi_{\text{eff}} = 1$ . This quantity plays an important role in determining the dependence of the viscosity of the emulsion on the filling fraction, as we will show next.

At low volume fractions, the shear viscosity  $\eta$  of an emulsion is given by Equation 8. In order to extend it to larger filling fractions  $\phi$ , we will use a differential effective medium approach in which a concentrated emulsion is obtained from an initial continuous phase by successively adding infinitesimally small quantities of droplets to the system until the final volume fraction of the dispersed phase is reached. The usual implementation of the differential theory to obtain a concentrated emulsion up to a given stage, consists in treat it as a homogeneous effective medium of viscosity  $\eta(\phi)$  into which we add a quantity  $\Delta\phi$  of new droplets. Then, the new viscosity  $\eta(\phi + \delta\phi)$  is calculated using Taylor's expression to give

$$\eta(\phi + \delta\phi) = \eta(\phi) \left( 1 + \frac{\eta(\phi) + 2.5\eta_d}{\eta(\phi) + \eta_d} \Delta\phi \right) \quad (11)$$

Here, it is important to notice that in order to allocate the new droplets maintaining constant the volume of the system, one has to remove part of the effective medium ( $1 - \Delta\phi$ ) in order to allocate the new quantity ( $\Delta\phi$ ) of droplets. Therefore, the new filling fraction is given by  $\phi + \delta\phi = \phi(1 - \Delta\phi) + \Delta\phi$ , from which one finds

$$\Delta\phi = \frac{\delta\phi}{1 - \phi} \quad (12)$$

A shortcoming of using Equation 11 and the bare filling fraction  $\phi$  is that it does not contains the correlations generated by the excluded volume effects, that is, it assumes that all the volume of the emulsion before new droplets are added is available to the new droplets. However, as we have mentioned previously, this is not possible since the droplets can occupy only the free volume and therefore scale according to  $\phi_{\text{eff}} = \phi/(1 - c\phi)$ , i.e. Equation 9.

These considerations suggest that the differential theory must be performed in terms of the scaling variable  $\phi_{\text{eff}}$  and not on the bare filling fraction itself. Therefore, making the substitution of  $\phi$  by  $\phi_{\text{eff}}$  in Equations 11 and 12 and integrating we obtain

$$\eta_r(\phi_{\text{eff}}) \left( \frac{2\eta_r(\phi_{\text{eff}}) + 5K}{2 + 5K} \right)^{3/2} = (1 - \phi_{\text{eff}})^{-5/2} \quad (13)$$

that, in terms of the bare filling fraction takes the form

$$\eta_r(\phi) \left( \frac{2\eta_r(\phi) + 5K}{2 + 5K} \right)^{3/2} = \left( 1 - \frac{\phi}{1 - c\phi} \right)^{-5/2} \quad (14)$$

Expressions 13 and 14 are similar to other ones based on the differential method, see, for example, Equations 2–4. However, our model crucially makes use of the geometrical information of the system from the start through  $\phi_{\text{eff}}$ . This makes an essential difference since, in contrast to the usual differential procedure, the use of  $\phi_{\text{eff}}$

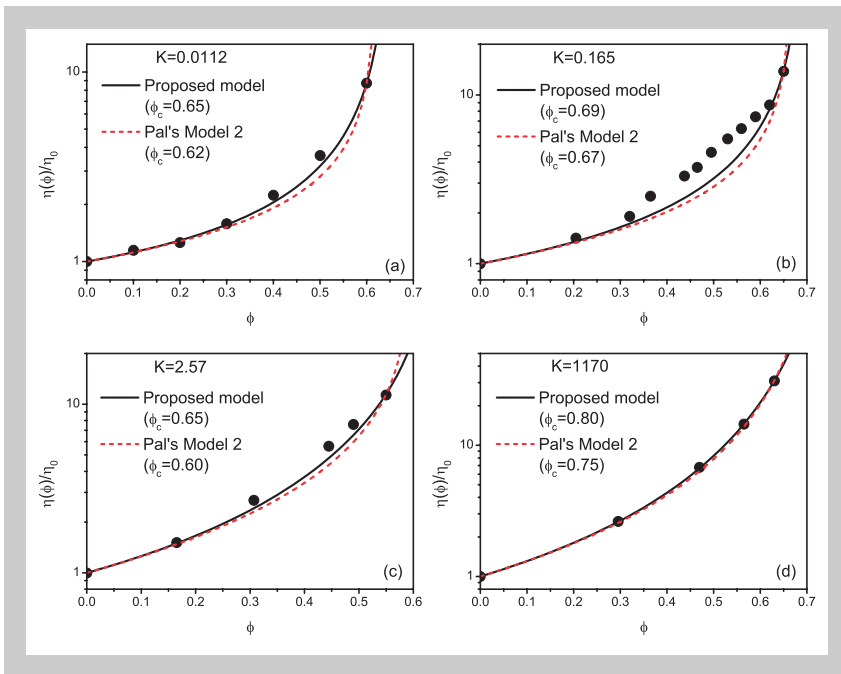
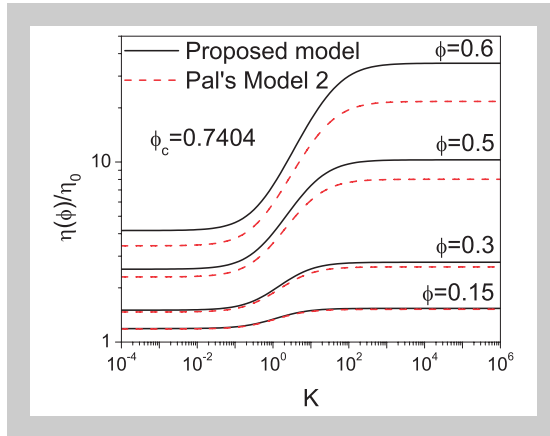


