

Other than attempts to provide empirical fits to experimental viscosity data at higher emulsion concentrations, two main theoretical approaches have been used to derive equations that can be used to predict the viscosity of emulsions at higher concentrations. The first approach begins with the dilute limit and attempts to extend it to higher concentrations using differential effective medium theory (D-EMT) [2]. The second approach starts in the concentrated regime, near the percolation threshold, and uses the theoretically expected scaling of the divergence of viscosity as a starting point to obtain a crossover equation that is applicable at lower concentrations. This latter approach is detailed in a review by Douglas and coworkers [3].

Of the two methods just described, the use of D-EMT has historically received the most attention. Using D-EMT, the relative viscosity is calculated incrementally, starting at a known dilute limit, and repeatedly adding differential volumes of the dispersed phase. The process is executed by always assuming that (1) the material surrounding the differential added volume is a homogeneous material with well-defined properties, (2) the property of the surrounding homogeneous material is unaffected by the addition of a differential volume of dispersed phase, and therefore, (3) the addition of a differential volume of dispersed phase produces a dilute composite, the change in property of which may be inferred from the known change in property in the dilute limit. Brinkman [4] and Roscoe [5] were the first to apply D-EMT to derive the following viscosity–concentration relationship for suspensions of hard spheres:

$$\eta_r = (1 - \phi)^{-[\eta]} \quad (3)$$

Krieger and Dougherty [6] modified Eq. (3) by introducing the concept of a maximum packing fraction, ϕ_m , at which the viscosity diverges, which they justified using the crowding effect originally introduced by Mooney [7] to account for volume exclusion as particles are added incrementally to the composite. Their resulting equation, also derived by D-EMT methods, is

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (4)$$

Later, Pal and Rhodes [8] appealed to D-EMT concepts to propose a simple form of Eq. (4) for emulsions,

$$\eta_r = [1 - K_0 K_\alpha \phi]^{-[\eta]} \quad (5)$$

In Eq. (5), K_0 and K_α are empirical correction factors that are interpreted as accounting for the influence of immobilized solvent volume due to, respectively, binding at the interface between the phases and entrapment in the interstitial spaces within flocs of the dispersed phase. K_0 is assumed to be a constant for a given emulsion, and K_α is assumed to depend on the shear rate. In practice, the product of the two parameters are fit to viscosity data, for a given emulsion, according to the equation

$$K_0 K_\alpha = 0.8415/\phi(100),$$

where $\phi(100)$ is the volume fraction at which $\eta_r = 100$. Equation (5) has been used widely to model the viscosity of emulsions in the non-dilute regime since it was introduced; as of this writing, Ref. [8] has been cited at least 89 times.

In emulsions, the relative viscosity depends not only on the concentration of the dispersed phase, but also on the ratio, z , of the viscosity of the dispersed phase to the viscosity of the pure solvent. To avoid confusion in terminology, we emphasize that z is the ratio of the viscosities of the two phases in the emulsion, whereas η_r is the ratio of the emulsion viscosity to the solvent viscosity. Pal [9] has incorporated z into D-EMT derivations of

viscosity–concentration relations for emulsions. In this case, the intrinsic viscosity $[\eta]$ was taken to be that derived by Taylor [10] for undeformable spherical droplets in a liquid medium,

$$[\eta] = 1 + \frac{3z/2}{1+z} \quad \text{undeformable spherical droplet.} \quad (6)$$

In addition, Pal utilized the concept of a crowding effect, originally introduced by Mooney [7] to account for volume exclusion as droplets are added incrementally to the composite. The resulting equation is

$$\eta_r \left[\frac{2\eta_r + 5z}{2 + 5z} \right]^{3/2} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}, \quad (7)$$

where ϕ_m is the maximum packing fraction of the liquid droplets, which must be determined separately either by fitting to experiment or by computer simulation.

In this paper, we scrutinize the applicability of D-EMT to emulsions more closely. In particular, the assumptions that underly the D-EMT approach are analyzed, and their validity is found to be questionable when solvation of the dispersed phase particles is possible. Because of the ambiguities involved, we revisit the derivation of Pal and Rhodes [8] using two different sets of starting assumptions about the way the emulsion is constructed. In so doing, we arrive at two different, yet somewhat complementary, equations for the relative viscosity. Afterward, we explore the second approach mentioned earlier, based on scaling of critical phenomena, to obtain an alternative viscosity–concentration equation for emulsions. We draw largely on the work by Douglas and coworkers [3] to account for influences of dispersed phase viscosity, deformability of the dispersed phase, and the possibility of interparticle forces. The resulting viscosity equation is compared with D-EMT results like Eq. (5) and Eq. (7), and is found to provide better fits to experimental data for oil–water emulsions covering a wide range of viscosity ratios.

2. D-EMT approach

In this section, we highlight some of the ambiguities that can arise when applying D-EMT to suspensions of particles that may themselves incorporate some of the solvent either by solvation or by occlusion in interstitial pores. We imagine a suspension or emulsion consisting of a continuous solvent phase and a number N of particles in suspension. The particles, shown schematically in Fig. 1, are modeled as a fixed volume of primary particles which may be flocculated to form a cluster, and a certain volume of liquid that is immobilized either by solvation or entrapment within the interstitial spaces between the primary particles. Both the solvent and the particles are assumed to be incompressible and, for the moment, we assume that the clusters are undeformable.

