

# The rheology of hard sphere suspensions at arbitrary volume fractions: An improved differential viscosity model

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We propose a simple and general model accounting for the dependence of the viscosity of a hard sphere suspension at arbitrary volume fractions. The model constitutes a continuum-medium description based on a recursive-differential method where correlations between the spheres are introduced through an effective volume fraction. In contrast to other differential methods, the introduction of the effective volume fraction as the integration variable implicitly considers interactions between the spheres of the same recursive stage. The final expression for the viscosity scales with this effective volume fraction, which allows constructing a master curve that contains all the experimental situations considered. 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. © 2009 American Institute of Physics. [DOI: 10.1063/1.3063120]

## I. INTRODUCTION

A large amount of work has been devoted to the understanding of the rheology of suspensions due to its ubiquity and the central role that they play in many technological processes. To control the structure and flow properties of such suspensions is of enormous practical importance. Due to its many body character, the study of the rheology of these systems is extremely difficult, even the simplest suspension composed of identical hard spheres shows rather complex rheological phenomena. Since Einstein's calculation for the viscosity for a dilute suspension of spheres<sup>1</sup> given by the expression,

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi \right), \quad (1)$$

where  $\eta_0$  is the solvent viscosity and  $\phi$  is the volume fraction, a lot of effort has been devoted to extend this result to more concentrated suspensions in which correlations among particles must be taken into account. However, in spite of the remarkable works, which make central contributions to the understanding of the rheology of concentrated suspensions,<sup>2-15</sup> the problem still constitutes a challenge for theoretical description.<sup>16</sup> Essentially, most of these works introduce particle correlations by taking into account hydrodynamic interactions and provide a conceptual framework that explains how these interactions modify the behavior of the viscosity as a function of the volume fraction  $\phi$  for arbitrary values of the wave vector and the frequency:  $\eta(k, \omega; \phi)$ . Sometimes, these approaches provide compact expressions for the effective viscosity, although usually a multipole expansion must be done in order to obtain numerical values.<sup>3,7-9</sup>

For example, Saito<sup>2</sup> derived an equation that accounts for hydrodynamic interactions between uncorrelated spheres

$$\eta(\phi) = \eta_0 \left[ 1 + \frac{5}{2} \left( \frac{\phi}{1 - \phi} \right) \right]. \quad (2)$$

In order to account for thermodynamic interactions between the spheres, Bedeaux<sup>17,18</sup> proposed the following expression for the viscosity:

$$\frac{\eta(\phi)/\eta_0 - 1}{\eta(\phi)/\eta_0 + \frac{3}{2}} = \phi(1 + S(\phi)), \quad (3)$$

where  $S(\phi)$  is an unknown function of the volume fraction giving the modification of the moment of the friction forces on the surface of a single sphere due to the ensemble-averaged hydrodynamic interactions with the other spheres.<sup>18</sup> By putting  $S(\phi)=0$ , one recovers Saito's expression. Using the conservation law for the total momentum density of the fluid and the suspended spheres, Bedeaux *et al.*<sup>7</sup> performed a multipole expansion of the one sphere response function to second order in the wave vector and an expansion in the volume fraction up to the second order, obtaining the expression

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 4.8 \phi^2 \right). \quad (4)$$

Beenakker,<sup>9</sup> by neglecting Brownian motion, gave a theory for the concentration and wave-vector dependence of the viscosity valid up to high concentrations that fully takes into account the many-body hydrodynamic interactions between an arbitrary number of spheres. Batchelor and Green<sup>4</sup> developed a theory for the evaluation of the bulk stress in semidilute suspensions of hard spheres. By neglecting Brownian motion and assuming a random particle distribution, they found the following expression for the viscosity

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$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 5.2 \phi^2 \right). \quad (5)$$

This result has been regarded as the high-frequency value of the real part of the complex shear viscosity.<sup>12</sup> A different result is obtained if Brownian motion is taken into account. Then appears an extra term accounting for the stresses generated in the dispersion by the random movements of the particles. Numerical calculations performed in Ref. 5 lead to the formula

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 6.17 \phi^2 \right), \quad (6)$$

considered as the low-shear and zero-frequency value of the real part of the complex shear viscosity because in the calculation Brownian motion dominates.<sup>12</sup>

Russel and Gast<sup>10</sup> formulated a theory for the nonequilibrium structure and stresses in a sheared suspension with a fluid rest state. Many-body interactions were handled exactly in the thermodynamics but truncated at the pair level for the hydrodynamics.

More recently, on the basis of the pair Smoluchowski equation, Cichocki and Felderhof<sup>19,20</sup> obtained exact results for  $\eta(\phi, \omega)$  to  $O(\phi^2)$ . Without Brownian motion contributions, their result for  $\omega=0$  is

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 5.00 \phi^2 \right), \quad (7)$$

while with Brownian motion contributions they find

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 5.91 \phi^2 \right). \quad (8)$$

Verberg *et al.*<sup>15</sup> presented an approximate theory based on the contribution of two physically relevant processes taking place at different time scales: (i) at short time scales, the viscosity of the suspension increases when compared with that of the pure solvent at infinite dilution due to the finite probability to find two particles at contact, whereas (ii) at long times it is difficult for a Brownian particle to diffuse out of the cage formed around it by its neighbors. For  $\omega=0$ , these authors obtain the approximate result

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi + 6.03 \phi^2 \right), \quad (9)$$

while for  $\omega \rightarrow \infty$  they propose

$$\eta(\phi) = \eta_0 \frac{1 - 0.5\phi}{(1 - \phi)^3}, \quad (10)$$

which is accurate for all  $0 < \phi < 0.55$ . Although their results compare reasonably well with experimental data, they are based in a number of assumptions not completely justified, as mentioned in Ref. 15.

