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 Viskositätsverhältnisbereich 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-récursive, 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: $\eta_r(\phi \longrightarrow \phi_c) \longrightarrow \infty$. 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 η_d of the dispersed phase and the vis-

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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 ϕ_{eff} , that naturally incorporates excluded volume effects into the description and has the property that approaches ϕ at low concentrations and becomes one at the critical concentration ϕ_c.

The effective volume fraction ϕ_{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 ϕ 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 $K \longrightarrow \infty$ [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-floculated 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-spherical shapes in both solid and liquid-like suspensions. This situation is currently under research.

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