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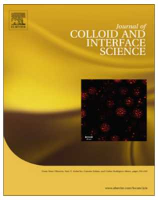

Viscosity of soft spherical micro-hydrogel suspensions

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ABSTRACT

The rheology of soft particle suspensions is considered to be a function of particle micromechanics and phase volume. However, soft particles such as microgels present a challenge because they typically contain solvent in their polymeric network structure, and their specific volume can alter in response to mechanical forces and physiochemical effects. We investigate how particle elasticity affects the viscosity of microgel suspensions as a function of effective phase volume (ϕ_0) using non-colloidal hydrogel spheres that, unlike many colloidal-scale microgels, are not highly responsive to physiochemical effects. In our unique approach, we compare the viscosity of microgel suspensions to a theoretical hard sphere viscosity model that defines the maximum packing fraction using the geometric random close packing fraction (ϕ_{rcp}) obtained from the measured particle size distribution. We discover that our harder microgels follow the hard sphere model up to random close packing, but softer microgels deviate around $\phi_0/\phi_{rcp} \sim 50\%$ which indicates that their specific volume is decreasing with increasing ϕ_0. This effect arises because microgels at high phase volumes do not fully re-swell during their preparation. We conclude that particle elasticity does not directly affect the viscosity of soft sphere suspensions up to the random close packing fraction. We highlight a convenient method for analysing the viscosity of microgel suspensions with potential to be applied to a wide variety of soft sphere suspensions.

1. Introduction

Most fundamental studies on suspension rheology focus on “hard” spheres, and a good understanding is emerging on their flow behaviour from experiment, theory and simulation [1]. In contrast, the rheological properties of soft particle suspensions are not so well defined, modelled or characterised. Soft particle suspension rheology is important to both natural and highly engineered systems, and they are the foundation of many soft materials [2,3]. Common suspensions of soft particles include: microgels, droplets, biological cells, swollen starch granules, star polymers, and polymer-stabilised/coated colloids. We are focused here on microgels, which are cross-linked polymeric particles swollen by the matrix fluid.

Microgel and other soft particle suspensions display interesting and useful rheological properties, particularly in the high concentration region where they exhibit viscoelastic and solid-like behaviour at low shear but yield and flow above a ‘yield’ stress [3]. These properties are widely exploited industrially in the coatings industry, mineral processing, oil recovery and drilling fluids, foods and personal care products, and for advanced materials such as biomaterials, lubricants, and pharmaceuticals [1,3,4]. Their rheological behaviour is complicated by particle deformability, porosity and volume changes that occur due to mechanical forces and physiochemical changes. The specific volume of microgels typically alters due to movement of fluid in or out of their gel structure in response to changes in temperature [5,6], pH [7] and compression [8]. Their phase volume is thus not well defined [3], unlike hard spheres [9], which creates a challenge when describing microgel suspension rheology analytically as a function of a concentration dependent parameter. Most articles concerning microgel suspensions do this by defining an effective phase volume (ϕ_0) that is based on their specific volume at dilute phase volumes (k_0) when they are in their most swollen state [10,11], as defined by Eq. (1) where c is concentration.

$$\phi_0 = k_0 \cdot c \tag{1}$$

The viscosity of suspensions bifurcates towards infinity upon reaching a critical phase volume, termed the maximum packing fraction (ϕ_m), which for non-interacting and (near) mono-disperse hard spheres occurs around 0.58–0.64 [12–14]. We recently showed that ϕ_m for many colloidal and non-colloidal hard sphere suspensions, and particularly those with some polydispersity, is reasonably predicted by the packing fraction of randomly close-

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Nomenclature

MPQ	Maron–Pierce–Quemada Eq. (2)
PSD	particle size distribution
rcp	random close packing
c	dry weight concentration (g/ml)
$d_{3,2}$	surface weighted mean (μm)
$d_{4,3}$	volume weighted mean (μm)
G'	bulk gel modulus (Pa)
G_P	particle modulus estimated from the bulk gel modulus (Pa)
k	specific volume (ml/g)
k_0	specific volume at maximum swelling (ml/g)
n	power law index
Q	swelling ratio – grams of swollen wet polymer/grams of dry polymer
η	viscosity (Pa s)
η_r	relative viscosity
η_s	solvent viscosity (Pa s)
σ^2	log normal particle size distribution, $\sigma^2 = \ln(d_{4,3}/d_{3,2})$
ϕ	phase volume
ϕ_0	effective phase volume
ϕ_m	maximum packing fraction
ϕ_{rcp}	geometric random close packing determined from particle size distribution

packed spheres, ϕ_{rcp} [15]. For suspensions of soft spheres, the critical ϕ_0 value (ϕ_{0m}) is not so well-defined as it increases with decreasing particle modulus [16] and cross-link density [17]; we note that values of $\phi_0 > 1$ and $\phi_{0m} > 1$ are commonly reported [3]. In this paper, we address this anomaly and seek to provide an analytical approach to using measured viscosity data to define how the specific volume of microgels alters with increasing concentration. We consider this situation experimentally using model "non-colloidal" soft spheres to ascertain the specific role that particle modulus has on defining the shear rheology and phase volume of soft particle suspensions. The outcomes are expected to provide insights that are equally applicable to colloidal-scale microgels. Having previously shown that a single theoretical model is applicable to both colloidal and non-colloidal hard spheres [15], we demonstrate here its applicability to non-colloidal soft spheres that do not contain long range interactive forces; these include emulsion droplets and microgel spheres.