The total liquid volume, $V_{L,\text{tot}}$, is the sum of the mobile liquid, solvated liquid, and interstitial liquid:

$$V_{L,\text{tot}} = V_{L,m} + V_{L,s} + V_{L,a}, \quad (8)$$

where $V_{L,m}$ is the volume of solvent that is free, i.e. not associated with any particle, $V_{L,s}/N$ is the average volume of solvent that is tightly bound to each particle by solvation, and $V_{L,a}/N$ is the average volume of solvent trapped in the interstitial spaces of a flocculated cluster. If V is the actual volume of dispersed phase, that is, the primary particles, then the volume of flocculated clusters is

$$V_c = V + V_{L,s} + V_{L,a}. \quad (9)$$

Normalizing Eqs. (8) and (9) to the total suspension volume, V_T , gives

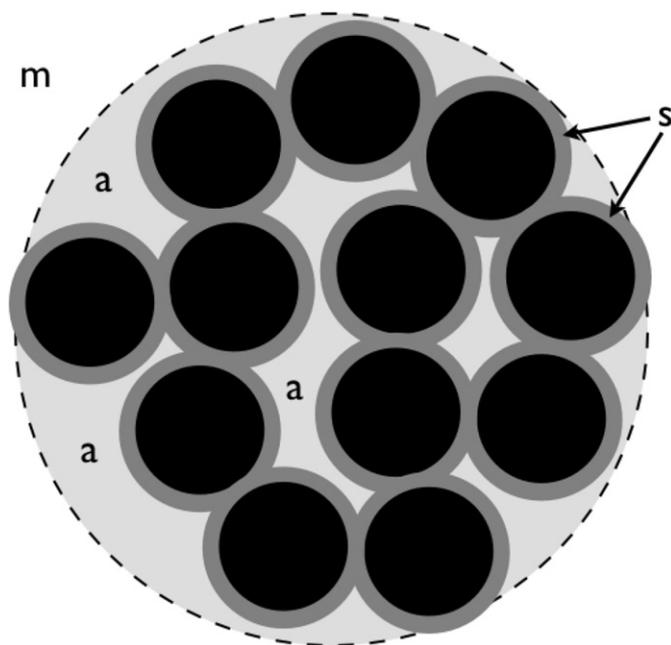


Fig. 1. Conceptual model of a particle, enclosed by the dashed circle. The particle, suspended in a mobile solvent denoted by “m,” consists of primary particles (black), solvated liquid that is tightly bound to the primary particle surfaces, denoted by “s,” and water that is trapped in the interstitial void space of the flocculated structure, denoted by “a.”

$$\phi_{L,tot} = \phi_{L,m} + \phi_{L,s} + \phi_{L,a}, \quad (10)$$

$$\phi_c = \phi + \phi_{L,s} + \phi_{L,a}, \quad (11)$$

where, for example, $\phi \equiv V/V_T$ is the volume fraction, or concentration, of primary particles.

Equation (11) can be rearranged as

$$\begin{aligned} \phi_c &= \frac{1 + (\phi_{L,s}/\phi)}{1 - (\phi_{L,a}/\phi_c)} \phi \\ &= K_0 K_\alpha \phi \equiv K \phi, \end{aligned} \quad (12)$$

where we follow Pal and Rhodes [8] in defining an empirical solvation factor, K_0 , an empirical flocculation factor, K_α , and an “effective solvation” factor, K , according to

$$K_0 \equiv 1 + \phi_{L,s}/\phi,$$

$$K_\alpha \equiv \frac{1}{1 - (\phi_{L,a}/\phi_c)} = \frac{1}{1 - \alpha},$$

$$K \equiv K_0 K_\alpha.$$

If we think of the effective volume of the particles as the area within the dashed circle in Fig. 1, then K represents the ratio of the effective volume to the volume of the primary particles in the cluster. This factor is decomposed into the product of two other factors: K_0 is the ratio of the solvated liquid volume to the primary particle volume, and K_α is the ratio of the effective particle volume to the combined volume of primary particles with their solvated liquid. As noted by Pal and Rhodes [8], K_0 should be a constant for a given suspension, but K_α depends on the flocculated cluster size and shape, which in turn can be influenced by the applied shear rate. Throughout this section, we will neglect the shear rate dependence of K_α , so it will be convenient to incorporate the effective volume through K alone. $K \geq 1$ by definition. Application of D-EMT is not as straightforward for solvated, flocculated clusters of primary particles as it is when the particles are dense and unsolvated. The source of the difficulty is the multiphase nature of the clusters. Specifically, in developing a D-EMT procedure for clusters, one has to decide on the source of the liquid of solvation

and occlusion. Basically, there are two choices: (1) The necessary extra liquid can be assumed to be added along with the primary particles at each step. This has the advantage that the composition of the surrounding medium will not be altered, but it has the disadvantage that the total liquid volume is not conserved. (2) The required liquid for solvation and occlusion can be assumed to be drawn from the mobile liquid in the surrounding medium after the particles are added. This assumption conserves the total liquid volume, but forces a reduction in the volume of mobile liquid in the surrounding medium and, therefore, an increase in its viscosity. But such an alteration in the medium viscosity violates one of the principle assumptions of D-EMT, namely that there is no differential change to the viscosity of the surrounding medium when a differential volume of new particles is added. Although a small effect during any differential step, the depletion of mobile solvent must increase the viscosity of the medium itself, and the accumulated effect can be significant.

