

# Simple heuristic for the viscosity of polydisperse hard spheres

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(Received 24 June 2014; accepted 13 November 2014; published online 1 December 2014)

We build on the work of Mooney [Colloids Sci. **6**, 162 (1951)] to obtain an heuristic analytic approximation to the viscosity of a suspension any size distribution of hard spheres in a Newtonian solvent. The result agrees reasonably well with rheological data on monodisperse and bidisperse hard spheres, and also provides an approximation to the random close packing fraction of polydisperse spheres. The implied packing fraction is less accurate than that obtained by Farr and Groot [J. Chem. Phys. **131**(24), 244104 (2009)], but has the advantage of being quick and simple to evaluate. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902439>]

## I. INTRODUCTION

The rheology of hard spheres in a Newtonian solvent of viscosity  $\eta_0$  is both a useful test case for rheological models and of practical importance as a first approximation to the behaviour of real suspensions. In 1906, Einstein<sup>1</sup> obtained the result that in the limit of low volume fractions  $\phi$ , the ratio of the viscosity  $\eta$  of the suspension to that of the solvent (known as the ‘relative viscosity’) is given by

$$\eta_r \equiv \eta/\eta_0 = 1 + [\eta]\phi + O(\phi^2), \quad (1)$$

where  $[\eta] = 2.5$  is the “specific viscosity,” and the expression is independent of the spheres’ sizes, or indeed polydispersity if the sizes are not all equal. Much work has subsequently been done to extend this result to higher volume fractions and polydisperse systems, but Einstein’s equation remains one of perhaps two results in the field which are both exact and uncontroversial.

As volume fraction increases, interactions between particles become important and terms of order  $\phi^2$  must be taken into account in Eq. (1). Let us assume hard sphere potentials, so forces such as electrostatics, van der Waals, and soft steric interactions are explicitly ruled out.<sup>2</sup> Nevertheless, both hydrodynamic interactions and Brownian forces, and the changes these induce in the spatial arrangements of the particles must, in general, be considered. For colloidal sized particles, where Brownian forces are important, the key distinction is between low shear rates, where diffusion can distribute the particles (in some sense) randomly, or induce crystallization,<sup>3</sup> and high shear rates, where hydrodynamic forces can lead to string phases or hydrodynamic clustering.<sup>4,5</sup> For macroscopic (neutrally buoyant) particles, the spatial arrangement will be history dependent, as any previous shear-induced order will persist. This makes the precise definition of the system of interest somewhat complex. Our primary concern is with colloidal particles in the limit of low shear rate, where we also assume that any equilibrium crystalline order has not yet emerged. We would also hope to be able to fit the behaviour of macroscopic spheres, provided they were initially

randomly distributed, and the experiment did not produce hydrodynamic ordering; for example, if small amplitude oscillatory rheometry were used. The experimental data we use for comparison are the low shear rate limit of colloidal sized spheres, except for Figure 8, where we accept the less clearly defined case of larger spheres averaged over a range of shear rates, in order to compare our predictions to a theory from the literature due to Qi and Tanner,<sup>6</sup> in a manner most favourable for the latter.

The first theory for monodisperse hard sphere viscosity at higher volume fraction was proposed by Arrhenius,<sup>7</sup> who argued that each subsequent addition of volume fraction  $\delta\phi$  would contribute an amount  $\delta\eta = \eta[\eta]\delta\phi$  to the suspension viscosity, for a final relative viscosity of

$$\eta_A = \exp([\eta]\phi). \quad (2)$$

An alternative approach can be based on the Bruggeman differential effective medium argument.<sup>8,9</sup> Here one imagines starting with a volume  $W$  of solvent, then adding a small volume  $\delta V$  of spheres, to achieve a relative viscosity of  $\eta_r(\delta V) = 1 + [\eta]\delta V/W$ . The next portion  $\delta V$  of spheres then sees an effective solvent of viscosity  $\eta_r(\delta V)$ , and volume  $W + \delta V$ . This leads to an equation for the relative viscosity as a function of the volume  $V$  of spheres added so far:

$$\eta_r(V + \delta V) = \eta_r(V) \left\{ 1 + \frac{[\eta]\delta V}{(W + V)} \right\}$$

so that, taking logarithms, one finds

$$\frac{d \ln \eta_r}{dV} = \frac{[\eta]}{W + V}.$$

If the total volume of spheres added is  $V_{\text{tot}}$  then  $\phi = V_{\text{tot}}/(W + V_{\text{tot}})$  and the relative viscosity is finally

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

Bruggeman’s equation (3) is interesting as it predicts a divergence in viscosity, in this case at  $\phi = 1$ . Studies in the 1950s however identified a reasonably well-defined (although still controversial<sup>10</sup>) concept of random close packing,<sup>11</sup> at a volume fraction around 0.63 or 0.64. One would therefore expect that both the low strain oscillatory viscosity and the

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low shear rate steady-state viscosity to diverge at this point (provided the spheres are in the metastable state where they have not crystallized<sup>3</sup>). This is because in these two cases, the shear will not have significantly perturbed the statistical arrangement of the spheres.

A very widely used approximation, which incorporates the idea of random close packing (or more generally, a maximum packing fraction), was provided by Krieger and Dougherty.<sup>12</sup> This can be seen as a modification of Arrhenius' argument, to take into account crowding effects:<sup>13</sup> suppose that the addition of a portion  $\delta\phi$  of the volume fraction leads to an extra increase in viscosity, over the Arrhenius result, namely,  $\delta\eta = [\eta]\eta\delta\phi + k\phi\delta\eta$ , then one obtains for the relative viscosity:

$$\eta_{KD} = [1 - (\phi/\phi_c)]^{-[\eta]\phi_c}, \quad (4)$$

where (in the low shear rate limit)  $\phi_c = 1/k$  is the random close packing fraction of hard spheres.