The simple formulas reviewed above are of fundamental importance for the understanding of the rheology of suspensions. However, they are far from satisfactory since they only give good quantitative results in the low volume fraction regime.<sup>12-14</sup>

This restriction has led to many works searching for simple procedures or semiempirical expressions to calculate the viscosity of suspensions and dispersions at frequencies and shear rates relevant to industrial applications.<sup>21</sup> Several phenomenological formulas<sup>22,23</sup> have been proposed in order

to fit experiments in the largest possible range of volume fractions. For example, Krieger and Dougherty<sup>22</sup> found empirically that the expression

$$\eta(\phi) = \eta_0 \left( 1 - \frac{\phi}{\phi_c} \right)^{-2.5\phi_c}, \quad (11)$$

with  $\phi_c$  the filling fraction at maximum packing, agrees reasonably well with the experimental data. Moreover, this relation reduces to the correct Einstein's equation in the limit of infinite dilution. Another example is the following expression obtained by Quemada:<sup>23</sup>

$$\eta(\phi) = \eta_0 \left( 1 - \frac{\phi}{\phi_c} \right)^{-2}, \quad (12)$$

which gives the right divergence for  $\eta$  as  $\phi$  approaches  $\phi_c$  but it does not reduce to Einstein's expression for low  $\phi$ . Nonetheless, although useful, these expressions lack physical support and therefore do not provide insight about the phenomenology of the system.

In this article, we explore a different approach to the problem leading to a simple and quantitatively powerful description of concentrated suspensions of mono- and polydisperse suspensions of colloidal particles. Our model assumes that at macroscopic length and time scales, the suspension can be considered as a truly continuum medium. However, the precise formulas are derived only by considering the discrete nature of the suspended phase through its possible configurations and correlations.

The technique we will adopt has been introduced long time ago in the context of different physical properties of dispersed systems,<sup>24-26</sup> including optical<sup>27,28</sup> and nonlocal dielectric systems.<sup>29</sup> In the case of rheological properties, a limited success has been obtained when comparing with the experimental results because the geometrical information of the system has poorly been included.<sup>24,26,30,31</sup> In this work, we improve previous results by incorporating structural information from the start through an effective filling fraction.

The article is organized as follows. In Sec. II we propose a first correction to Einstein's formula that takes into account excluded volume effects and is the starting point of our differential effective medium model that we introduce in Sec. III. In Sec. IV we compare the predictions of our model with previous theories and with various experimental results. Finally, Sec. V is devoted to conclusions.

## II. EXCLUDED VOLUME CORRECTIONS TO EINSTEIN'S EXPRESSION FOR THE VISCOSITY

At very low volume fractions, the shear viscosity  $\eta$  of a suspension of hard spheres can be predicted by Eq. (1) that Einstein calculated from the viscous dissipation produced by the flow around a single sphere.<sup>1,32</sup> More explicitly, expression (1) can be obtained after assuming that the solution of the fluid flow can be expressed as a sum of two contributions,  $\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1$ , where  $\mathbf{v}_0 = \nabla \mathbf{v}_0 \cdot \mathbf{r}$  is the imposed shear flow and  $\mathbf{v}_1$  is the perturbation on the fluid's velocity due to the presence of a particle. In Ref. 32, it has been shown that the

effective viscous stress tensor of the suspension  $\bar{\Pi}^V$  can then be calculated after performing an average over the volume  $V$

$$\bar{\Pi}^V \approx \eta_0 \overline{\nabla \mathbf{v}_0^0} + \frac{N}{V} \int [\Pi - \eta_0 \nabla \mathbf{v}_0^0] dV, \quad (13)$$

where  $\Pi$  is the total stress tensor of the suspension and the upper  $V$  stands for the volume average and the factor  $N$  accounts for the contribution of the  $N$  independent particles. The first term in Eq. (13) is the contribution to the viscous stresses of the fluid under the imposed flow, whereas the second term is the contribution to the viscous stresses due to the presence of the particles  $\bar{\Pi}_p^V$ , given by<sup>32</sup>

$$\bar{\Pi}_p^V \approx 5 \eta_0 \phi \overline{\nabla \mathbf{v}_0^0}. \quad (14)$$