Figure 1 (below): Relative viscosity  $\eta_r(\phi) = \eta(\phi)/\eta_0$  predicted from our model (Equation 14, solid line) and Pal's model 2 (Equation 3, dashed line).  $\phi_c$  is taken to be 0.7404.

Figure 2 (above): Comparisons between the experimental data [17] and best fits of the theoretical predictions for the volume dependence of the relative viscosity for different values of the viscosity ratio  $K$ . The solid line is the result of our model and the dashed line the prediction of Pal's model 2.



as the integration variable incorporates correlations between droplets of the same recursive stage, resulting in an improvement of the quantitative description when compared to experimental data, as will be shown in the next section.

### 3 RESULTS

In Figure 1 we show the relative viscosities predicted from the present model (Equation 14) and Pal's model 2 (Equation 3) as a function of the viscosity ratio  $K$ . Both models have a sigmoidal shape characterized by an increase in the range  $0.1 < K < 1000$ , approximately, and predict a growth of the viscosity for higher values of the filling fraction  $\phi$ . From Figure 1 it also follows that our Equation 13 predicts larger values of the relative viscosity than Equation 3 over the full range of  $K$  and that the difference between both curves grows for larger values of  $\phi$ .

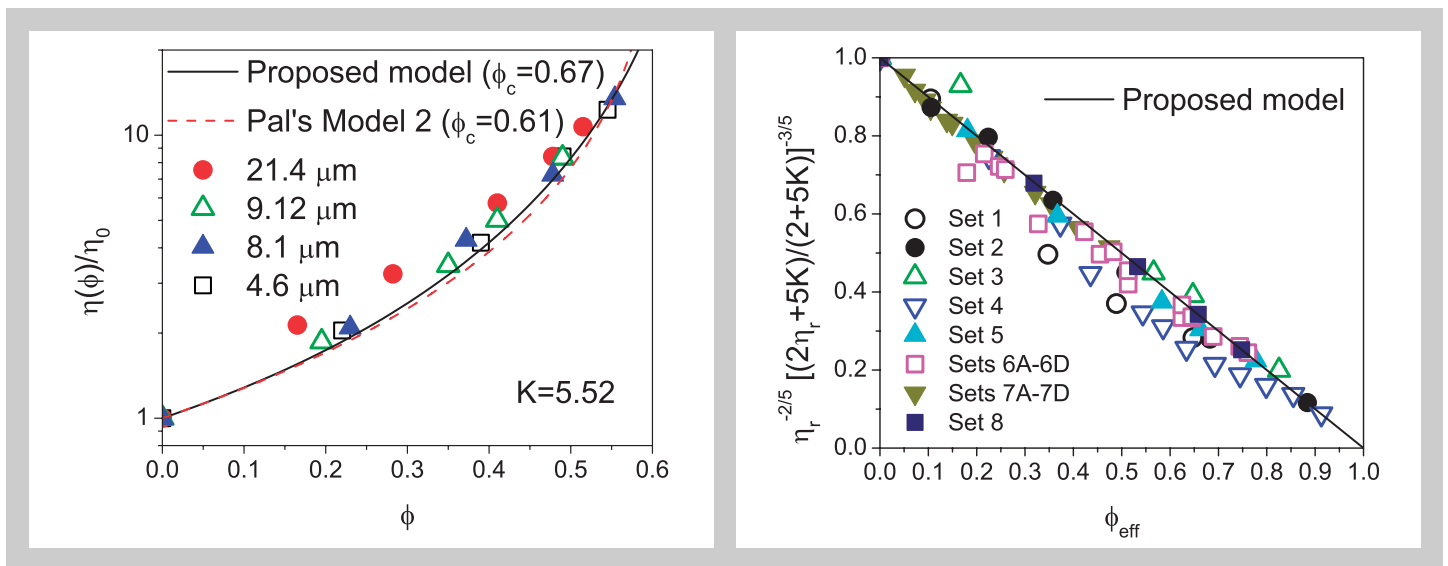
This behavior can be understood in the following way: Pal's model 2 can be obtained from Taylor's expression by introducing the effective filling fraction  $\phi_{eff}^p = \phi/\phi_c$ , which is larger than  $\phi$ . This definition of  $\phi_{eff}^p$  underestimates the avail-