1.1. Background and approach

1.1.1. Hard sphere theory

In our recent study [15], we show that Eq. (2) with $\phi_m = \phi_{rcp}$ provides a reasonably accurate theoretical prediction of the viscosity of suspensions of polydisperse hard spheres (colloidal and non-colloidal) beyond the dilute regime. The model was derived by Maron and Pierce [18] and later by Quemada [19], and we refer to it as the MPQ model. This model is also theoretically derived by Brady [20] based on the evolving pair-distribution between hard spheres with increasing volume fraction [15,21]. ϕ_{rcp} is independently determined from the particle size distribution [15], and is easily obtained analytically using the model of Farr and Groot [22], discussed in detail in Supplementary material. η is the Newtonian plateau viscosity and η_s is the solvent viscosity. The linear form of the model is included as Eq. (3); this form demonstrates that for the model to be valid, a straight line should be observed when $1/(\eta_r)^{0.5}$ is plotted against ϕ and that ϕ_m is the x-intercept when $1/(\eta_r)^{0.5} \rightarrow 0$. The significance of our recent findings is that the viscosity of hard sphere suspensions can be predicted directly using the MPQ model without need for any fitting parameters [15].

$$\frac{\eta}{\eta_s} = \eta_r = \left(1 - \frac{\phi_0}{\phi_m}\right)^{-2} \tag{2}$$

$$\left(\frac{1}{\sqrt{\eta_r}}\right) = 1 - \frac{\phi_0}{\phi_m} \tag{3}$$

1.1.2. Soft sphere suspensions

Here we employ the same approach to ascertain how microgel suspensions deviate from hard sphere behaviour. We note that previous literature on the rheology of microgel suspensions, including the well-cited works of Senff and Richtering, Tan et al., and Adams et al. [5,6,16], Eq. (2) or similar (as detailed below) is used with ϕ_m determined as a free-fitting parameter from a plot of η_r against ϕ_0. In most of our work presented here using spherical microgels, we set $\phi_m = \phi_{rcp}$ and obtain ϕ_{rcp} from the particle size distribution using the Farr and Groot [22] model. We refer to this as the MPQ-rcp model. This provides an unambiguous way in which to compare our microgel suspensions to hard sphere behaviour. In this context, we reinterpret in a new way the data from Tan et al. [11] and Cloitre et al. [10] to demonstrate the applicability of the MPQ approach to their soft spheres that exhibit osmostic de-swelling as phase volume is increased.

Rather than use ϕ_0, Tan et al. [11] define ϕ by determining the specific volume (k) as a function of concentration (i.e. $\phi = k \cdot c$) using the viscosity predicted from the Krieger–Dougherty and Batchelor equations for mono-disperse hard-sphere suspensions. They assumed their PMMA suspensions were completely monodisperse and consequently used $\phi_m = 0.63$. k_0 varies with concentration above a critical concentration required for osmotic de-swelling to occur. Cloitre et al. [10] utilised an ion specific electrode to measure the increase in free counter ions with increasing microgel concentration to independently calculate the influence of osmotic de-swelling. This confirmed that microgel specific volume decreases with increasing concentration. In Fig. 1, the relative

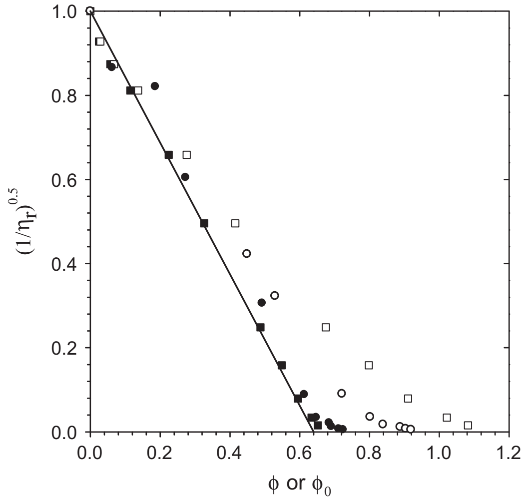

Fig. 1. A linear plot of $1/(\eta_r)^{0.5}$ against phase volume for both ϕ (filled symbols) and ϕ_0 (open symbols) for polyelectrolyte microgels (~100 nm diameter in the collapsed state) from Cloitre et al. [10] (□■) and Tan et al. [11] (○●). The solid line represents the MPQ model with $\phi_m = \phi_{rcp} = 0.64$ for these monodisperse suspensions.