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Analytically predicting the viscosity of hard sphere suspensions from the particle size distribution

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ABSTRACT

Suspension rheology is of widespread importance to industry and research. Hard spheres represent a benchmark by which to compare other particle suspensions, and there are a variety of analytical and numerical models available to describe their rheology. However, it is experimentally challenging to produce ideal hard spheres, where surface forces are negligible between particles, and where phase volume is precisely defined. Beyond the dilute regime, the model by Maron and Pierce [1] and Quemada [2], which we refer to as the MPQ model, is commonly used analytically to describe the relative viscosity of hard sphere suspensions as a function of phase volume and a maximum packing fraction (ϕ_{m}). We show that obtaining ϕ_m from empirical fits can lead to misinterpretation of experimental data. We reveal that reasonable prediction of the viscosity is obtained using the MPQ model when ϕ_m is set to the geometric random close packing fraction ϕ_{rcp}, which is independently defined from the particle size distribution using the packing model of Farr and Groot [3]. This 'theoretical' approach is tested using a wide variety of experimental data on colloidal and non-colloidal hard spheres without need for any fitting parameters or empiricisms. In addition, plotting the inverse of the square-root of viscosity as a function of phase volume, which linearises the MPQ model, provides a convenient means by which to clearly see where suspensions deviate from the model due to such effects as particle aggregation, particle softness and measurement errors. We also demonstrate the necessity of this approach by accurately predicting the viscosity of microgel suspensions up to ϕ_{rcp}; empirical fits across the full data set are erroneous because particle deformation and viscoelasticity lead to values of $\phi > \phi_{\mathrm{rcp}}$. This approach provides a suitable unambiguous theoretical baseline for comparison to experimental studies on suspension rheology involving polydisperse size distributions.

1. Introduction

The rheology of both colloidal (>1 μm) and non-colloidal (<1 μm) hard sphere suspensions is of interest to researchers and industry alike. Suspension rheology is defined by the matrix rheology and suspension microstructure, which is dependent on the particle volume fraction and particle size distribution, as well as particle interactions, morphology and softness. These latter three factors are negligible for ideal 'hard' spheres, which represent a benchmark against which to compare other suspensions. The region of particular interest occurs at particle phase volumes (ϕ) approaching maximum packing fraction (ϕ_m), where suspensions become highly viscous. It is usual to simply determine ϕ_m empirically by fitting various models to viscosity-phase volume data. There is still debate about the theoretical definition of ϕ_m, nevertheless, it is *widely accepted* that it is dependent on particle size distribution although this is rarely quantified in studies on rheology.

For *monodisperse hard sphere* suspensions, ϕ_m is considered to be theoretically defined as one of two points [4], either: (1) at $\phi = 0.58$, which corresponds to the glass transition (ϕ_g); or (2) at $\phi = 0.64$, which corresponds to random close packing (ϕ_{rcp}). ϕ_g is described thermodynamically by Mode Coupling Theory as the point where a particle is only able to relax within a cage formed by its nearest neighbours, thus limiting diffusion and flow [5]. In contrast, for suspensions of hard spheres, ϕ_{rcp} is defined geometrically as the most consolidated packing achievable by 'tapping' or vibrating a large container of spheres [6]. This is highly repeatable experimentally and hence is considered to be a well-defined transition. For this reason, we favour defining ϕ_m for hard sphere suspensions as being equivalent to ϕ_{rcp}, an approach also supported by theoretical and experimental literature in studies on the rheology of hard sphere suspensions [7–9]. In addition, both

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analytical and numerical models are now available that accurately predict ϕ_{rcp} for polydisperse spheres from measurements of particle size distribution [3], making it an easily defined parameter that is independent of viscosity measurement.

We investigate whether use of the particle size distribution and ϕ_{rcp} provides an unambiguous parameter with which to theoretically predict the viscosity of hard sphere suspensions from phase volume and the matrix phase viscosity. We review the experimental literature on the viscosity of hard sphere suspensions, covering the full spectrum of sizes (colloidal and non-colloidal) and size-distributions (mono, bi and polydisperse), in addition we provide our own experimental data on suspensions containing non-colloidal agarose microgel spheres and poly(methyl methacrylate) (PMMA) spheres. We use these extensive data sets to validate our proposed approach and find that it provides a superior method for determining where systems deviate from hard sphere behaviour due to effects such as particle softness, aggregation and migration. In regards to particle softness, we discover that the theoretical model overcomes the difficulties encountered when empirically defining ϕ_m for particles that deform at phase volumes beyond random close packing.