able volume for the particles at low  $\phi$  (and therefore, overestimates  $\phi_{eff}^p$ ) while tends to the correct limit at high  $\phi$ . In order to obtain the correct Taylor's expression at low  $\phi$ , the overestimation of  $\phi_{eff}^p$  has to be compensated by decreasing the hydrodynamic drag factor by the same constant factor  $\phi_c$ , that is, from Equation 1 we have

$$\eta_r(\phi) = \left( 1 - \frac{1 + 2.5K}{1 + K} \phi_c \phi_{eff}^p \right) \quad (15)$$

Now Equation 3 can be derived from Equation 1 by following the differential method used in Section 2 with the effective filling fraction  $\phi_{eff}^p$  (instead of  $\phi_{eff}$ ) and the corresponding extra factor  $\phi_c$  in the drag term. Such a derivation of Equation 3 is different than the one used in [17] and illustrates the generality of the method we propose. For the sake of clarity, it is convenient to stress here that in his original derivation, Pal contended that the increase in the volume of the dispersed phase when new particles are added is  $d\phi/(1 - \phi/\phi_c)$  whereas in our derivation it is  $d\phi_{eff}^p/(1 - \phi_{eff}^p)$  and the hydrodynamic drag factor has the extra factor  $\phi_c$  (both derivations are linked by a simple change of variable).

However, the present derivation is interesting because it shows that the overestimation on the filling fraction  $\phi_{eff}^p$  at low  $\phi$  has to be compensated with an underestimation of the hydrodynamic drag factor in order to recover the correct low-concentration limit given by Taylor's expression. This compensation is unnecessary in Equation 13 since the effective filling fraction  $\phi_{eff}^p$  naturally tends to  $\phi$  in this limit. As a result, in the low concentration limit both approaches reduce to Taylor's expression and give similar quantitative results. However, the situation is quite different for larger values of  $\phi$ . To prove this statement, one can use the relative difference  $(\phi_{eff}^p - \phi_{eff})/(\phi_{eff}^p)$  between the effective filling fractions which is a decreasing function of  $\phi$  that vanishes at  $\phi_c$  (assumed to be the same for both models in this analysis). This behavior implies that the overestimation of the filling fraction in  $\phi_{eff}^p$  is progressively less important with increasing  $\phi$  and therefore, the difference between both models due to the constant underestimation of the hydrodynamic drag term in Pal's model 2 is more important with increasing filling fraction since at large  $\phi$  it cannot be compensated by  $\phi_{eff}^p$ . The same rea-



soning explains why the alternative model given by Equation 4 gives very good results at high  $\phi$  but fails at low  $\phi$ .

Figure 2 shows comparisons between the experimental data and predictions of Equations 14 and 3 for different values of the viscosity ratio  $K$ . The various data sets considered in this figure are identical to the ones used in [17]. They consist on stable (unfloculated) emulsions covering the viscosity ratio  $3.87 \cdot 10^{-4} < K < 3.25 \cdot 10^5$  and having small capillary numbers. Although accurate fits are difficult to obtain due to the scattering of the experimental data, particularly in panel (b), the comparison with experiments allows us to conclude that our model describes the experimental results slightly better than Pal's model 2. Moreover, from this comparison it also follows that the more significant difference between both models is that the values of the fitting parameter  $\phi_c$  predicted by our model, and which varies for different values of  $K$ , are, in all cases, larger than those reported in [17].

