Model for the shear viscosity of suspensions of star polymers and other soft particles

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Abstract

We propose a model to describe the concentration dependence of the viscosity of soft particles. We incorporate in a very simple way the softness of the particles into expressions originally developed for rigid spheres. This is done by introducing a concentration-dependent critical packing, which is the packing at which the suspension looses fluidity. The resultant expression reproduces with high accuracy the experimental results for suspensions of star polymers in good solvents. The model allows to explain a weak increase of the viscosity observed in the case of diblock copolymer stars suggesting that the reason for this peculiar behavior is mainly a consequence of the softness of the particles. In the semi-dilute regime, suspensions of star polymers are modeled using the Daoud-Cotton picture to complete the description in the whole concentration regime.

It is of basic and applied importance to understand the flow behavior of fluids containing colloidal particles and macromolecules. The range of industrial applications of such complex fluids range from motor oils, coatings, drilling fluids and food products among others. Many colloidal suspensions consist of hard particles whose rheological properties have been studied profusely. By contrast, much less attention has been paid to suspensions containing soft colloids. Representatives of soft colloids include deformable particles and particles that in addition may interpenetrate to some extent.

The interest in studying soft particles stems from the desire to explore the behavior of a number of complex fluids composed of nonrigid structures such as polymerically stabilized colloidal spheres [1], block copolymer micelles [2], star polymers [3], hard spheres with a grafted polymer brush [4], dendritically branched polymers [5] and others. In particular, star polymers which are branched macromolecules with a small central core from where \( f \) arms of identical linear polymer chains, each one containing \( N \) segments emerge are considered an important prototypical model of soft particle because their size

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and architecture can be tailored between that of linear polymers and ultra-soft colloids to nearly hard-spheres.

Pioneering theoretical work to calculate the viscosity of dilute colloidal suspensions was initiated by Einstein who obtained an expression to calculate the viscosity as function of the concentration of dilute suspensions of spherical hard particles. Various models to calculate the viscosity of dilute suspensions of particles other than solid spheres have been proposed. Among them we can mention the case of emulsions of spherical droplets, homogeneously porous rigid spheres and uncharged spherical soft particles.

For non-dilute systems, the suspension rheology is determined by the interplay between the direct particle-particle interactions and the solvent-mediated hydrodynamic interactions (HIs). Their many body nature impose a formidable difficulty for the calculation of rheological quantities such as the shear viscosity of the system. The fact that many particles are soft complicates even more the calculation. Nonetheless, it is a common practice to correlate the concentration dependence of the viscosity of star polymers and other hairy particles using phenomenological models designed for solid hard spheres. In particular, experimental data are frequently compared with the expression proposed by Krieger and Dougherty for hard colloidal particles:

\[
\eta(\phi) = \eta_0 \left[ 1 - \left( \frac{\phi}{\phi_{\text{max}}} \right)^{\frac{1}{[\eta]}} \right], \tag{1}
\]

where \(\eta(\phi)\) is the viscosity of the suspension, \(\eta_0\) the viscosity of the background solvent, \(\phi\) is the volume fraction of the colloidal particles, \(\phi_{\text{max}}\) is the volume fraction at maximum packing and \([\eta] = 5/2\) is the intrinsic viscosity of hard spheres. Comparing experimental data for star polymers with this expression might be accurate for stars with a large number of short arms since they behave essentially as hard spheres. However, such comparisons do not give satisfactory results in the case of stars with larger arms because in this case the particles are much softer. In addition to this, it has been shown that the Krieger and Dougherty expression underestimates the viscosity of the suspension at large volume fractions even in the case of hard spheres, as explained thoroughly in Ref.

Alternative expressions have been devised to predict the viscosity for concentrated suspensions including in a more accurate way hydrodynamic and excluded volume interactions. Using a differential effective medium technique based on a progressive addition of particles to the sample in which the new particles interact in an effective way with those added in previous stages, we have shown that the static and high-frequency viscosities of suspensions of colloidal particles can be correlated with the expression:

\[
\eta(\phi) = \eta_0 \left( 1 - \frac{\phi}{1 - k\phi} \right)^{-[\eta]}, \tag{2}
\]

where \([\eta]\) is the intrinsic viscosity and \(k\) a fitting constant related to the critical
volume fraction \( \phi_c \) at which the suspension loses its fluidity and is given by

\[
k = \frac{1 - \phi_c}{\phi_c}.
\]

Expression (2) incorporates crowding effects and hydrodynamic interactions [17]-[20] and has been applied successfully to suspensions of hard spheres [18], emulsions of spherical droplets [19], suspensions of arbitrarily-shaped hard particles [17], suspensions of rigid core-shell permeable particles [20] and suspensions with power-law matrices [21] with excellent results. However, as in the case of the Krieger and Dougherty model, when applied to soft (interpenetrable) particles, Eq. (2) fails to reproduce the viscosity-concentration curves satisfactorily.

The purpose of the present work consists in propose a method to incorporate the softness of the particles in the above mentioned expressions to obtain a model that better correlates with experimental results.