Over time, various modifications have been made to the Krieger-Dougherty result, to agree better with rheological studies. As an example, we mention a recent expression due to Mendoza and Santamaria-Holek<sup>14</sup>

$$\eta_{MS} = (1 - \phi_{\text{eff}})^{-[\eta]}, \quad (5)$$

where  $\phi_{\text{eff}} = \phi/(1 - c\phi)$  and  $c = (1 - \phi_c)/\phi_c$ .

An alternative effective medium approach, which treats all the added portions of spheres on an equal footing, was first suggested by Mooney.<sup>15</sup> Suppose we split the volume  $V_{\text{tot}}$  of spheres up into equal, differential portions  $\delta V$  (the number of such portions thus being  $V_{\text{tot}}/\delta V$ ). Next, suppose that each fraction contributes a multiplicative factor to the viscosity,  $1 + [\eta]\delta V/(W - kV_{\text{tot}})$ , which implies that the other fractions present exclude it from some part of the volume occupied by the solvent. The resulting relative viscosity is then

$$\eta_M = \left[1 + \frac{[\eta]\delta V}{(W - kV_{\text{tot}})}\right]^{V_{\text{tot}}/\delta V} = \exp\left\{\frac{[\eta]\phi}{1 - (\phi/\phi_c)}\right\}, \quad (6)$$

where  $\phi_c = 1/(k + 1)$ . A comparison of these theories against experimental data is shown in Figure 1.

The pursuit of expressions to capture polydispersity has attracted a similarly vigorous literature to the monodisperse case. The only exact result in this field however, is the observation by Farris<sup>16</sup> that if a suspension consists of a number of monodisperse fractions, which all have very different radii, then a given sphere sees an effective solvent consisting of the actual solvent, plus all the (much) smaller spheres. The overall suspension viscosity can therefore be found by multiplying factors for monodisperse spheres in an effective medium, in order, up to the largest size class. This result will be recovered analytically for the model in this paper, in Sec. III E.

When looking at distributions of particles containing size classes of very different radii, another issue immediately arises: if some particles are small enough for Brownian motion to be important, they can cause depletion forces<sup>17</sup> between the larger particles, and ultimately induce a phase separation.<sup>18</sup> In this paper, we assume that such a phase separation has not occurred; either because the size distribution is not conducive, or because the measurement of viscosity is performed before it has happened. This issue will not be

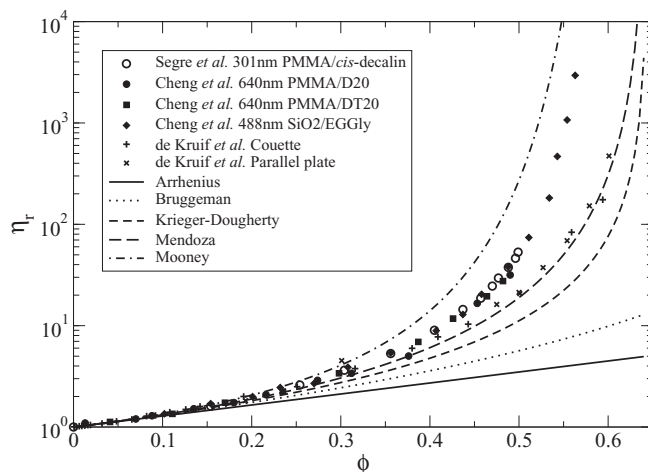


FIG. 1. Comparison of the rheological models described in Sec. I to rheological data from Segrè *et al.*,<sup>22</sup> Cheng *et al.*,<sup>23</sup> and de Kruif *et al.*<sup>21</sup> The data from Segrè *et al.* use PMMA spheres in *cis*-decalin; Cheng *et al.* use PMMA and SiO<sub>2</sub> spheres of the stated size, in decalin (D20), decalin-tetralin (DT20), and ethylene glycol-glycerol (EGGly) as solvents. The data from de Kruif *et al.* use 78 nm silica spheres in cyclohexane. Further details of experimental data are in Table I. The rheological models use a random close packing volume fraction for monodisperse spheres of  $\phi_{\text{rcp}} = 0.6435$ .<sup>19</sup>

present for macroscopic spheres, but then the preparation history could lead to poor reproducibility of measurements in this case.

More generally, predicting the viscosity of a polydisperse system is a much greater challenge than for the monodisperse case. In the former, we are seeking to approximate a functional; that is to say a function of an infinite number of arguments, corresponding to the volume fractions of all size classes in a potentially continuous distribution; whereas the latter is a function of only one variable (the volume fraction  $\phi$ ). Any estimate for the polydisperse case at low shear rate must also implicitly solve the problem of predicting the random close packed volume fraction of polydisperse spheres; an issue for which good approximants have only recently emerged.<sup>19,20</sup>

Progress has nevertheless been made in this area. For example, Farris<sup>16</sup> introduced an empirical “crowding factor”  $f$ , and more recently, Dörr *et al.*<sup>24</sup> have adopted a matched asymptotic expansion for  $\eta_r(\phi)$  and an effective medium approach to tackle cases of mixed sphere sizes where the classes have large, but not infinite, size ratios. An interesting empirical approach was in fact raised by Mooney in his work on the monodisperse case,<sup>15</sup> where he suggested that “ $k$ ” could be taken as a function of the ratios of sphere radii, and sketched the form that this function would then require. Due to the symmetric nature of his expression under swapping sphere classes, predictions by this route would be independent of the order in which size classes were included. However, the rather poor performance of the Mooney equation (Figure 1) has apparently discouraged further work on this idea.