Based on these considerations, we need to examine the application of D-EMT carefully when solvated clusters are involved. A previous paper [8] in which Eq. (5) was introduced, used the second assumption from the preceding paragraph, i.e. that the required liquid of solvation and occlusion is drawn from the surrounding medium after primary particles are added. Because of a couple of mathematical errors introduced in the derivation, Eq. (5) was obtained in Ref. [8]. As shown in Appendix A, however, the equation that should result from these assumptions is actually

$$\eta_r = (1 - \phi)^{-K[\eta]_c}, \quad (13)$$

where $[\eta]_c$ is the intrinsic viscosity of the solvated and flocculated clusters, a quantity that will likely depend on the shear rate applied to the suspension because the degree of flocculation is likely to be reduced at higher shear rates. In addition to this difficulty and the fact that it diverges only when $\phi \rightarrow 1$, Eq. (13) probably is not valid because, as described already, its derivation violates the assumption that the addition of a differential volume of particles does not alter the viscosity of the surrounding effective medium.

It is important to remember that, in the D-EMT method, the medium is assumed to be a *homogeneous pure solvent* at each step even though its composition and viscosity change incrementally with each step. Therefore, ϕ in the dilute limit must be interpreted as just the volume fraction that is *added* during one step, not the actual volume fraction. To emphasize this point, the dilute limit of Eq. (1) is rewritten in finite difference form as follows:

$$\Delta \eta_r = \eta_r [\eta] \Delta \phi', \quad (14)$$

where the prime superscript on the volume fraction means that it is the incremental volume fraction added to the effective medium during each step.

In Appendix A, we derive the following equation using D-EMT, based on the assumption that the differential extra volume of liquid required for solvation and occlusion is added to the medium along with the differential volume of primary particles during each step:

$$\eta_r = (1 - K\phi)^{-[\eta]/K}. \quad (15)$$

When $K = 1$ and when there is no flocculation, then $[\eta]_c = [\eta]$ and Eq. (15) reduces to Eq. (3) obtained for hard spheres by Brinkman [4] and Roscoe [5]. The D-EMT result also is similar in form to Eq. (5) proposed by Pal and Rhodes [8], except that the exponent in Eq. (5) is now shown to be $[\eta]/K$ instead of $[\eta]$. We can compare the form of Eq. (15) to the virial expansion in Eq. (1) expanding the former as a Maclaurin series:

$$\begin{aligned} \eta_r &= (1 - K\phi)^{-[\eta]/K} \\ &= 1 + [\eta]\phi + \frac{1}{2}([\eta]^2 + K[\eta])\phi^2 + \dots \end{aligned} \quad (16)$$

The expansion agrees with Eq. (1) to first order, and comparison of the second-order terms provides a general approximation suggested by Douglas [11]:

$$k_H = \frac{1}{2}[\eta]([\eta] + K). \quad (17)$$

For undeformable, repulsive spherical particles, theoretical calculations of k_H predict values between 5.0 [12,13] and 5.2 [14] when only hydrodynamic effects are considered. If the spheres are sufficiently small, influences of Brownian motion increase the theoretical estimates to between 6.0 [12,13] and 6.2 [14]. For these same particles, $K = 1$ and $[\eta] = 2.5$, so Eq. (17) suggests that $k_H \approx 4.4$, which for large spheres is about 90% of the theoretical values. Thus, Eq. (15) provides approximate corrections to the dilute limit that are only approximate to second order. The effective medium approach is more accurate at low concentrations, so these corrections are expected to be quite an effective approximation in the absence of further information about k_H , even for particles of general shape. When a dispersion becomes increasingly concentrated, the assumptions of D-EMT become increasingly dubious. Particles added to a more concentrated suspension will begin to interact with the particles that are already present. This interaction may be due to interparticle forces or to the onset of a percolation transition, as described in the Introduction. The concentration beyond which these interactions become important will depend on the nature of the dispersion, such as the range of interparticle forces and the shape and deformability of the particles. In many cases, interactions can become important in the semidilute regime, but even suspensions composed of rigid inert spheres will undergo interactions in the concentrated regime due to the onset of percolation. In any event, once the interactions become important, the assumptions of D-EMT are no longer strictly valid, and therefore the validity of Eq. (15) becomes questionable. For these reasons, in the next section we propose an alternate approach that may better address these complications.

3. Approach based on critical phenomena

In 1995, Douglas and Garboczi [15] demonstrated, both theoretically and computationally, that the viscosity of suspensions in the dilute regime has an exact correspondence to the electrical conductivity of composites, formed by embedding conducting inclusions in an insulating matrix. In [3], Douglas and coworkers argued that, for suspensions of rigid particles at high concentrations, the relative viscosity diverges as $\phi \rightarrow \phi^*$ according to an asymptotic universal relationship,

$$\eta_r \sim \left(1 - \frac{\phi}{\phi^*}\right)^{-2}, \quad (18)$$

which is independent of the shape of the particles in suspension.