This difference in the values of  $\phi_c$  can be understood on the light of the discussion of the previous paragraphs. As we have mentioned, for the same  $\phi_c$  Pal's model 2 predicts viscosities much smaller than those obtained with our model for large  $\phi$  due to the underestimation of the hydrodynamic drag. Thus, if both models are intended to give good fits to the same data set, then the underestimation of the viscosity in Equation 3 must be compensated with a smaller  $\phi_c$  to produce a rapid increment of  $\phi$ . As a consequence, the shape of the viscosity curve is slightly more bend for Pal's model 2 than for Equation 14. Additionally, it is interesting to notice that for the largest value of  $K$ , for which the system should be similar to hard spheres, both models predict values of  $\phi_c$  larger than the close packing value for a system of identical-sized spheres. A question then emerges: Can these abnormally high values of  $\phi_c$  be attributed to the experi-

mental system which maybe does not consist of spherical droplets of identical or similar sizes? We conjecture that the answer to this question is yes because our model gives an excellent fit of many experimental data reported for uniform-sized hard spheres ( $K \rightarrow \infty$ ) and predicts very realistic values of  $\phi_c$  lying between random close packing and FCC packing for low and high shear rates, respectively [8]. Thus, we consider that more precise experimental data are needed in order to assess which of the two models give more reliable predictions. Figure 3 shows the independence of the relative viscosity on the mean droplet size. This is to be expected since the original Taylor's expression is independent of this parameter. The comparison between theoretical models and experiments was performed by assuming that all the samples consist of identical-sized spheres and shows again a slightly better fit for our model. However, it is convenient to consider here that for a system with dispersion of sizes the viscosity curve should be different since the close packing value should be also different.

According to Equation 13, the viscosity, plotted in the form  $\eta_r(\phi)^{-2/5} [2\eta_r(\phi) + 5K] / (2 + 5K)^{-3/5}$  versus  $\phi_{eff}$  should be system independent. This is almost confirmed in Figure 4 which shows all that the viscosity data tend to collapse in a master curve that compares well with the one predicted by our model. In order to produce this plot, the values of  $\phi$  for the experimental data points should be transformed to  $\phi_{eff}$  by using Equations 9 and 10. The values of  $\phi_c$  used in these transformations were the ones that gave the best fits in the previous comparisons and therefore were different for each data set. Note that a similar master curve cannot be obtained from the scaling of Equation 3 since it produces different curves for different values of  $\phi_c$ . The agreement between the data points and our model is fairly good considering the large scattering of the experimental data.

Figure 3 (left): Comparisons between the experimental data and predictions of our model (Equation 14, solid line) and Pal's model 2 (Equation 3, dashed line). The best fit for our model was obtained with  $\phi_c = 0.67$  and for Pal's model 2  $\phi_c = 0.61$ .

Figure 4: Master curve of  $1 - \phi_{eff}$  consisting of all the experimental viscosity data. The solid line is the result of our model.

## 4 CONCLUSION

We have obtained a novel viscosity relation for concentrated emulsions of spherical droplets that contains excluded volume effects and compares well with experiments and previous theories. The relation has been derived by starting from a modified version of Taylor's equation for the viscosity of very dilute emulsions [8] and using a differential effective medium approach. The difference of the method we propose with previous ones comes from the fact that we have used as an integration variable the so-called effective volume fraction  $\phi_{eff}$ , that naturally incorporates excluded volume effects into the description and has the property that approaches  $\phi$  at low concentrations and becomes one at the critical concentration  $\phi_c$ .

The effective volume fraction  $\phi_{eff}$  contains a constant  $c$  that incorporates the geometrical information that not all the free volume of the system can be occupied by the droplets. This constant can be written in terms of the critical value of the bare volume fraction  $\phi$  at which the divergence of the viscosity occurs, which sometimes corresponds to the maximum packing of the droplets under low or high shear rate conditions. This apparently simple correction leads to a model that slightly improves the comparison with experimental data as compared with the results obtained with other models containing a different proposal of the effective volume fraction [16, 17]. Our model also reduces to Taylor's expression at low concentrations in contrast to other models considered for comparison which fail at low filling fractions in one case (Equation 4), and in the high filling fraction in the other (Equation 3). Our theory reduces to a recently found expression for a suspension of hard spheres in the limit  $K \rightarrow \infty$  [8]. This limiting behavior is important when considering that the comparison with experiments in this last case shows to be excellent.

The model proposed in this article is ready to be used in the description of the rheological properties of non-flocculated emulsions of spherical droplets with small capillary numbers. Its relevance comes from the fact that it can be used to identify different scaling properties of the viscosity of these systems and thus to better understand their interactions. As a final remark, we want to mention that the model can be generalized to consider polydispersion and non-spheri-

cal shapes in both solid and liquid-like suspensions. This situation is currently under research.

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