The present analysis implements an heuristic modification of Mooney’s approach, choosing a plausible (but arbitrary) form for the  $k$  function, but goes beyond Mooney’s suggestion by also introducing a second level of particle-to-particle variability, potentially representing different local

environments that spheres of even the same size may encounter. This extra variability allows for a much better match to experimental data and a simple scheme for predicting the viscosity arising from any size distribution, but at the cost of introducing two free parameters.

## II. CONSTRUCTING A FUNCTIONAL

### A. Requirements

Suppose we seek a functional which maps sphere size distribution (and overall volume fraction) to a predicted viscosity. What are the constraints such a functional must satisfy? We suggest the following:

- At low volume fractions, Einstein's equation [Eq. (1)] should be recovered.
- The relative viscosity  $\eta_r$  for monodisperse spheres should diverge at the random close packed volume fraction  $\phi_{\text{rcp}} = 0.64 \pm 0.005$ , provided we are interested in the low shear rate limit of colloidal particles, or small strain oscillatory behaviour.
- If one size fraction in the size distribution is divided into several parts added separately, this should not affect the prediction for the viscosity.
- For a bidisperse mixture with a very large size ratio, the small spheres should behave as an effective medium for the large spheres, increasing both the volume and viscosity of this effective solvent.
- For such a bidisperse mixture, the viscosity of the small sphere dispersion between the large spheres should, to leading order, be that of the small spheres in the solvent alone. To next order in the radius ratio, the surfaces of the large spheres should exert a depletion effect on the small spheres, slightly increasing their effective viscosity (discussed below). This observation applies only away from the jamming transition (at which point small spheres may get incorporated into the jammed network<sup>25</sup>), and in cases where hydrodynamic ordering is not important (the low shear rate limit of colloidal particles, or small strain oscillatory flow).
- Analogous "effective medium" results to the previous two points should apply to mixtures of more than two fractions when all the sizes are very different.<sup>16</sup>
- A reasonable approximation for the viscosity as a function of  $\phi$  for the monodisperse case should be recovered.
- The functional should agree with known values for random close packed volume fractions of different size distributions, in particular the two-parameter family of bidisperse spheres, and the one parameter family of lognormal distributions.
- The predicted random close packing fraction should be least for the monodisperse case.
- The functional should give plausible answers for all size distributions, in the sense of predicting neither unexpected divergences, nor unphysical viscosities below that of the solvent.

### B. A symmetric differential effective medium approach

Can the requirements of Sec. II A be met by a simple analytic expression? Suppose we split the total volume of spheres  $V_{\text{tot}}$  into small portions  $\delta V$ , each being sufficiently small that we can consider all the spheres in one portion to have the same radius. Next, we imagine that the different spheres composing the portion  $\delta V$  need not all behave identically in the dispersion; they may, for example, have different neighbours, and so contribute differently to the rheological properties. We capture this dispersity in behaviour by labelling the spheres with a real parameter  $q \in (0, 1)$ , and suppose that a fraction  $f(q)dq$  have the label  $q$ . Because  $q$  is an arbitrary label, we are free to choose  $f(q) \equiv 1$  without loss of generality, but for the moment, we keep  $f(q)$  in the calculation, since future work may indicate a more natural choice for the label. We have therefore split our actual population of spheres into a two-dimensional distribution, parameterised by radius  $r$  and the new label  $q$ . We will assume, for calculational convenience, that we are adding spheres sequentially, in order of size, so that the radius  $r$  can be deduced from the volume  $V$  we have already added. That is to say, there is a function  $V(r)$ , which specifies the overall sphere size distribution through

$$P_{3D}(r) = \frac{1}{V_{\text{tot}}} \frac{dV(r)}{dr}, \quad (7)$$

where  $P_{3D}(r)dr$  is the fraction of the volume of spheres that have radii between  $r$  and  $r + dr$ . Therefore,  $V$  and  $r$  are both labels implying sphere size.

We now ask: what effective solvent volume does a sphere with radius  $r$  and label  $q$  "see"? The first (wrong) guess would simply be "the actual volume  $W$  of solvent that is present." However, other spheres may alter this. In particular, if there are spheres of radius  $r' \ll r$ , these will behave as an effective solvent, adding to  $W$ . On the other hand, spheres that are similar in size to  $r$  may have a crowding effect, lowering the effective volume of available solvent. If we consider a fraction of spheres that have radius  $r'$ , and label in the range  $q'$  to  $q' + \delta q'$ , they will constitute a volume  $\delta V' f(q') \delta q'$ . Let us suppose that these spheres reduce the effective solvent volume available to our original spheres (which have radii  $r$ ) by an amount  $k_{\text{net}} \delta V' f(q') \delta q'$ , where  $k_{\text{net}}$  is a function of  $V$ ,  $V'$ ,  $q$ , and  $q'$ . The net result for the spheres of radius  $r$ , is a solvent volume

$$W_{\text{eff}}(V, q) = W - \int_{V'=0}^{V_{\text{tot}}} \int_{q'=0}^1 f(q') k_{\text{net}}(V, V', q, q') dV' dq'. \quad (8)$$

The fraction of spheres with radii between  $r$  and  $r + \delta r$ , and labels between  $q$  and  $q + \delta q$  will therefore provide a factor to the relative viscosity given by  $(1 + [\eta] \delta V f(q) \delta q / W_{\text{eff}})$ . By multiplying up all the contributions to the increment of viscosity from all the sphere fractions, we obtain a final estimate of the suspension relative viscosity, given by

$$\ln \eta_r = \int_{V=0}^{V_{\text{tot}}} \int_{q=0}^1 \frac{f(q)[\eta] dV dq}{\left[ W - \int_{V'=0}^{V_{\text{tot}}} \int_{q'=0}^1 f(q') k_{\text{net}} dV' dq' \right]}. \quad (9)$$

Without loss of generality, we now take  $f(q) = 1$ , but we also impose two restrictions on  $k_{\text{net}}$ : First that it depends on the radius ratio  $R(V, V') \equiv r(V)/r(V')$  rather than the radii individually. This is necessary to ensure that if a suspension of spheres is magnified (with the solvent viscosity remaining the same), then the overall viscosity will also be unchanged. Second, we assume that  $k_{\text{net}}$  a linear function of  $(q + q')/2$ . This is not motivated on physical grounds, but allows us to obtain a simple analytic solution to all the equations.