Using Eq. (18) as a starting point, Douglas and coworkers [3] proposed a crossover equation between it and the virial expansion in Eq. (1), which provides a smooth transition between the semidilute and concentrated regimes:

$$\eta_r = \left(1 - \frac{\phi}{\phi^*}\right)^{-2} \left[1 + C_1 \left(\frac{\phi}{\phi^*}\right) + C_2 \left(\frac{\phi}{\phi^*}\right)^2\right] \quad (19)$$

to second order in ϕ , where

$$C_1 = [\eta]\phi^* - 2, \quad (20)$$

$$C_2 = k_H\phi^{*2} - 2[\eta]\phi^* + 1. \quad (21)$$

The critical exponent of 2 in Eq. (19) is strictly valid for rigid particles in three-dimensional (3-D) suspensions [15]. The correspondence shown by Douglas and Garboczi also predicts that the

critical exponent is 4/3 for 2-D suspensions [15], a prediction that is confirmed by experiments on thin films of oil containing small spherical particles [16]. Although there is some question in the literature about its universality, the value of 2 has been shown to be, at the very least, a good approximation of the exponent for a wide range of 3-D suspensions [3,17–20,26]. The numerical value of the critical exponent is not as well established for emulsions near ϕ^* , but there is experimental evidence that the viscosity of emulsions typically diverges near a critical concentration with a critical exponent that is often near 2 [8]. Therefore, lacking further information we will assume that a critical exponent of approximately 2 is also valid for emulsions. In any case, the advantage of Eq. (19) is that it incorporates, into one continuous relation, both the generalized scaling of the divergence of η_r near ϕ^* , as well as the linear and second-order terms of the virial expansion for more dilute suspensions. Therefore, this equation should be appropriate for dilute, semidilute, or concentrated suspensions.

In the next section, we apply Eq. (19) to emulsions and compare the results to Eq. (7) and Eq. (15). Therefore, we now require some means of estimating $[\eta]$, k_H , and ϕ^* for emulsions. We will assume that the particles in suspension are the solvated clusters from earlier sections of the paper, the shapes of which are basically spherical due to surface tension effects. If the interfacial tension between the particles and the surrounding liquid is sufficiently high, or if the shear rate is sufficiently low, then the particle shapes will remain approximately spherical and

$$[\eta] = \frac{1 + z[\eta]_\infty}{1 + z} \quad \text{undeformable spherical droplet} \quad (22)$$

will describe the intrinsic viscosity, where we have written Eq. (6) in an equivalent form and $[\eta]_\infty$ refers to an infinite-viscosity particle of the same shape (e.g. 2.5 for a hard sphere). Equation (22) is usually a good approximation for $[\eta]$ at low shear rates when the dispersed phase has a high surface tension in the solvent, and often is appropriate both for liquid-in-liquid emulsions and for gas-in-liquid dispersions [3,9]. But for particles that can deform easily, the following equation for the intrinsic viscosity holds [15]:

$$[\eta] = \frac{z - 1}{1 + (z - 1)/[\eta]_\infty} \quad \text{freely deformable liquid droplet.} \quad (23)$$

Like Eq. (22), Eq. (23) recovers the rigid particle value, $[\eta]_\infty$, in the limit $z \rightarrow \infty$, but Eq. (23) also predicts negative values of $[\eta]$ when $z < 1$. That is, Eq. (23) predicts that emulsions will become less viscous with increasing concentration when particles are added that have lower viscosity than the pure liquid medium. In contrast, Eq. (22) always predicts $1 \leq [\eta] \leq 2.5$.

The quantity ϕ^* can be thought of as a viscosity percolation threshold, which generally is greater than the purely geometrical percolation threshold of the particles but less than or equal to the maximum packing fraction ϕ_m [3]. ϕ^* is interpreted as the concentration at which the dispersion loses its fluidity, and this same interpretation was implicitly used as a working definition of ϕ_m [6,8,9]. As with other percolation phenomena, the value of ϕ^* is expected to depend sensitively on particle shape, aggregation tendency, and the shear rate applied to the suspension [3]. Wildemuth and Williams [21] analyzed experimental data on hard-sphere dispersions and found that $\phi^* \approx 1.7/[\eta]$ is a good approximation over a wide range of shear rates in which both ϕ^* and $[\eta]$ vary. Bicerano et al. [3] further suggested that the inverse relation between ϕ^* and $[\eta]$ is universal for monodisperse spheres. For polydisperse spheres, the simple inverse relation is questionable because $[\eta] = 2.5$ for rigid spheres of any size but ϕ^* for rigid spheres can increase from the random close packing fraction of approximately 0.64 for monodisperse spheres, to much higher values for polydisperse spheres.

We have already noted that the Huggins coefficient, k_H , depends sensitively on particle interactions and on $[\eta]$. Equation (17) was given earlier as an approximate relationship between k_H and $[\eta]$. Other investigators [22] have suggested $k_H \sim [\eta]^2$ as a good approximation for spherical particles, but this is likely to be valid only over a modest range of intrinsic viscosities near the hard-sphere value of 2.5. When the dispersed phase tends to flocculate, $[\eta]$ and k_H depend greatly on the degree of flocculation. Furthermore, if weak flocs can be broken down by application of high shear rates, then both $[\eta]$ and k_H will depend on shear rate, too, decreasing as the shear rate increases.