It is important to stress that in obtaining Eq. (14), excluded volume effects have not been taken into account, and therefore the validity of the relation is restricted to volume fractions in which the particles can be considered as mass points. In the first approximation, Eq. (14) can be improved by considering the excluded volume effects, i.e., by performing the average over the free volume accessible to the particles, which we define through the relation:  $V_{\text{free}} = V - cNV_p$ . Here,  $V_p$  is the volume of one particle and  $c$  is a constant taking into account the fact that the complete free volume cannot be filled with spheres. Notice also that, for different symmetries of the suspended particles, the value of the constant  $c$  will be different. This fact suggests that it contains information about the maximum packing of spheres the system may allocate. Thus, if this excluded volume effect is taken into account when performing the volume average, the second term on the right-hand side of Eq. (13) becomes

$$\bar{\Pi}_p^{V_{\text{free}}} \approx \frac{N}{(V - cNV_p)} \int [\Pi - \eta_0 \nabla \mathbf{v}_0^0] dV, \quad (15)$$

and the contribution to the viscous stress tensor coming from the particles is

$$\bar{\Pi}_p^{V_{\text{free}}} \approx 5 \eta_0 \left( \frac{\phi}{1 - c\phi} \right) \overline{\nabla \mathbf{v}_0^0}. \quad (16)$$

From expression (16), we may finally obtain the modified Einstein's expression for the viscosity of a suspension of particles with excluded volume effects

$$\eta(\phi) = \eta_0 \left[ 1 + \frac{5}{2} \left( \frac{\phi}{1 - c\phi} \right) \right]. \quad (17)$$

From this formula, Einstein's expression is recovered in the limit of small volume fractions ( $\phi \rightarrow 0$ ). This fact is important since Eq. (1) may be applied to any polydisperse distribution of spheres at low volume fractions, giving to it its universal character. Equation (17) is interesting because it explains the experimental fact that the viscosity diverges at a critical volume fraction  $\phi_c < 1$ , implying that this effect is related to the fact that the spheres cannot occupy all the volume of the sample due to geometrical restrictions. For example, for a face centered cubic (fcc) arrangement of identical spheres, the maximum volume that the spheres may occupy is larger than for a random arrangement of spheres.

Notice that, in the general case, the excluded volume effect may be modified by the presence of hydrodynamic interactions, which introduce an effective particle radius through the penetration length.<sup>7,32</sup>

### III. THE DIFFERENTIAL EFFECTIVE MEDIUM THEORY

The formula (17) only incorporates the excluded volume corrections to the Einstein relation for the viscosity of a suspension. To improve it, further corrections must appear due to the interactions between particles, in a similar way as the thermal equation of state is obtained in the classical theory of real gases. In the system under consideration, these interactions are the hydrodynamic interactions, which become increasingly important when increasing the filling fraction. Accounting for the correlations arising from these interactions is a very hard task. A microscopic approach to the problem suggests the use of an  $N$ -particle description, as it was formulated in different ways (see, for instance, Refs. 7–9 and 15).

However, the mentioned correlations can also be accounted for by following a phenomenological approach called differential effective medium theory (DEMT). This theoretical method is based on a progressive addition of spheres to the sample in which the new particles interact with those added in previous stages.<sup>26</sup> Frequently, Einstein's expression is used as the starting point of the DEMT. However, by proceeding in using it, one is implicitly neglecting correlations between spheres of the same generation. To avoid this limitation, instead of Einstein's formula we propose to use Eq. (17) since it contains the correlations due to excluded volume effects through the scaling factor  $\phi(1 - c\phi)^{-1}$ . Thus, in order to implement the differential procedure, it is convenient to realize that in Eq. (17) the relevant quantity is  $\phi(1 - c\phi)^{-1}$ , which allows us to define an *effective* filling fraction

$$\phi_{\text{eff}} = \frac{\phi}{1 - c\phi}, \quad (18)$$

and therefore, rewrite Eq. (17) in the form

$$\eta(\phi) = \eta_0 \left[ 1 + \frac{5}{2} \phi_{\text{eff}} \right]. \quad (19)$$

Taking Eq. (19) as the starting point, suppose that we increase by  $\delta\phi_{\text{eff}}$  the particle concentration in the suspension of viscosity  $\eta(\phi_{\text{eff}})$  by adding a small quantity  $\Delta\phi_{\text{eff}}$  of few new particles. If we treat the suspension into which we add these particles as a *homogeneous* effective medium of viscosity  $\eta(\phi_{\text{eff}})$ , then the new viscosity can be written as

$$\eta(\phi_{\text{eff}} + \delta\phi_{\text{eff}}) = \eta(\phi_{\text{eff}}) \left( 1 + \frac{5}{2} \Delta\phi_{\text{eff}} \right), \quad (20)$$

where the added quantity of new spheres is related to  $\delta\phi_{\text{eff}}$  by

$$\Delta\phi_E = \frac{\delta\phi_{\text{eff}}}{1 - \phi_{\text{eff}}}. \quad (21)$$

The normalizing factor that appears in Eq. (21) is due to the fact that one has to remove part of the effective medium in order to allocate the new particles, that is, the new fraction of spheres is given by  $\phi_{\text{eff}} + \delta\phi_{\text{eff}} = \phi_{\text{eff}}(1 - \Delta\phi_{\text{eff}}) + \Delta\phi_{\text{eff}}$ , from

which we find  $\Delta\phi_{\text{eff}}$ . Integrating Eq. (20), we finally obtain

$$\eta(\phi) = \eta_0(1 - \phi_{\text{eff}})^{-5/2}, \quad (22)$$

or, using the definition of  $\phi_{\text{eff}}$

$$\eta(\phi) = \eta_0 \left[ 1 - \left( \frac{\phi}{1 - c\phi} \right) \right]^{-5/2}. \quad (23)$$