We also note that the volume fraction is related to  $W$  and  $V_{\text{tot}}$  trivially via

$$\phi = V_{\text{tot}}/(W + V_{\text{tot}}),$$

which means that Eq. (9) simplifies to

$$\ln \eta_r = \int_{V=0}^{V_{\text{tot}}} \int_{q=0}^1 \frac{[\eta]\phi(dV/V_{\text{tot}})dq}{\left[1 - \phi - \phi \int_{V'=0}^{V_{\text{tot}}} \langle k_{\text{net}} \rangle (dV'/V_{\text{tot}})\right]}, \quad (10)$$

where  $\langle k_{\text{net}} \rangle \equiv \int k_{\text{net}} dq'$ , and is a linear function of  $q$  (as well as depending on  $R$ ).

What properties should  $\langle k_{\text{net}} \rangle$  have? The maximum value it can attain over all values of  $V'$ ,  $V$ , and  $q$ , determines the random close packing volume fraction through

$$\phi_c = \left\{ 1 + \max_{V,q} \left[ \int \langle k_{\text{net}}(V, V', q) \rangle (dV'/V_{\text{tot}}) \right] \right\}^{-1}, \quad (11)$$

since this is the lowest volume fraction at which Eq. (10) diverges. Thus, for the monodisperse case, we require  $\phi_c$  to be the random close packing fraction for monodisperse spheres,  $\phi_{\text{rcp}} = 0.64 \pm 0.005$ , and furthermore we require that this is the lowest volume fraction for random close packing out of all choices of  $r(V')$ ,  $r(V)$ , and  $q$ .

Next, consider the limits of small and large size ratios. If  $r(V') \ll r(V)$ , that is say the fraction of spheres we are integrating over is much smaller than those we are considering, then these tiny spheres just act to increase the effective volume of the solvent. Hence  $\langle k_{\text{net}} \rangle \approx -1$  in this limit. For the opposite case when  $r(V') \gg r(V)$ , the large spheres should, to leading order, have no effect on the effective volume of solvent, so that  $\langle k_{\text{net}} \rangle \approx 0$ . To next order, we argue in Figure 2 that  $\langle k_{\text{net}} \rangle = O(r(V)/r(V'))$ .

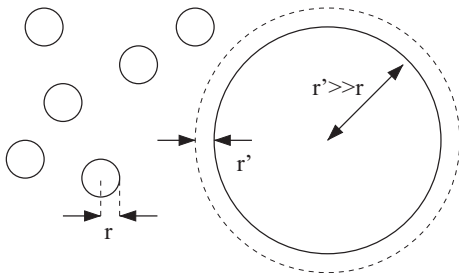


FIG. 2. How should  $\langle k_{\text{net}} \rangle$  scale in the limit  $r' \gg r$ ? We assume that the large spheres exclude the small spheres from a portion of the solvent which has a volume proportional to the depletion zone around the large spheres. If we are considering a small portion of the large spheres, occupying a volume  $\delta V'$ , then the depletion volume produced by this fraction will be proportional to  $(r/r')\delta V'$ . This will be  $\langle k_{\text{net}} \rangle \delta V'$ , so in the limit  $r/r' \rightarrow 0$ , we expect  $\langle k_{\text{net}} \rangle \propto r/r'$ .

With these considerations in mind, we choose a simple (but arbitrary) functional form for the lower and upper bounds on  $\langle k_{\text{net}} \rangle$  as a function of  $q$ . We then reconstruct the full function using linearity in  $q$ :

$$\begin{aligned} \langle k_{\text{net}}(V, V', q) \rangle &= k_{\text{min}} + (k_{\text{max}} - k_{\text{min}})q, \\ k_{\text{min}} &\equiv K(\phi^*), \\ k_{\text{max}} &\equiv K(\phi_{\text{rcp}}), \\ K(x) &\equiv \frac{(m/x)R - R^m}{[(m-1)/(1-\phi_{\text{rcp}})] + R^m}, \\ R &\equiv r(V)/r(V') \end{aligned} \quad (12)$$

where  $m$  and  $\phi^*$  are free parameters with which we attempt to fit all the experimental and simulation data. Note that the predicted random close packing fractions depend on  $m$  only, while viscosities depend on both  $m$  and  $\phi^*$ . The limits are shown in Figure 3 for the parameters which we find to give the best fit to the experimental data (two cases are shown, because the experimental data are not mutually consistent).