2. Viscosity-phase volume relationships for hard sphere suspensions

2.1. Analytical models

Suspension rheology is strongly dependent on particle phase volume and the viscosity of the matrix phase. Phase volume (ϕ) is the volume of particles in suspension (V_P) relative to the total volume of suspension (V_T), $\phi = V_P/V_T$. For hard particles at dilute ($\phi < 0.05$) and semi-dilute ($\phi < 0.15$) concentrations, viscosity is predicted from the phase volume according to the Einstein [10] and Batchelor models [11], given respectively as:

$$\eta_r = 1 + [\eta]\phi \tag{1}$$

$$\eta_r = 1 + 2.5\phi + C\phi^2 \tag{2}$$

η_r is the relative viscosity, $\eta_r = \eta/\eta_s$ where η is the viscosity of the suspension (usually the zero-shear viscosity η_0 if the suspension is shear-thinning) and η_s is the solvent or matrix phase viscosity. Einstein's equation includes the intrinsic viscosity term that has a value of $[\eta] = 2.5$, although this only applies at dilute concentrations where there is substantial experimental uncertainty. Batchelor's equation includes the addition of a second order term to Einstein's equation to account for pair-wise interactions that occur beyond the dilute regime at increasing phase volumes. The constant (C) can have a range of values from 4.2 to 6.2, depending on the underlying assumptions and approach to the derivation [6,9,11,12]. Batchelor [11] derived a value of $C = 6.2$ for Brownian spheres and Ball and Richmond [12] found $C = 5.2$ to be most accurate for non-colloidal systems.

With increasing phase volume, particles come into close contact and many body interactions must be taken into account. At phase volumes greater than about 0.2, the following model developed by Maron and Pierce [1] accounts for these multi-body interactions to give:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \tag{3}$$

This model, which was also independently obtained by Quemada [2] and referred to here as the MPQ model, is commonly used to predict the viscosity of suspensions with volume fraction up to phase volumes where the relative viscosity diverges towards infinity at ϕ_m [6,13,14]. This model is mathematically derived for concentrated suspensions following two paths; (1) using the theory of 'two phase flow' to minimise the rate of viscous energy dissipation during shear [2,7] and; (2) by developing the equation of a pair distribution function of Brownian hard spheres [8]. Using a simple starting point of a monodisperse suspension of hard spheres that experience hydrodynamic and Brownian forces, Brady [8] shows that as $\phi \rightarrow \phi_{\mathrm{rcp}}$ the divergence of relative viscosity is proportional to $(1 - \phi/\phi_{\mathrm{rcp}})^{-2}$. This comes from two factors: the first is proportional to the number of particles in contact as maximum packing is approached and diverges as $(1 - \phi/\phi_{\mathrm{rcp}})^{-1}$; the second, self-diffusivity, vanishes as $(1 - \phi/\phi_{\mathrm{rcp}})$ because particles become trapped by their nearest neighbours. The relative viscosity (or deviatoric stress) is proportional to the first factor divided by the second factor, resulting in $(1 - \phi/\phi_{\mathrm{rcp}})^{-2}$ [7,8,15]. Close to maximum packing fraction, the short term diffusivity of colloidal particles vanishes [16], which matches the situation with non-colloidal spheres that do not undergo short term diffusivity. For this reason, the model also appears to be applicable to non-colloidal suspensions in this region.

The papers of Brady [8], Maron and Pierce [1] and Quemada [2] are highly cited and Eq. (3) has been used to describe an extensive range of experimental data [2,17–19] and found to match Stokesian dynamic simulations [20]. The MPQ model is very similar to the well-used Krieger–Dougherty model [21]; they have exactly the same form except that the exponent "2" is replaced by the product $[\eta]\phi_m$. Hence the Krieger–Dougherty model may predict experimental data better when empirically fitted because it includes two adjustable parameters. It is indeed rare for $[\eta]$ to be determined independently of ϕ_m, although technically it should only be determined through viscosity measurements under dilute solution conditions. In this case, the Krieger–Dougherty model reduces to Einstein's equation at low volume fraction when $[\eta] = 2.5$, which is why it is favoured by many researchers. However, the error resulting from difference between MPQ and Einstein in this regime is not significant and is within experimental error (<10%). A similar model to MPQ and Krieger–Dougherty is that of Mendoza and Santamaria-Holek [9], which we refer to as the Mendoza model, who define viscosity in terms of an excluded volume (ϕ_{excl}) and reduces to Einstein's model at low phase volume:

$$\eta_r = (1 - \phi_{\mathrm{excl}})^{-2.5} \tag{4}$$

$$\phi_{\mathrm{excl}} = \frac{\phi}{1 - [(1 - \phi_m)\phi/\phi_m]} \tag{5}$$

Both colloidal and non-colloidal hard sphere suspensions follow the same relative viscosity-phase volume profile, but there are some distinct differences. Non-colloidal hard spheres are mainly influenced by hydrodynamic interactions without the additional forces arising from Brownian motion and electrostatic forces that are significant for colloidal particles. This results in differences in rheology at low to moderate volume fraction; non-colloidal hard sphere suspensions show Newtonian behaviour up to large volume fractions ($\phi \sim 0.5$) but colloidal suspensions are usually non-Newtonian and shear thinning even at very low volume fractions [6]. Differences in rheology between colloidal and non-colloidal hard sphere suspensions also occur at phase volumes in the vicinity of ϕ_m; Menut et al. [16] suggest that surface roughness plays a role in the inter-particle contact between non-colloidal particles, while Brownian motion limits particle contact for colloidal particles by promoting a lubricating fluid layer between particles.

The MPQ, Krieger–Dougherty, and Mendoza models are found to provide very good (empirical) predictions for the viscosity of hard sphere suspensions as a function of phase volume if freely fitted by adjusting ϕ_m. Fig. 1 shows a large collection of experimental data from the literature on η_r for colloidal and non-colloidal hard

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