This relation for the effective viscosity of a suspension of solid spherical particles constitutes a powerful improvement of previous theoretical results and empirical proposals, as we will show in Sec. IV. The main characteristic of  $\phi_{\text{eff}}$  is that it is the most simple way to incorporate geometrical information and has the property that  $\phi_{\text{eff}} \sim \phi$  at low volume fractions and  $\phi_{\text{eff}} = 1$  at the critical packing  $\phi_c$ , which is related to the constant  $c$  by

$$c = \frac{1 - \phi_c}{\phi_c}. \quad (24)$$

It is convenient to stress here that, although Eq. (23) is similar to the empirical proposals of Refs. 22 and 23 [Eqs. (11) and (12), respectively] and also to other differential effective medium theories,<sup>24–26</sup> our model crucially makes use of the correlations between the spheres from the start through  $\phi_{\text{eff}}$ . Using it as the integration variable in the differential procedure means that interactions between the spheres of the same generation are being considered, in contrast to the usual DEMT in which  $\phi$  is used instead of  $\phi_{\text{eff}}$ . This simple consideration results in a huge improvement of the quantitative description when compared with experimental data ranging from disordered to ordered system of spheres, or to systems with polydispersion of sizes. Even more, by an appropriate choice of the coefficient of the  $\phi$  term in Eq. (1) it can also be applied to other systems ranging from emulsions to arbitrarily shaped particles.

#### IV. RESULTS AND COMPARISON WITH EXPERIMENTS

In this section, we compare the predictions of the improved DEMT with several experimental results and with the results obtained from other theories. To carry out these comparisons, it is important to notice that the value of  $\phi_c$  in Eq. (24) is a free parameter of the theory to be chosen in order to best fit the experimental results. Nonetheless, this parameter can be chosen beforehand based on physical arguments and then used to compare with specific experimental situations.

This is done in Fig. 1, where the behavior of the relative viscosity  $\eta(\phi)/\eta_0$  is compared with experimental results of de Kruif *et al.*<sup>33</sup> and of Krieger<sup>34</sup> for high- and low-shear rates as a function of the volume fraction  $\phi$ . The lower curve is the prediction of Eq. (23) with  $\phi_c = 0.7404$ , which corresponds to fcc close packing. This gives an excellent agreement with the experimental results for the case of high-shear rates. The upper curve represents the prediction of Eq. (23) with  $\phi_c = 0.63$ , which corresponds to the random close packing (RCP) of identical spheres. The comparison with the experimental results for low-shear rates is again excellent. These results are consistent with the known fact that for low-shear rates the spheres remain disordered while at high-shear rates the equilibrium microstructure of the dispersion is com-

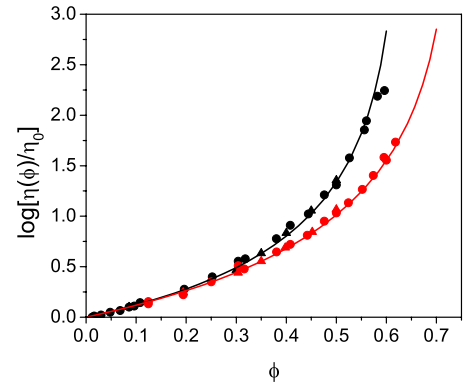


FIG. 1. (Color online) Relative viscosity  $\eta(\phi)/\eta_0$  at low- and high-shear rates as a function of the volume fraction  $\phi$ . The lines correspond to the predictions of the improved DEMT with RCP  $\phi_c = 0.63$  (upper line) and close packing at fcc  $\phi_c = 0.7404$  (lower line). The measured data are from Refs. 33 (circles) and 34 (triangles).

pletely destroyed and the spheres adopt an ordered fcc configuration. In Fig. 2, we use again the value  $\phi_c = 0.63$  to compare our theory with the experimental results obtained by Saunders,<sup>35</sup> by Krieger,<sup>34</sup> and by Kops-Werkhoven and Fijnaut.<sup>36</sup> We also plot the calculated values obtained by Beenakker<sup>9</sup> with a theory that fully takes into account the many-body hydrodynamic interactions between an arbitrary number of spheres. Notice again that the agreement with the experimental results is excellent over the entire fluid range.

In Fig. 3(a), we compare  $\eta(\phi)/\eta_0$  with the reduced viscosity measurements by van der Werff *et al.*<sup>12</sup> and by Zhu *et al.*<sup>37</sup> at high frequencies. We also plot the values obtained by Cichocki and Felderhof<sup>20</sup> and the predictions using a proposal by Verberg *et al.*<sup>15</sup> which considers the fraction of colloidal particle pairs at contact, Eq. (10). We used as a parameter to fit the data  $\phi_c = 0.8678$ . We note that Verberg's predictions lie below the experimental points while the results of the improved DEMT fits the data very well. Similarly, Fig. 3(b) shows the zero frequency low-shear viscosity as obtained by our model using  $\phi_c = 0.63$ , and it is compared with experimental results and the model of Verberg *et al.*<sup>15</sup> Again, a very good agreement is found.