### C. Analytic solution for the polydisperse case

Suppose that we have a mixture of  $n$  monodisperse sphere classes, where  $n$  may be arbitrarily large, and suppose that sphere class  $i$  has radius  $r_i$ , and occupies a volume fraction  $\phi_i$

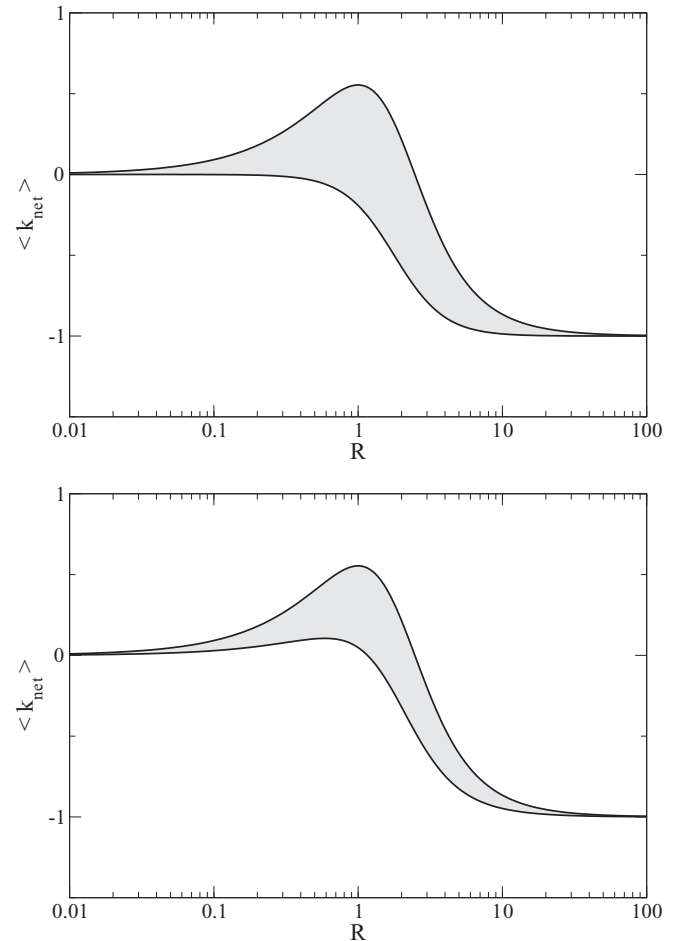


FIG. 3. The range of values of  $\langle k_{\text{net}} \rangle$  from Eq. (12). First plot uses  $\phi^* = \infty$ . Second plot uses  $\phi^* = 2$ .

TABLE I. Experimental data points used in Figures 1 and 6 for the low shear rate viscosity of monodisperse, hard spheres of various sizes in different solvents, as a function of volume fraction  $\phi$ . The data are extracted from plots in Refs. 22 (first two columns) and 23 (last four columns). The other data shown in Figures 1 and 6 can be read from tables in the references cited.

301 nm PMMA/decalin		640 nm PMMA/D20		640 nm PMMA/DT20		488 nm SiO <sub>2</sub> /EGGly	
$\phi$	$\log_{10} \eta_r(\dot{\gamma} = 0)$	$\phi$	$\log_{10} \eta_r(\dot{\gamma} = 0)$	$\phi$	$\log_{10} \eta_r(\dot{\gamma} = 0)$	$\phi$	$\log_{10} \eta_r(\dot{\gamma} = 0)$
0.000	0.000	0.013	0.04	0.041	0.05	0.102	0.13
0.154	0.205	0.070	0.08	0.111	0.13	0.154	0.23
0.254	0.415	0.088	0.11	0.170	0.24	0.201	0.30
0.304	0.560	0.135	0.18	0.235	0.35	0.232	0.39
0.356	0.725	0.180	0.24	0.298	0.53	0.270	0.43
0.405	0.955	0.216	0.32	0.387	0.84	0.308	0.59
0.437	1.160	0.274	0.46	0.426	1.07	0.356	0.73
0.457	1.270	0.312	0.53	0.464	1.29	0.407	0.95
0.470	1.390	0.376	0.70	0.482	1.44	0.437	1.11
0.477	1.470	0.453	1.22			0.458	1.31
0.488	1.575	0.490	1.50			0.488	1.58
0.496	1.665					0.511	1.87
0.499	1.725					0.534	2.26
						0.543	2.67
						0.554	3.03
						0.563	3.47

in the final dispersion. The total occupied volume fraction is therefore  $\phi = \sum_{i=1}^n \phi_i$ , which must be less than 1. We place no restrictions on the radii  $r_i$ : they do not need to be ordered, and they do not need to all be different. In this scenario, the normalized volume-weighted particle size distribution is

$$P_{3D}(r) = \sum_{i=1}^n [(\phi_i/\phi)\delta(r - r_i)]. \quad (13)$$

We can now directly perform the integrals in Eq. (10) to obtain

$$\ln \eta_r = \sum_{i=1}^n \frac{[\eta](\phi_i/\phi)}{[S_i(\phi_{\text{rcp}}) - S_i(\phi^*)]} \ln \left[ \frac{1 - [1 + S_i(\phi^*)]\phi}{1 - [1 + S_i(\phi_{\text{rcp}})]\phi} \right], \quad (14)$$

$$S_i(x) \equiv \sum_{j=1}^n \frac{(\phi_j/\phi)[(m/x)(r_i/r_j) - (r_i/r_j)^m]}{[(m-1)/(1 - \phi_{\text{rcp}})] + (r_i/r_j)^m}. \quad (15)$$

As we will see below, from comparison of the predictions to known experimental and simulation data, the following values for  $m$  and  $\phi^*$  give reasonable agreement:

$$m = 2.5, \quad \phi^* = \infty, \quad \text{or} \quad \phi^* = 2, \quad (16)$$

where the choice of  $\phi^*$  arises from inconsistencies in the literature data on the viscosity of monodisperse spheres (Ref. 21 versus Refs. 22 and 23).

Equations (14)–(16) provide the solution we seek, which can be used to predict the viscosity of any distribution of hard sphere sizes.

