THE VOLUME FRACTION DEPENDENCE OF THE EFFECTIVE VISCOSITY OF HARD SPHERE SUSPENSIONS AND EMULSIONS OF NEARLY SPHERICAL DROPLETS

I. Santamaria-Holek[a], Carlos I. Mendoza[b]
[a]Facultad de Ciencias, Universidad Nacional Autónoma de México, Circuito Exterior de Ciudad Universitaria 04510, México D. F., México
[b]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 70-360, 04510, México D. F., México

Introduction

A general continuum-medium description accounting for the experimental dependence of the effective viscosity of hard sphere suspensions and nearly spherical droplets at arbitrary volume fractions ϕ can be performed in simple form by taking into account the correct scaling properties of these systems [1]. This description is based on a recursive/differential method that introduces correlations between particles through an effective volume fraction containing excluded volume effects, which are responsible for the scaling properties and show to be universal for hard-sphere suspensions [1]. The details of the recursive/differential method are given in Refs. [1,2]. This description can also be applied to describe emulsions of nearly spherical droplets with small capillary numbers by taking into account the adequate boundary conditions between the particles constituting the dispersed phase and the host fluid having dynamical viscosity η_0 [1]. The agreement of our expression for the viscosity with experiments at low- and high-shear rates and in the high-frequency limit is remarkable for all volume fractions [1].
The differential method has been introduced long time ago in the context of different physical properties of dispersed systems [2]. The limited success of the method was due to the fact that geometrical information of the system had poorly been included since they used as starting points Einstein's [3] and Taylor's [4] expressions. These expressions implicitly assumes that particles are point size and have two main ingredients: a) They contain a factor expressing the effect of hydrodynamic drag on each suspended particle and b) a factor, the filling fraction, accounting for the collective effect of this friction force. Implicit in this second ingredient is the point particle assumption.
Einstein's and Taylor's formulas are given by

$$\eta_E(\phi)=\eta_0(1+2.5\phi) \text{ and } \eta_T(\phi)=\eta_0\left(1+A\phi\right), \quad (1)$$

where $A=(1+2.5k)/(1+k)$, with $k = \eta_d/\eta_0$ and η_d the viscosity of the dispersed phase. The factors 2.5 and A, are hydrodynamic drag factors for the solid particles and the liquid droplets, respectively [3,4]. These formulas correctly describe the behavior of the effective viscosity for *very* dilute suspensions.

To obtain these formulas, similar physical considerations have to be taken into account. For the case of a solid-liquid suspension, these conditions are that the velocity of the fluid at the surface of the particles must be equal to the velocity of the particle. In the case of liquid-liquid suspensions, these conditions are, essentially: *i)* The droplets 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 droplets.

Improving the low concentration expression for the effective viscosity

When equations (1) are used in the recursive/differential method as the starting information, only a poor improvement of Einstein's and Taylor's results has been obtained [2], because these expressions constitute point particle approximations. A considerable improvement of the description is obtained when one considers the finite size of the particles in the collective contribution.
To explain this point, let us consider that Einstein's formula can be calculated from the viscous dissipation produced by the flow around a single sphere [3,5]. The solution of the fluid flow around the sphere can be expressed as: v_0+v_1, where v_0 is an imposed shear flow, $v_1=\nabla v_0\cdot r$ is the flow perturbation due to the presence of the particle and $\nabla=\partial/\partial r$ [5]. The effective viscous stress tensor of the suspension is then calculated after performing an average over the volume of the sample

$$\overline{\sigma}^V=\eta_0\overline{\nabla v_0}^V+(N/V)\int\eta_0\nabla v_1 dV \,. \quad (2)$$

The first term is the contribution of the the host fluid whereas the second term is the contribution of the N independent suspended particles which, after performing the integral, becomes: $5\eta_0\phi\overline{\nabla v_0}^V$ (see Ref. [5]). The second term in RHS of Eq. (2) implicitly assumes that the particles may fill the entire volume V of the sample. This is not true since the particles can only fill the *free* volume, $V_{free}=V-cNV_p$, of the sample. Here V_p is the volume of a particle and c a constant taking into account the geometry of the particles and the fact that the complete free volume of the sample cannot be filled with spheres due to their spatial distribution.