As discussed by Bedeaux,<sup>17</sup> a more sensitive representation of the relative viscosity data is the one given in Eq. (3)

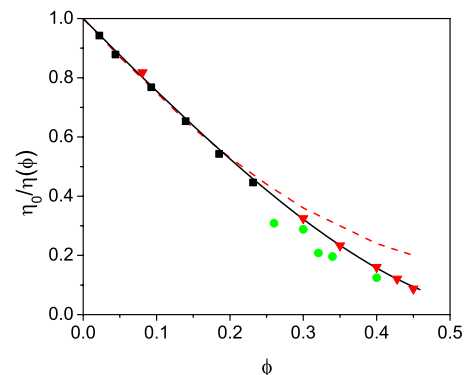


FIG. 2. (Color online) Volume fraction dependence of the reciprocal of the relative viscosity  $\eta_0/\eta(\phi)$ . The solid line is the result of the improved DEMT with  $\phi_c = 0.63$ . The dashed line is taken from Ref. 9. The measured data are from Refs. 35 (squares), 34 (triangles), and 36 (circles).

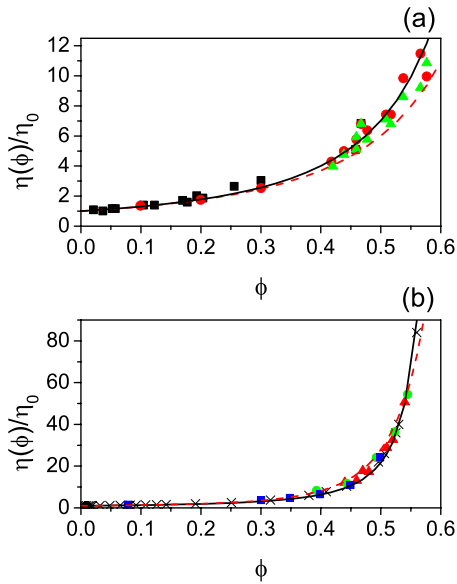


FIG. 3. (Color online) (a) Relative infinite-frequency viscosity  $\eta(\phi)/\eta_0$  as a function of the volume fraction  $\phi$ : Squares, Zhu *et al.* (Ref. 37); circles, van der Werff *et al.* (Ref. 12); and triangles, Cichocki and Felderhof (Ref. 20). The dashed line corresponds to the prediction by Verberg *et al.* (Ref. 15), and the solid line is the result of the improved DMT with  $\phi_c = 0.8678$ . (b) Relative zero-frequency viscosity  $\eta(\phi)/\eta_0$  at low shear rate as a function of the volume fraction  $\phi$ : triangles, van der Werff *et al.* (Ref. 12); crosses, van der Werff and de Kruijff (Ref. 13); circles, Jones *et al.* (Ref. 38); and squares, Papir and Krieger (Ref. 39). The dashed line corresponds to the prediction by Verberg *et al.* (Ref. 15), and the solid line is the result of the improved DMT with  $\phi_c = 0.63$ .

since its expansion in powers of  $\phi$  converges much better. For this reason, the differences between the predictions of the different models are more noticeable in this representation. In Fig. 4, we plot the function  $S(\phi)$  for various experimental results obtained in a variety of experimental situations and compare with the values obtained with our model. We take the same values of  $\phi_c$  used previously for the low-shear, high-shear, and high-frequency cases. The agreement with the experimental data is very good especially at large

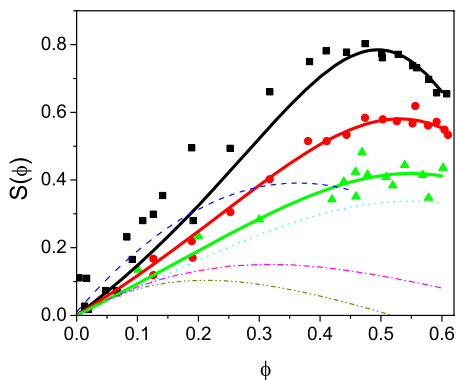


FIG. 4. (Color online) Representation of various viscosity data as suggested by Bedeaux (Ref. 17): Squares, SJ18 low-shear limit (Refs. 1 and 33); circles, SJ18 high-shear limit (Refs. 13 and 33); triangles, high-frequency limit of the real part of the complex shear viscosity (Ref. 12). Thick solid lines are the results of the improved DMT with  $\phi_c = 0.63$  (upper),  $\phi_c = 0.7404$  (medium), and  $\phi_c = 0.8678$  (lower); thin dashed line is Beenakker's result (Ref. 9), thin dotted line is Verberg *et al.* prediction (Ref. 15), thin dash-dot line is the result of Russel and Gast (Ref. 10), and the thin dash-dot-dot line is the prediction of Batchelor and Green (Ref. 4).