Furthermore, if we use the size distribution described by Eq. (13) but add more and more of the dispersed phase, in order to achieve higher and higher volume fractions  $\phi$ , then we will find that there is a maximum volume fraction  $\phi_c$  permitted, at which Eq. (14) diverges. This is the random close packed volume fraction of the polydisperse spheres, and is

predicted from Eq. (13) to be given by

$$\phi_c = \{1 + \max_i [S_i(\phi_{\text{rcp}})]\}^{-1}. \quad (17)$$

### III. COMPARISON TO KNOWN RESULTS

#### A. Random close packing of bidisperse spheres

The results from Eq. (17) can be compared directly to simulation results for random packing of bidisperse spheres from Refs. 19 (based on soft sphere packing in the zero pressure limit) and 25 (based on an efficient sequential linear programming method to generate disordered, strictly jammed states). Suppose the ratio of sphere sizes is  $R \geq 1$ , and the fraction of occluded volume in the large spheres is  $w$ , then Eqs. (15) and (17) lead to

$$S_1(x) = \frac{(1-x)}{x} \left[ 1 - w + \frac{w \cdot (mR^{-1} - xR^{-m})}{m-1 + (1-x)R^{-m}} \right], \quad (18)$$

$$S_2(x) = \frac{(1-x)}{x} \left[ \frac{(1-w)(mR - xR^m)}{m-1 + (1-x)R^m} + w \right], \quad (19)$$

$$\phi_c = \frac{1}{1 + \max[S_1(\phi_{\text{rcp}}), S_2(\phi_{\text{rcp}})]}. \quad (20)$$

The comparison to simulation data is shown in Figure 4, where we see that  $m = 2.5$  gives a reasonable level of agreement.

#### B. Random close packing of lognormal distributions

Another set of simulation data that can be used for comparison, is the random close packing fraction of lognormal distributions of spheres, in Refs. 19 and 20 (shown in Table II). The comparison is shown in Figure 5, and here the best fitting value of  $m$  is around 3; although  $m = 2.5$  gives

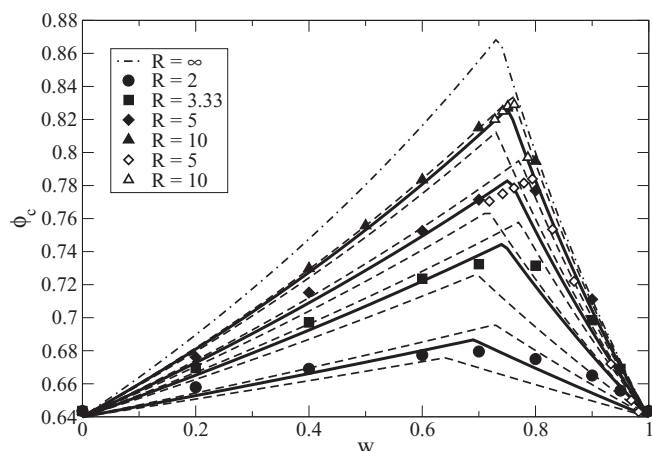


FIG. 4. Comparison of predictions for random close packing of bidisperse spheres to simulation data from Refs. 19 (closed symbols) and 25 (open symbols). The parameter  $w$  is the fraction of the occluded volume occupied by the large spheres. For each of the sphere size ratios  $R$ , we plot predictions for different values of the parameter  $m$ : the bold solid line is for  $m = 2.5$ , and the thin dashed lines below and above are for  $m = 2$  and  $m = 3$ , respectively.

moderately good agreement, provided the polydispersity is not too extreme.

### C. Viscosity of monodisperse spheres

In this case, Eq. (14) reduces to the form

$$\eta_r(\phi) = \left[ 1 + \frac{(\phi/Q)}{1 - (\phi/\phi_{rcp})} \right]^{[\eta]Q}, \quad (21)$$

where

$$Q = \frac{(m - \phi_{rcp})\phi_{rcp}\phi^*}{m(1 - \phi_{rcp})(\phi^* - \phi_{rcp})}. \quad (22)$$

TABLE II. Simulation results for random close packing volume fractions of lognormal distributions of spheres, using a soft particle simulation method on 6000 spheres (column 3; data from Ref. 19), and results using the hard sphere particle simulation method of Ref. 28 on 1024 spheres (columns 4-6; data from Ref. 20).

$\sigma$	$d_{4,3}/d_{3,2}$	$\phi_c$ (Ref. 19)	$\phi_c$ (Ref. 20)	$\phi_c$ (Ref. 20)	$\phi_c$ (Ref. 20)
0.000	1.000	0.6430	0.64353	0.64502	0.64406
0.000	1.000	0.6438			
0.000	1.000	0.6436			
0.050	1.003	0.6434	0.64505	0.64461	
0.100	1.010	0.6485	0.64566	0.64637	0.64766
0.150	1.023	0.6514	0.65202	0.65007	
0.200	1.041	0.6564	0.65466	0.65565	0.65587
0.250	1.064	0.6624	0.66049	0.66275	
0.300	1.095	0.6713	0.66801	0.66902	0.66680
0.350	1.130	0.6786	0.67372	0.67608	
0.400	1.174	0.6864	0.68282	0.68317	0.68316
0.426	1.199	0.6952			
0.491	1.273	0.7072			
0.500	1.284	0.7028	0.70009	0.70181	0.70189
0.521	1.312	0.7118			
0.550	1.353	0.7178			
0.600	1.433	0.7296			

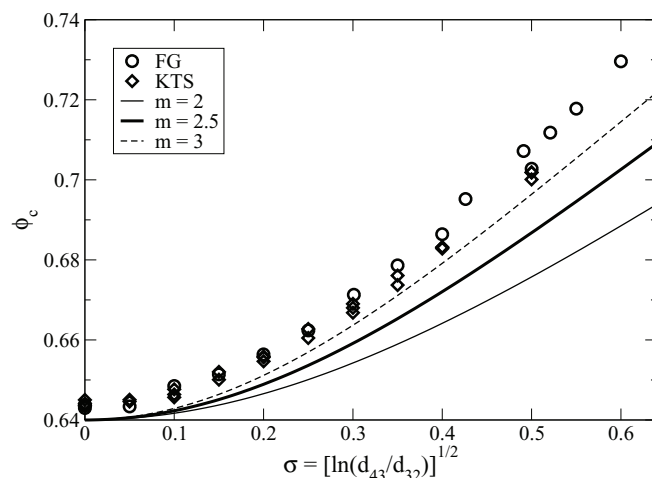


FIG. 5. Comparison of predictions for random close packing of lognormal distributions of spheres against simulation data from Refs. 19 (FG) and 20 (KTS). The predictions are shown for three values of the parameter  $m$ : the solid line uses  $m = 2$ , the bold solid line uses  $m = 2.5$  and the dashed line uses  $m = 3$ .