4. Comparison of D-EMT and percolation equations

In this section, we compare the predictions of Eqs. (7), (15), and (19). All three equations involve parameters such as ϕ^* , k_H , and z , that depend on the particular emulsion being studied. However, a parametric study of the equations seems to have limited value outside the context of experimental measurements on real emulsions. Therefore, we prefer to compare the theoretical equations to measurements on several emulsions to determine how well each equation fits the data when reasonable values are chosen for the parameters. The aim of this paper is primarily theoretical, and generating new experimental measurements of emulsion viscosity lies outside its scope. Therefore, we have chosen to use measurements on emulsions previously reported by Pal [9]. These experimental data were chosen for two reasons. First, the emulsions span five orders of magnitude in the viscosity ratio, z , ranging from 0.0112 to 1170. Second, Pal used these same experimental data for validating his own viscosity equation, Eq. (7). He chose those four particular emulsions—a polymer-thickened emulsion, two mineral oil emulsions, and one emulsion of heavy oil in water—because their properties were known to be consistent with the assumptions that “(a) the capillary number is small so that deformation of droplets can be neglected, and (b) the emulsions are stable (unfloculated), consisting of noncolloidal droplets with negligible colloidal interactions” [9]. Therefore, although we do not have further knowledge of those emulsions nor the details surrounding the measurement techniques that were used, it is appropriate to use these experimental data for comparing the other two equations considered here. Nevertheless, our choice of previously published experimental data is intended only to show how Eq. (19) can give at least as good a fit to the experimental data as either Eq. (7) or Eq. (15). We do not consider this cursory comparison to be a full validation of any of the equations, and we invite other experimentalists to make more stringent tests of these equations in the future.

We first note that the D-EMT result, Eq. (15), diverges as $K\phi \rightarrow 1$, with critical exponent $[\eta]/K$. In this respect, the inverse solvation factor, $1/K$, plays the role of a critical concentration. Indeed, if we assign $1/K = \phi^*$, then Eq. (15) is identical to the Krieger–Dougherty equation, Eq. (4), if ϕ^* is equated to the maximum packing fraction ϕ_m . Therefore, although there is a significant physical difference between ϕ^* and ϕ_m [3], there is no mathematical distinction between Eq. (15) and the Krieger–Dougherty equation. This point will be taken up in the Discussion, but to make comparisons between Eq. (7), Eq. (15), and Eq. (19), we will simply assume that $K = 1/\phi^*$. Also, because we have no detailed information on the polydispersity of the emulsions to which we are comparing, we will assume that $\phi_m \approx \phi^*$ in Eq. (7) which, as already mentioned is entirely consistent with the definition given to ϕ_m in the derivations of Eqs. (4) and (7) [6,9]. When using Eq. (19), we will estimate k_H using Eq. (17) with $K = 1$. As already shown, Eq. (17) is required for consistency between the D-EMT equation (15), and it also agrees reasonably well with earlier theoretical calculations [12–14,22]. In addition, we will assume for both equations that the

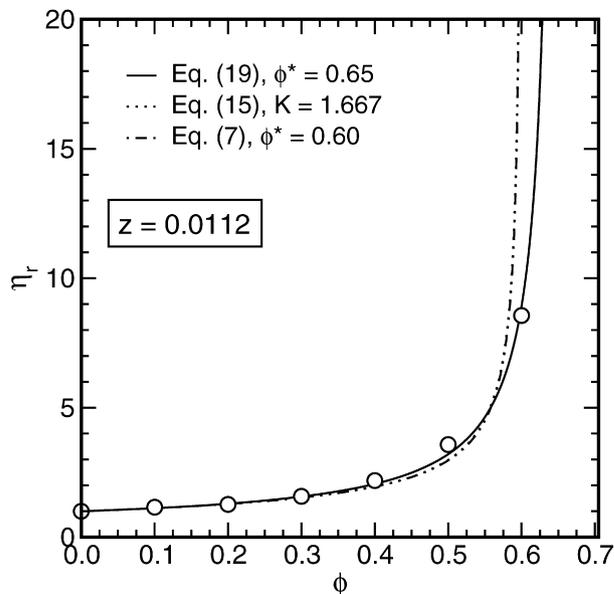


Fig. 2. Comparison of viscosity equations against experimental data (open circles) given in [9] for a polymer-thickened emulsion with $z = 0.0112$. Equations (7) and (15) are indistinguishable.

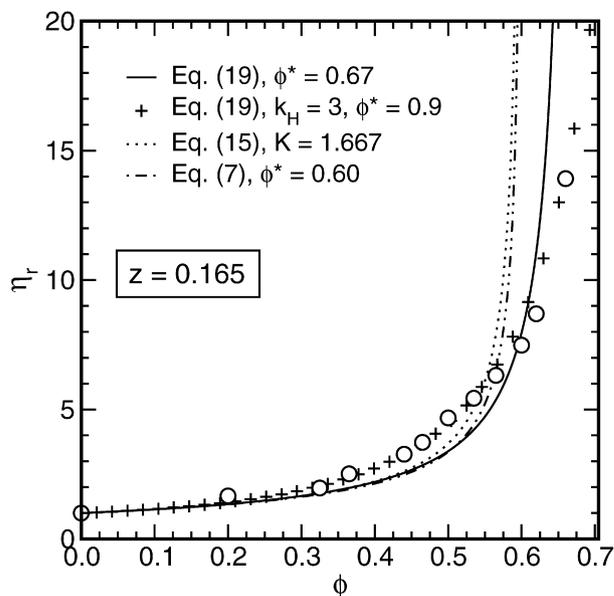


Fig. 3. Comparison of viscosity equations against experimental data (open circles) given in [9] for a mineral oil emulsion with $z = 0.165$.

intrinsic viscosity is given by Eq. (22). Finally, because of the difficulty associated with estimating ϕ^* when the polydispersity of the emulsion is not known, we will treat it as a fitting parameter when comparing the equations to experimental data.