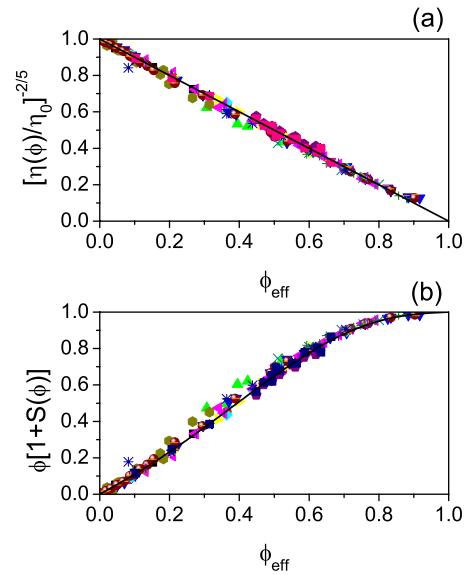


FIG. 5. (Color online) (a) Relative viscosity  $[\eta(\phi)/\eta_0]^{-2/5}$  as a function of the effective volume fraction  $\phi_{\text{eff}}$ . Symbols correspond to all the data sets of the previous figures and the solid line corresponds to the prediction of the improved DMT [Eq. (23)]. (b) Same as (a) but in the representation suggested by Bedeaux [Eq. (3)] as a function of the effective volume fraction  $\phi_{\text{eff}}$ . Symbols correspond to all the data sets of the previous figures and the solid line corresponds to the prediction of the improved DMT [Eq. (23)].

values of  $\phi$ . Note, that for small values of  $\phi$ , the experimental accuracy of  $S(\phi)$  is unsatisfactory which explains the large scatter in the experimental points.<sup>17</sup> The last set of experimental points corresponds to the high-frequency limit of the real part of the complex viscosity as obtained by the linear dynamic measurements performed by van der Werff *et al.*<sup>12</sup> The best fit to the real part, obtained with  $\phi_c = 0.8678$ , gives an excellent agreement with the experimental values. As a comparative, we also show the predictions for the high-frequency limit, obtained by Beenakker,<sup>9</sup> by Batchelor and Green,<sup>4</sup> by Russel and Gast,<sup>10</sup> and by Verberg *et al.*<sup>15</sup> In this very sensitive representation, it is seen that only the improved DMT matches the data at all volume fractions.

Finally, let us notice that the functional form for the reduced viscosity in the improved DMT in terms of  $\phi_{\text{eff}}$  as given by Eq. (22) makes no reference to any material parameter neither to the geometrical information of the system. This means that a plot of the reduced viscosity  $\eta(\phi)/\eta_0$  versus  $\phi_{\text{eff}}$  should be independent of the experimental details or of the material parameters of the sample. This is confirmed in Fig. 5(a) where we plot  $[\eta(\phi)/\eta_0]^{-2/5}$  versus  $\phi_{\text{eff}}$  for all the data sets considered in the previous figures. The straight line is the master curve predicted by the improved DMT [Eq. (22)]. In Fig. 5(b), we show  $\eta(\phi)/\eta_0$  but in the representation suggested by Bedeaux [Eq. (3)]. The agreement between theory and experiments shown in Fig. 5 provides a strong support to our definition of  $\phi_{\text{eff}}$ .

It is interesting to compare Eqs. (3) and (23) for the effective viscosity of the suspension by first performing a series expansion of Eq. (3) for  $\eta(\phi)$  in powers of  $\phi$ . We obtain

$$\eta(\phi) = \eta_0 \left[ 1 + \frac{5}{2}\phi + \frac{5}{2}(1 + S_1)\phi^2 + \dots \right],$$

where we have also used the expansion<sup>18</sup>  $S(\phi) = S_1\phi + S_2\phi^2 + \dots$ . The series expansion of Eq. (23) gives

$$\eta(\phi) = \eta_0 \left[ 1 + \frac{5}{2}\phi + \left( \frac{35}{8} + \frac{5}{2}c \right) \phi^2 + \dots \right]. \quad (25)$$

By comparing terms having the same order in  $\phi$ , we find relationships between the constant  $c$  and the constants  $S_i$  arising from the series expansion of  $S(\phi)$ . For instance, for the first two orders, we obtain  $S_1 = 3/4 + c$  and  $S_2 = -35/8 - (12/8)c + c^2$  that together yield the relation

$$S_2 = \left( S_1 - \frac{3}{2} \right)^2 - \frac{79}{16}. \quad (26)$$

Similar relations exist for the higher order coefficients  $S_i$  (with  $i > 2$ ) in terms of  $S_1$ , implying that for the improved DENT higher order correlations between the spheres can be reduced to combinations of the lower order correlations.

Other interesting comparisons can be performed with the different expressions for the effective viscosity. For instance, putting  $\phi = \phi_c$  in the denominator of Eq. (18) and replacing the factor  $5/2$  by  $2$  in Eq. (19), we obtain the well known empirical expression obtained by Quemada,<sup>23</sup> Eq. (12). This expression although gives the right divergence at high filling fractions does not have the correct low volume fraction limit given by Einstein's expression. On the other hand, putting  $\phi_{\text{eff}} = \phi / \phi_c$  in the denominator of Eq. (21), we recover the empirical expression obtained by Krieger and Dougherty<sup>22</sup> [Eq. (11)]. Nonetheless, the virial expansion of this expression gives values for the second virial coefficient  $k_2$  that are too small.<sup>26</sup> A generalization of this model but including a dependence of the crowding factor on the volume fraction was proposed by van de Ven.<sup>26</sup> However, this model has the shortcoming that gives rise to an expression for the viscosity that is more involved and it includes a second adjustable parameter besides  $\phi_c$ , which is chosen in order to adjust the second virial coefficient to the values predicted by other theories. In contrast, our proposal does not contain adjustable parameters besides  $\phi_c$  and the series expansion gives the right values for the second virial coefficient in a natural way, as it is shown below.