Equation (21) depends on the fitting parameters  $\phi^*$  and  $m$ , which have no physical interpretation, as they come from an arbitrarily chosen functional form. Figure 6 shows the comparison to rheological data, from which we see that a value of  $\phi^* = \infty$  agrees reasonably well with the data from de Kruif *et al.*,<sup>21</sup> while  $\phi^* = 2$  gives a better fit (at least up to volume fractions of 0.5) for the more recent data from Refs. 22 and 23. Hence we find

$$Q = 1.3 \quad \text{if } \phi^* = \infty, \quad (23)$$

$$Q = 2.0 \quad \text{if } \phi^* = 2. \quad (24)$$

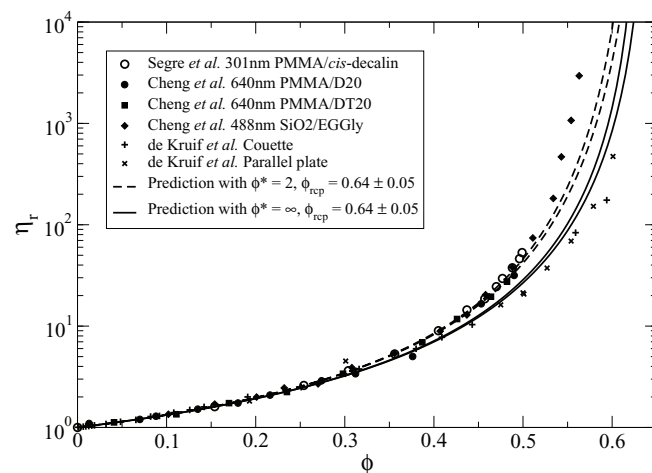


FIG. 6. Comparison of the predictions for the viscosity of monodisperse spheres against experimental data. The experimental results are for zero shear rate viscosity, and are taken from Refs. 22, 23, and 21 (see Figure 1 and Table I for a detailed description). The predictions use Eq. (21) with  $m = 2.5$  and  $\phi^* = \infty$  (solid lines) and  $\phi^* = 2$  (dashed lines). The two lines for each case cover the possible range of values for  $\phi_{rcp}$ , which is not accurately known; namely  $\phi_{rcp} = 0.635$  and  $0.645$ .

Out of interest, one can also expand the predicted viscosity to second order in  $\phi$  to obtain

$$\eta_r = 1 + [\eta]\phi + \left\{ \frac{[\eta]}{\phi_{\text{rcp}}} + \frac{[\eta]^2}{2} - \frac{[\eta]}{2Q} \right\} \phi^2 + O(\phi^3). \quad (25)$$

which gives a coefficient of  $\phi^2$  of 6.1 when  $\phi^* = \infty$ , or 6.4 when  $\phi^* = 2$ . This is consistent with the range 4.8–7.03 of reported values from the literature,<sup>24</sup> which arise according to the manner in which hydrodynamics and Brownian forces are included in the calculations. Specifically, Batchelor and Green<sup>26</sup> showed that the purely hydrodynamic contribution to the coefficient of  $\phi^2$  from a thermal distribution of spheres is 5.2. Later, Batchelor<sup>27</sup> showed that Brownian forces in the same system made an extra contribution of 1, so that the predicted value for our case of low shear rate Brownian spheres should be 6.2.

#### D. Viscosity of bidisperse spheres

A comparison to zero shear rate viscosity data on colloidal spheres from Rodriguez *et al.*,<sup>29</sup> using  $\phi_{\text{rcp}} = 0.64$ ,  $m = 2.5$ , and  $\phi^* = \infty$  is shown in Figure 7. We see that reasonable agreement is found, with no further adjusting of parameters. The experimental data are for a single sphere size ratio ( $R = 141/84 \approx 1.68$ ), and various volume fractions.

We note that for bidisperse spheres with a large size ratio (and potentially other size distributions), it is quite possible for a depletion-induced phase separation to occur<sup>18</sup> in the low shear rate regime when particles are small enough for Brownian forces to be important and a low shear rate viscosity is clearly defined. However, for the relatively modest value of  $R$  in Ref. 29, this may not be a concern.<sup>30</sup>

Finally, we show some experimental data for larger, non-colloidal spheres in Figure 8. The experimental viscosity data

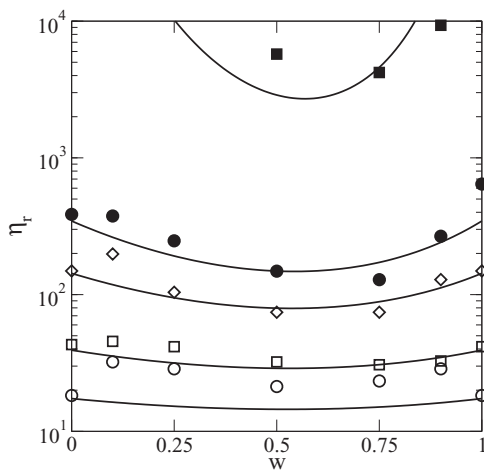


FIG. 7. Comparison of the predictions for the relative viscosity  $\eta_r$  of bidisperse spheres against experimental data (as a function of the proportion  $w$  of the volume of spheres that are in the large size class). The experimental results are for zero shear rate viscosity, and are taken from Ref. 29, which uses latex spheres of diameter 84 nm and 141 nm in bromoform. The total volume fraction of the spheres is (bottom to top)  $\phi = 0.473$  ( $\circ$ ),  $\phi = 0.517$  ( $\square$ ),  $\phi = 0.562$  ( $\diamond$ ),  $\phi = 0.582$  ( $\bullet$ ),  $\phi = 0.634$  ( $\blacksquare$ ). The predictions use Eq. (14) with  $\phi_{\text{rcp}} = 0.64$ ,  $m = 2.5$ , and  $\phi^* = \infty$ .