Figs. 2–5 compare the crossover equation, Eq. (19), the D-EMT equation, Eq. (15), and the equation of Pal, Eq. (7), to experimental data on the four emulsions previously described here and in Ref. [9]. Each plot in Figs. 2–5 show the three equations as curves, with ϕ^* or K chosen to provide the best qualitative fit to the experimental data. The experimental data were obtained from the figures in [9] by high-resolution electronic scans, using the coordinates of the four corners of the scanned figure and interpolating the values from the coordinates of each point. The uncertainties in the experimental data were not reported.

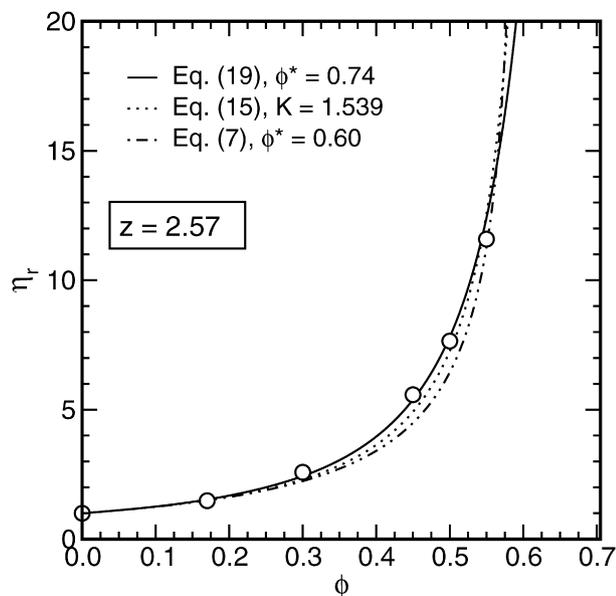


Fig. 4. Comparison of viscosity equations against experimental data (open circles) given in [9] for a mineral oil emulsion with $z = 2.57$.

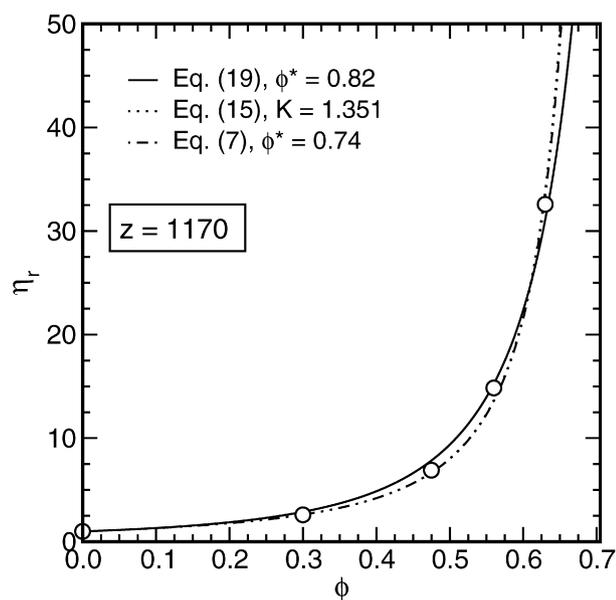


Fig. 5. Comparison of viscosity equations against experimental data (open circles) given in [9] for an emulsion of heavy oil in water with $z = 1170$. Equations (7) and (15) are indistinguishable.

In each of the figures, all three equations give reasonable fits to the experimental data at lower volume fractions, and the values of the fitting parameter are within a reasonable range. However, Eq. (19) provides a better fit to the data in each plot, over the entire range of volume fractions measured but especially at higher volume fractions. We also note that the D-EMT equation (15) and the more complicated equation (7) proposed in [9] nearly coincide over the range of volume fractions measured, and are basically indistinguishable when $z = 0.0112$ and $z = 1170$.

Despite the better fit of Eq. (19) to the experimental data, there is still some discrepancy at higher concentrations when $z = 0.165$ in Fig. 3. Without more information about the nature of this particular emulsion, it is difficult to pinpoint why its measured viscosity is lower than predicted at higher concentrations. One possible explanation is a mild attraction between the dispersed phase particles, in which case we would expect k_H to be higher than the

value of 1.3 predicted by Eq. (17). In fact, if we assign $k_H = 3$ for this emulsion, then the fit of Eq. (19) is even better, as shown by the “+” symbols in Fig. 3, although ϕ^* also must be increased to 0.9 to obtain the fit. For this emulsion, the dispersed phase has a significantly lower viscosity than the solvent, so higher values of ϕ^* are plausible. But without more information about the emulsion, we will not speculate further on the meaning of the better fit.