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That is, c contains the information about the maximum packing of spheres the system may allocate.
Thus, if excluded volume effects are taken into account, the pre-factor in the second term on the RHS of Eq. (2) becomes $\phi(1-\phi)^{-1} = N/(V - cNV_p)$, and consequently

$$\eta(\phi) = \eta_0\left[1 + B\phi(1-c\phi)^{-1}\right], \qquad (3)$$

where the constant B may take the values 2.5 or A. From (3), Einstein's (or Taylor's) expression is naturally recovered in the limit $\phi \to 0$.

Differential viscosity model: Scaling and excluded volume effects

If we now define the effective filling fraction $\phi_{eff} = \phi/(1-c\,\phi)$, Eq. (2) simply becomes

$$\eta(\phi_{eff}) = \eta_0\left[1 + B\phi_{eff}\right]. \qquad (4)$$

This result suggests that the natural variable of the system is not the bare filling fraction ϕ, but the effective one, ϕ_{eff}. The differential method essentially consists in a progressive addition of particles in a host medium that contains the contribution to the viscosity due to the previously added particles. Thus, if one applies the recursive/differential method using ϕ_{eff} as the integration variable, it is possible to show that the relative viscosity $\eta_r = \eta/\eta_0$ for hard-sphere suspensions takes the form [1]

$$\eta_r(\phi_{eff}) = \left(1 - \phi_{eff}\right)^{-5/2}. \qquad (5)$$

The effective viscosity for emulsions of nearly spherical droplets is similarly given by

$$\eta_r(\phi_{eff})\left(\frac{2\eta_r(\phi_{eff}) + 5k}{2 + 5k}\right)^{3/2} = \left(1 - \phi_{eff}\right)^{-5/2}. \qquad (6)$$

Equations (5) and (6) represent powerful generalizations of previous theories (cf. Refs. [1,2] and references therein). A comparison of Eq. (5) with experiments is shown in Figure 1, whereas for Eq. (6) this is performed in Fig. 2.

Conclusions

The expressions (5) and (6) obtained for the viscosities of hard- and liquid-sphere suspensions allow to construct a universal master curve in which all the experimental data collapse (including low- and high-shear and high frequency limit), see Fig. (1). This curve strongly supports the validity of the assumptions done and the conclusion that ϕ_{eff} is the natural scaling function of these systems. Comparison with experimental values is remarkable for hard-spheres suspensions and also for emulsions.

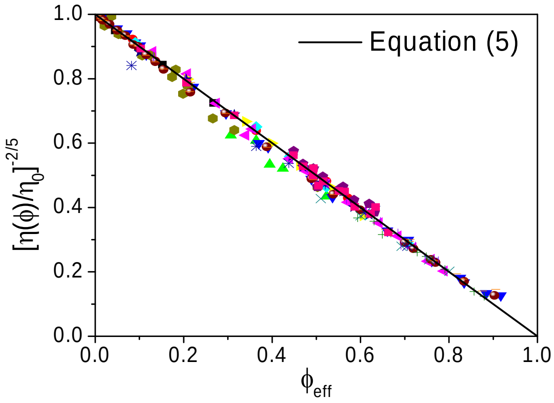

Fig.1: Master curve for the viscosity as a function of ϕ_{eff} for hard-sphere suspensions. Symbols represent experiments and the solid line our theory, Eq. (5).

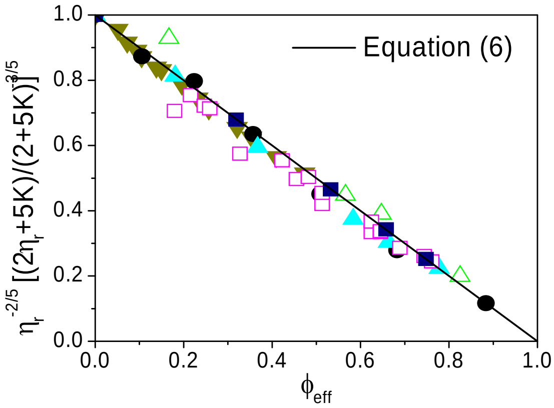

Fig.2: Master curve for the viscosity as a function of ϕ_{eff} for emulsions. Symbols represent experiments and the solid line our theory, Eq. (6).

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