Choosing the RCP value for the volume fraction at critical packing,  $\phi_c = 0.63$ , we obtain from Eq. (25) up to  $O(\phi^3)$

$$\eta(\phi) / \eta_0 = 1 + \frac{5}{2}\phi + 5.84325\phi^2 + 12.5673\phi^3 + O(\phi^4),$$

which compares very well up to second order with the result that Cichoki and Felderhof<sup>20</sup> obtained on the basis of the pair Smoluchowski equation, which are exact to  $O(\phi^2)$ . With Brownian motion contributions they find for the second virial coefficient  $k_2 = 5.91$  [see Eq. (8)]. Batchelor and Green,<sup>4</sup> including Brownian motion obtained  $k_2 = 6.17$ , as shown in Eq. (6). Our result differs from the exact one by 1.2%, while the result by Batchelor and Green differs by 4.4%.

Taking fcc close packing  $\phi_c = 0.7404$ , and expanding Eq. (23) up to  $O(\phi^3)$ , we obtain

$$\eta(\phi) / \eta_0 = 1 + \frac{5}{2}\phi + 5.25155\phi^2 + 9.93777\phi^3 + O(\phi^4),$$

which compares well up to second order with the result by Bedeaux and collaborators<sup>7</sup>  $k_2 = 4.8$ , as shown in Eq. (4) and

even better with the result of Cichocki and Felderhof without including Brownian motion  $k_2 = 5.00$ , as shown in Eq. (7). Our result differs from the exact one by 5%, while the result by Bedeaux by 4%.

Using the value that best fits the high-frequency regime  $\phi_c = 0.8678$ , one finds for the real part of the complex relative viscosity

$$\eta(\phi) / \eta_0 = 1 + \frac{5}{2}\phi + 4.75566\phi^2 + 7.95275\phi^3 + O(\phi^4),$$

which compares well with the result by Batchelor and Green,<sup>4</sup>  $k_2 = 5.2$ , as shown in Eq. (5), and in which Brownian motion is not taken into consideration.

Finally, it is interesting to find a value for  $\phi_c$  that best fits the theoretical results obtained by Verberg *et al.*<sup>15</sup> in the high-frequency limit [Eq. (10)]. This value is  $\phi_c = 0.95238$  and produces the following series expansion up to  $O(\phi^7)$ , just to show a few terms

$$\begin{aligned} \eta(\phi) / \eta_0 = & 1 + \frac{5}{2}\phi + 4.5\phi^2 + 7.006\phi^3 + 10.041\phi^4 \\ & + 13.6358\phi^5 + 17.8297\phi^6 + 22.6673\phi^7 \\ & + O(\phi^8), \end{aligned}$$

which is exact up to  $O(\phi^2)$  with the series expansion of the result by Verberg *et al.*,<sup>15</sup> which reads

$$\begin{aligned} \eta(\phi) / \eta_0 = & 1 + \frac{5}{2}\phi + 4.5\phi^2 + 7\phi^3 + 10\phi^4 + 13.5\phi^5 \\ & + 17.5\phi^6 + 22\phi^7 + O(\phi^8), \end{aligned}$$

and the higher order terms are also amazingly close.

## V. CONCLUSIONS

We have formulated an improved differential effective medium theory that accounts for the dependence of the viscosity of hard spheres suspensions at arbitrary volume fractions. This theory incorporates correlations between the spheres arising from excluded volume effects and hydrodynamic interactions that lead to scaling of the viscosity as a function of an effective filling fraction  $\phi_{\text{eff}}$ . This scaling behavior is essential to determine the expression for the viscosity when taking  $\phi_{\text{eff}}$  as the integration variable in the differential procedure. Physically, this scaling implicitly considers correlations between the spheres of the same generation in contrast to the usual differential methods where the bare filling fraction is used.

The agreement with experimental data at low- and high-shear rates and in the high-frequency limit is remarkable and superior to all other theories. Also, the virial expansion of our model compares well with the second virial coefficient obtained by a number of different theories in all the regimes considered. In the particular case of the high-frequency limit, it is possible to find a value for  $\phi_c$  for which the virial expansion is amazingly close to higher orders to that of the model by Verberg *et al.*<sup>15</sup> Although our proposal can be generalized to describe the viscoelastic behavior at  $\omega \neq 0$  by simply allowing  $\phi_c$  to take complex values, we do not have a derivation based on simple physical arguments to justify this generalization. Such a goal requires further research.