5. Discussion

As mentioned already, the D-EMT equation (15) given here, which corrects the equation derived by Pal and Rhodes [8], is mathematically identical to the Krieger–Dougherty equation if one identifies the solvation factor K with $1/\phi_m$ although, as previously noted [3], it is more proper to think of ϕ_m as the viscosity percolation threshold ϕ^* instead of the maximum packing fraction of the dispersed phase. Not only mathematically, but physically there should be qualitative similarities between K and $1/\phi^*$. For example, K increases as the volume of solvent bound to the dispersed phase increases, either by solvation or by occluding the internal porosity of flocculated droplets. But flocculation also decreases ϕ^* relative to its value for unflocculated systems, and Bicerano et al. suggest a semiquantitative relationship for relating ϕ^* to the average size and fractal dimension of the flocs [3]. Also, in flocculated suspensions both K and $1/\phi^*$ decrease with increasing shear rate if the flocs are weak enough to be broken down [3,8]. But the physical analogy between K and $1/\phi^*$ cannot be taken too far because a change in ϕ^* may not always cause an inverse change in K . For example, increasing the polydispersity of a suspension of unsolvated/deflocculated hard spheres ($K \equiv 1$) will generally increase ϕ^* . Similarly, changing the shape of the dispersed phase can have a dramatic influence on ϕ^* [3,23] without influencing K at all. Therefore, when fitting K to experimental viscosity data, as in [8], differences in K among different emulsions cannot necessarily be interpreted physically solely in terms of degree of solvation or flocculation.

In this paper, we have assumed that emulsions possess a finite viscosity percolation threshold. That is, we have assumed that there is some concentration $\phi^* < 1$ at which the viscosity diverges and the emulsion loses its fluidity. A number of experiments [8,9] seem to indicate this divergent behavior. However, viscosity measurements can be difficult in the concentrated regime, and a rapid increase in viscosity may not necessarily indicate divergence. Indeed, zero-shear viscosity measurements on some polymer solutions indicate a power law relation between viscosity and concentration [24,25]:

$$\eta_r \propto \phi^\alpha,$$

where the exponent α is related to the exponent in the relationship between the radius of gyration of the polymer and its molecular weight. For some emulsions, especially those with a highly deformable dispersed phase, the suspension might not undergo gelation or lose fluidity at any finite concentration. Instead, such suspensions might exhibit a continuous, but not necessarily monotonic, viscosity–concentration relationship involving power-law behavior up to intermediate concentrations followed by an asymptotic approach to the viscosity of the dispersed phase as $\phi \rightarrow 1$. Considerably more experimental work is necessary to determine if such behavior by emulsions can be observed.

Finally, we have not addressed temperature effects on the relative viscosity of emulsions in this paper. Predicting the influence of temperature on relative viscosity can be extremely complicated and is outside the scope of this paper, but a few general comments can be made. At low shear rates and above the glass transition temperature, the viscosity of a pure liquid often approaches an Arrhenius-like dependence on absolute temperature T ,

i.e. $\eta \sim \exp(E_\eta/RT)$, where E_η is an activation energy for viscous flow and R is the gas constant. In a suspension of large, non-interacting hard particles that are chemically inert with respect to the solvent, η_r should not be a strong function of temperature because the relative viscosity normalizes the viscosity of the suspension to that of the solvent. In emulsions, however, temperature effects can be manifested in several ways. First, the viscosity of both the solvent and the dispersed phase can change by different amounts with changes in temperature, which means that z is a function of temperature. A temperature dependence of z in turn implies a temperature dependence of $[\eta]$ according to Eq. (22) or Eq. (23), which further implies a temperature dependence of k_H and ϕ^* . Secondly, the magnitude of interparticle interactions, due to electrostatic or steric effects, for example, can be functions of temperature which influence k_H and ϕ^* . Furthermore, changes in temperature can influence the degree of miscibility of the dispersed phase with the solvent, thereby changing the composition (and viscosity) of the solvent and also altering the volume fraction of the dispersed phase.

6. Summary

We have suggested two alternative equations for the shear viscosity of emulsions. One of them, Eq. (15) is based on differential effective medium theory, which attempts to extend the known dilute limit to higher volume fractions. This equation is mathematically identical to the Krieger–Dougherty equation if the solvation factor K is identified as the inverse of the critical concentration ϕ^* . The other relation, Eq. (19)d, first suggested by Bicerano and coworkers [3] and generalized by Martys and Flatt [26], is based on known scaling relations in the concentrated regime near ϕ^* , and is also consistent with the virial expansion of the viscosity to second order in concentration. Both equations account for the effect on the intrinsic viscosity of the emulsion's viscosity ratio. Consistency with Eq. (15) requires that $k_H \sim [\eta]^2$ in the absence of other complicating effects, and we have assumed that $k_H = [\eta]^2$ in using Eq. (19). Comparison of both equations to published experimental data, covering a wide range of viscosity ratios, shows that Eq. (19) agrees more closely with the data, particularly at high concentrations.

In addition to its better fit to experimental data, we believe that the form of Eq. (19) provides a closer tie to the physics and chemistry of emulsions than does Eq. (15). In particular, the stability of a given emulsion might be directly connected to k_H and ϕ^* , since these properties are related to interactions among dispersed-phase particles. The fitting of solvation constants to viscosity data on asphalt binders already has been used as a predictor of their stability [27–29], and we expect that similar analyses using Eq. (19) could have important practical implications for transport and long-term storage of emulsions.

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Appendix A

A.1. Derivation of Eq. (15)

As a starting point, consider an homogenized medium with the following composition:

V° = volume of primary particle phase,

$V_{L,m}^\circ$ = volume of mobile solvent,

$V_c^\circ = KV^\circ$ = volume of clusters,

$V_T^\circ = V_{L,m}^\circ + V_c^\circ$ = total volume.