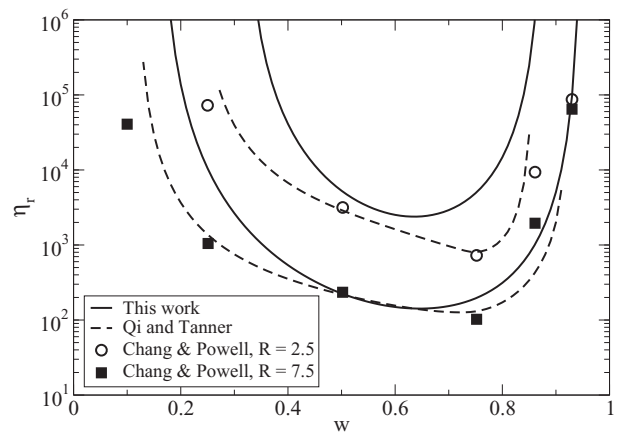


FIG. 8. Comparison of the predictions for the relative viscosity  $\eta_r$  of bidisperse spheres against experimental data and the model from Ref. 6 at a fixed volume fraction of 0.67 and  $R = 2.5$  and 7.5. The proportion of the volume of spheres that are in the large size class is  $w$ . The experimental results in this case are viscosities averaged over a range of shear rates, and are taken from Ref. 31, which uses polystyrene and PMMA spheres of diameters  $40 \pm 10 \mu\text{m}$ ,  $100 \pm 20 \mu\text{m}$ , and  $300 \pm 25 \mu\text{m}$ . The predictions from this work use Eq. (14) with  $\phi_{\text{rcp}} = 0.64$ ,  $m = 2.5$ , and  $\phi^* = \infty$ .

taken from Chang and Powell,<sup>31</sup> have been averaged over a range of shear rates. This is therefore a sub-optimal data set, due to the possibility of hydrodynamic ordering, which would make the choice of the static random close packed volume fraction for the divergence of viscosity suspect. Nevertheless, we choose this data set to compare to our predictions, because another rheological model (due to Qi and Tanner<sup>6</sup>) uses this data set to choose their fitting parameters and functions. We see that reasonable agreement is obtained with no further adjustment of parameters.

#### E. The limit of large sphere size ratios

Suppose that we have a set of  $n$  sphere size fractions, occupying volume fractions  $\phi_1, \phi_2, \dots, \phi_n$ . Furthermore, assume (which has not been necessary so far) that they are all very different in radius, and are ordered such that

$$r_1 \ll r_2 \ll \dots \ll r_n. \quad (26)$$

It follows immediately from Eq. (15) that

$$S_i(x) = \frac{(1 - \phi_{\text{rcp}})[(m/x) - 1](\phi_i/\phi)}{(m - \phi_{\text{rcp}})} - \sum_{j=1}^{i-1} \left( \frac{\phi_j}{\phi} \right). \quad (27)$$

The relative viscosity of the system can be calculated from Eq. (14), and after some manipulation one finds

$$\ln \eta_r = \sum_{i=1}^n H_r(\Psi_i), \quad (28)$$

$$H_r(\Psi_i) = [\eta]Q \ln \left[ 1 + \frac{(\Psi_i/Q)}{1 - (\Psi_i/\phi_{\text{rcp}})} \right], \quad (29)$$

$$\Psi_i \equiv \frac{\phi_i}{1 - \sum_{j=i+1}^n \phi_j}, \quad (30)$$

while the random close packing fraction from Eq. (17) is

$$\phi_c = \left\{ \max_i \left[ \frac{(\phi_i/\phi)}{\phi_{\text{rcp}}} + \sum_{j=i+1}^n \left( \frac{\phi_j}{\phi} \right) \right] \right\}^{-1}. \quad (31)$$

Here  $H_r(\phi)$  the monodisperse relative viscosity, defined in Eq. (21). This is the exact result obtained by Farris in Ref. 16, where spheres of one size fraction move in an effective medium defined by the solvent plus all the smaller spheres.

#### IV. CONCLUSIONS

The core result of this paper is contained in Eqs. (14)–(17), which together provide a simple and computationally cheap method to estimate the viscosity and random close packed volume fraction of any size distribution of hard spheres in a Newtonian solvent.

The resulting model yields moderately good agreement with known experimental and simulation data (some compromises are necessary in choosing numerical values for the two free parameters), gives physically plausible answers even for unusual size distributions, and reproduces known exact limits for the cases where sphere sizes are very different to one another.

Although the results for random close packing are notably less accurate than those obtained from the recent one dimensional rod-packing model of Farr and Groot,<sup>19,20</sup> we believe that the crowding and effective medium approach used in this paper has the potential to describe a broader class of rheological behaviour, including cases where the interaction between particles is not simply a hard sphere potential plus hydrodynamics. We hope to develop these possibilities in future work.

#### ACKNOWLEDGMENTS

Thanks are due to William Frith, Andy Hoddle, and Patrick Warren for many useful discussions.

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