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- <sup>1</sup>A. Einstein, *Investigations on the Theory of Brownian Movement* (Dover, New York, 1975); *Ann. Phys.* **34**, 591 (1911).
- <sup>2</sup>N. Saito, *J. Phys. Soc. Jpn.* **5**, 4 (1950).
- <sup>3</sup>J. M. Peterson and M. Fixman, *J. Chem. Phys.* **39**, 2516 (1963).
- <sup>4</sup>G. K. Batchelor and J. T. Green, *J. Fluid Mech.* **56**, 401 (1972).
- <sup>5</sup>G. K. Batchelor, *J. Fluid Mech.* **83**, 97 (1977).
- <sup>6</sup>P. Mazur and D. Bedeaux, *Physica (Amsterdam)* **76**, 235 (1974).
- <sup>7</sup>D. Bedeaux, R. Kapral, and P. Mazur, *Physica A* **88**, 88 (1977).
- <sup>8</sup>C. W. J. Beenakker, W. van Saarloos, and P. Mazur, *Physica A* **127**, 451 (1984).
- <sup>9</sup>C. W. J. Beenakker, *Physica A* **128**, 48 (1984).
- <sup>10</sup>W. B. Russel and A. P. Gast, *J. Chem. Phys.* **84**, 1815 (1986).
- <sup>11</sup>G. Bossis and J. F. Brady, *J. Chem. Phys.* **91**, 1866 (1989).
- <sup>12</sup>J. C. van der Werff, C. G. de Kruiff, C. Blom, and J. Mellema, *Phys. Rev. A* **39**, 795 (1989).
- <sup>13</sup>J. C. van der Werff and C. G. de Kruiff, *J. Rheol.* **33**, 421 (1989).
- <sup>14</sup>J. Mellema, C. G. de Kruiff, C. Blom, and A. Vrij, *Rheol. Acta* **26**, 40 (1987).
- <sup>15</sup>R. Verberg, I. M. de Scheper, and E. G. D. Cohen, *Phys. Rev. E* **55**, 3143 (1997).
- <sup>16</sup>R. A. Lionberger and W. B. Russel, *Adv. Chem. Phys.* **111**, 399 (2000).
- <sup>17</sup>D. Bedeaux, *J. Colloid Interface Sci.* **118**, 80 (1987).
- <sup>18</sup>J. Smeets, G. J. M. Koper, J. P. M. van der Ploeg, and D. Bedeaux, *Langmuir* **10**, 1387 (1994).
- <sup>19</sup>B. Cichocki and B. U. Felderhof, *Phys. Rev. A* **43**, 5405 (1991).
- <sup>20</sup>B. Cichocki and B. U. Felderhof, *Phys. Rev. A* **46**, 7723 (1992).
- <sup>21</sup>B. Dames, B. R. Morrison, and N. Willembacher, *Rheol. Acta* **40**, 434 (2001).
- <sup>22</sup>I. M. Krieger and T. J. Dougherty, *Trans. Soc. Rheol.* **3**, 137 (1959).
- <sup>23</sup>D. Quemada, *Rheol. Acta* **16**, 82 (1977).
- <sup>24</sup>R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford, New York, 1999).
- <sup>25</sup>R. Pal and E. Rhodes, *J. Rheol.* **33**, 1021 (1989).
- <sup>26</sup>T. G. M. van de Ven, *Colloidal Hydrodynamics* (Academic, London, 1989).
- <sup>27</sup>D. A. G. Bruggeman, *Ann. Phys.* **416**, 636 (1935).
- <sup>28</sup>R. Chang, H.-P. Chiang, P. T. Leung, D. P. Tsai, and W. S. Tse, *Solid State Commun.* **133**, 315 (2005).
- <sup>29</sup>I. O. Sosa, C. I. Mendoza, and R. G. Barrera, *Phys. Rev. B* **63**, 144201 (2001).
- <sup>30</sup>Z. Arrhenius, *Biochem. J.* **11**, 112 (1917).
- <sup>31</sup>R. Ball and P. Richmond, *Phys. Chem. Liq.* **9**, 99 (1980).
- <sup>32</sup>L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, Fluid Mechanics* (Pergamon, New York, 1980), Vol. 6.
- <sup>33</sup>C. G. de Kruif, E. M. F. van Iersel, A. Vrij, and W. B. Russel, *J. Chem. Phys.* **83**, 4717 (1985).
- <sup>34</sup>I. M. Krieger, *Adv. Colloid Interface Sci.* **3**, 111 (1972).
- <sup>35</sup>F. L. Saunders, *J. Colloid Sci.* **16**, 13 (1961).
- <sup>36</sup>M. M. Kops-Werkhoven and H. M. Fijnaut, *J. Chem. Phys.* **77**, 2242 (1982).
- <sup>37</sup>J. X. Zhu, D. J. Durian, J. Muller, D. A. Weitz, and D. J. Pine, *Phys. Rev. Lett.* **68**, 2559 (1992).
- <sup>38</sup>D. A. R. Jones, B. Leary, and D. V. Boger, *J. Colloid Interface Sci.* **147**, 479 (1991); **150**, 84 (1992).
- <sup>39</sup>Y. S. Papir and I. M. Krieger, *J. Colloid Interface Sci.* **34**, 126 (1970).

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