Suppose that a small volume ΔX of material is added to the homogenized medium, including both primary particles and the volume of liquid required to solvate them and occlude their flocculated pore structure. The volume of the medium changes by ΔX , but the volume of primary particles changes by only $\Delta X/K$, so the added volume fraction of primary particles is

$$\begin{aligned} \Delta\phi' &= \frac{\Delta X/K}{V_T^\circ + K\Delta X} \\ &= \frac{\Delta X}{KV_T^\circ} \left(1 + \frac{\Delta X}{V_T^\circ}\right)^{-1}. \end{aligned} \quad (\text{A.1})$$

Since $\Delta X < V_T^\circ$, the second factor on the right can be expanded as a convergent geometric series, giving

$$\begin{aligned} \Delta\phi' &= \frac{\Delta X}{KV_T^\circ} \left(1 - \frac{\Delta X}{V_T^\circ} + \mathcal{O}(\Delta X^2)\right) \\ &= \frac{\Delta X}{KV_T^\circ} + \mathcal{O}(\Delta X^2). \end{aligned} \quad (\text{A.2})$$

The actual change in the volume fraction of primary particles in the medium is

$$\Delta\left(\frac{V}{V_T}\right) = \frac{V^\circ + \Delta X/K}{V_T^\circ + \Delta X} - \frac{V^\circ}{V_T^\circ}. \quad (\text{A.3})$$

Expanding the denominator and rearranging gives

$$\Delta\left(\frac{V}{V_T}\right) = \left(1 - \frac{KV^\circ}{V_T^\circ}\right) \frac{\Delta X}{KV_T^\circ} + \mathcal{O}(\Delta X^2). \quad (\text{A.4})$$

Solving for $\Delta X/(KV_T^\circ)$ and rewriting in terms of volume fractions,

$$\frac{\Delta X}{KV_T^\circ} = \frac{\Delta\phi}{1 - K\phi^\circ} + \mathcal{O}(\Delta X^2). \quad (\text{A.5})$$

Substituting into Eq. (14), taking the limit as $\Delta\phi \rightarrow 0$ and $\Delta X \rightarrow 0$, and integrating gives

$$\int_1^{\eta_r} \frac{dx}{x} = [\eta] \int_0^\phi \frac{dx}{1 - Kx}. \quad (\text{A.6})$$

The result this time is Eq. (15),

$$\eta_r = (1 - K\phi)^{-[\eta]/K}. \quad (\text{A.7})$$

A.2. Derivation of Pal–Rhodes equation in Ref. [8]

Pal and Rhodes [8] assumed that primary particles are added to the suspension without including the liquid of solvation or liquid necessary to fill the internal pores of the cluster that forms. The cluster was assumed to form immediately, but the required liquid was assumed to be drawn from the surrounding medium. It was assumed that this withdrawal of liquid from the medium had a negligible impact on its viscosity. If we use these assumptions, even though they are at odds with the principles of D-EMT, then it is equivalent to adding pre-assembled clusters without the associated liquid. Therefore, we must use $[\eta]_c$ as the intrinsic viscosity in what follows, and the appropriate dilute limit is

$$\Delta\eta_r = \eta_r[\eta]_c \Delta\phi'_c, \quad (\text{A.8})$$

where ϕ'_c is the effective volume fraction of clusters corresponding to the addition of the primary particles in one incremental step of the D-EMT procedure.

If a volume ΔX of primary particles is added to the medium without including the additional liquid volume needed for cluster formation, then that volume of mobile solvent, $(K - 1)\Delta X$, must be withdrawn from the surrounding medium. The net effect is to add a volume $K\Delta X$ of clusters to the medium. In other words, the effective volume of clusters added is $K\Delta X$, but the total volume increases by just ΔX , the volume of material added to the system.

$$\begin{aligned}\Delta\phi'_c &= \frac{K\Delta X}{V_T^\circ + \Delta X} = \frac{K\Delta X}{V_T^\circ} \left(1 + \frac{\Delta X}{V_T^\circ}\right)^{-1} \\ &= \frac{K\Delta X}{V_T^\circ} + \mathcal{O}(\Delta X^2),\end{aligned}\quad (\text{A.9})$$

where the last form comes from expanding second term as a Maclaurin series. The rest of the mathematics is like that in Section 2. The actual change in the volume of clusters in the medium is

$$\begin{aligned}\Delta\left(\frac{V_c}{V_T}\right) &= \frac{V_c^\circ + K\Delta X}{V_T^\circ + \Delta X} - \frac{V_c^\circ}{V_T^\circ} \\ &= \left(1 - \frac{V_c^\circ}{KV_T^\circ}\right) \frac{K\Delta X}{V_T^\circ} + \mathcal{O}(\Delta X^2).\end{aligned}\quad (\text{A.10})$$

Rearranging produces

$$\frac{K\Delta X}{V_T^\circ} = \frac{\Delta\phi_c - \mathcal{O}(\Delta X^2)}{1 - (\phi_c^\circ/K)},\quad (\text{A.11})$$

and substituting into Eq. (A.8), taking the limit as $\Delta\phi_c \rightarrow 0$ and $\Delta X \rightarrow 0$, and integrating gives

$$\int_1^{\eta_r} \frac{dx}{x} = K[\eta]_c \int_0^{\phi_c} \frac{dx}{K-x}\quad (\text{A.12})$$

or, after integration,

$$\eta_r = (1 - \phi)^{-K[\eta]_c}.\quad (\text{A.13})$$

This is the result given in Eq. (13).

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