Since we have in mind to apply the model to suspensions of star-branched polymers we have to take into account the possibility that the particles are permeable to some extent to the surrounding solvent. To do so, we consider a core-shell particle consisting of a spherical hard core of radius \( a \) coated with a surface soft layer of thickness \( \delta \). The soft layer may represent a grafted polymer brush [22] or the outer sections of a star polymer, as represented in Fig. 1. Thus, the polymer-coated particle or star polymer has a non-porous inner radius \( a \) and an a permeable outer shell of radius \( b = a + \delta \). The volume fraction \( \phi \) is defined as the volume occupied by the particles including the shell, divided by the volume of the sample. To model the permeability of the outer shell, the polymer segments are regarded as resistance centers distributed in the permeable polymer layer, exerting frictional forces \( -\gamma u \) on the liquid flowing in the layer, where \( u \) is the liquid velocity relative to the particle and \( \gamma \) is the frictional coefficient. The result of this model is [12] \( [\eta] = (5/2)L_2(\lambda b, a/b)/L_1(\lambda b, a/b) \), where \( \lambda = \sqrt{\gamma/\eta_0} \). Expressions for \( L_1(\lambda b, a/b) \) and \( L_2(\lambda b, a/b) \) can be found in Ref. [20]. Therefore, the permeability of the outer shell is incorporated in the intrinsic viscosity \([\eta]\) of the core-shell spheres.

If we consider that the outer core of the soft sphere do not exert frictional forces on the liquid flowing through it, that is, \( \lambda = 0 \), then the expression for \([\eta]\) simplifies considerably and one gets

\[
[\eta] = \frac{5}{2} \left( \frac{a}{b} \right)^3.
\]

The present model, Eq. (2) together with Eq. (4) allows to obtain the viscosity as a function of the concentration of rigid porous core-shell particles and has been successfully applied to calculate the static viscosity of surfactant coated particles and the high-frequency viscosity of homogeneous porous particles [20]. However it does not give satisfactory results for suspensions of star polymers.

As mentioned above, experimental results of the concentration-dependent viscosity of star polymers can not be satisfactorily reproduced with models developed for hard colloids like the Krieger-Dougherty model, Eq. (1) or the
one given by Eq. (2) even when the intrinsic viscosity for core-shell particles, Eq. (4), is used. The problem with these expressions is that they assume that the particles are rigid. It is apparent that the softness of the stars must be taken into account to obtain better results. Here we propose to model the softness of the particles by assuming that the critical volume fraction, $\phi_c$, is larger than the random close packing value $\phi_{RCP}$ since soft particles can interpenetrate each other. Specifically, we propose the following ansatz

$$\phi_c = \phi_{RCP} + \beta \phi^\alpha,$$

where $\alpha$ and $\beta$ are unknown constants that should be determined from the fitting to the experimental data. Expression (5) can be interpreted as follows, when the volume fraction is very low, the soft particles do not interact too much with each other and therefore they do not overlap too much on average. In this situation they behave as rigid impenetrable spheres and $\phi_c = \phi_{RCP}$. As the volume fraction is increased, the particles are forced to collide more often increasing the average overlap which in turn increases the value of $\phi_c$. Eq. (5) then proposes that this increase follows a power law on the volume fraction.

To test the correctness of this proposal we compare the predictions of our model given by Eq. (2) including the possibility that the outer sections of the star are solvent permeable, using the intrinsic viscosity (4). Finally and most importantly, we incorporate the softness of the particles substituting Eq. (5) in Eq. (3). This is done in Fig. 2 where we compare the predictions of our model with the experimental results of Roovers, Ref. [15] for the relative viscosity of polybutadiene star polymers in the good solvent toluene. Typically, the viscosity vs concentration curves for star polymers are plotted in terms of the polymer concentration $c/c^*$, where $c^*$ is the overlap concentration defined by $c^* = \left[\left(N_A/M\right) (4\pi/3) R_V^3\right]^{-1}$, where $N_A$ is Avogadro’s number, $M$ the molecular weight, and $R_V$ the viscosimetric equivalent hard-sphere radius of the polymer coil. On the other hand, models for the viscosity of colloidal suspensions like Eq. (2) are written in terms of the particle volume fraction $\phi$. In the dilute regime these two quantities are related by

$$\phi = c/c^*,$$

which allows to plot our model in terms of the polymer concentration. In Fig. 2 we perform such plot. Panel (a) shows the experimental results for stars with $f = 128$ arms. Notice that the viscosity-concentration curve is not very different from the hard-sphere result at low concentrations. However at large concentrations a slight departure from the hard sphere behavior is observed. Our model reproduces very well this departure with the fitting parameters shown in Table 1. If the number of arms is decreased, one expects a smaller steric repulsion between the arms of different stars allowing a larger overlap and therefore a larger departure from the hard-sphere behavior. This is shown in Fig. 2 (b) where results for a star with 64 arms are shown. The softness of the star is larger than in the case of the star with 128 arms and the departure from the hard-sphere behavior is larger. Our model predicts correctly the experimental
data and the increased softness of this case is reflected in a larger value of the parameter $\beta$, as shown in Table 1. Panel (c) shows the results for a star with 32 arms. The low number of arms of this case allows a much larger overlap allowing that concentrations above $c^*$ can be reached. Experimental data show clearly a different behavior below and above $c^*$. The region below $c^*$ can still be described with our model with an even larger value of $\beta$ than in the previous cases. However, above $c^*$, the overlap is so large that the conformation of the star polymers should be described differently. Here we use the Daoud and Cotton picture [23] to describe the star conformation in this semi-dilute regime.

In the Daoud and Cotton model [23], a single star polymer is regarded as a spherical region of a semi-dilute polymer solution with a local, position dependent screening length $\xi(r)$, where $r$ is the distance from the center. This is represented pictorially by associating with each arm a string of blobs of increasing size $\xi(r)$ as shown in Fig. 3. The blob size varies as $\xi(r) \simeq rf^{-1/2}$ and the corresponding local polymer volume fraction as $c_s(r) \simeq f^{2/3}(b/r)^{4/3}$. The size of the star can be obtained from monomer conservation [24] to obtain $R \simeq \beta \xi_p N f^{1/5}$, where $\xi_p$ is the Kuhn length. Above the overlapping concentration $c^* = f N \xi_p^3 / R^3$, the outer sections of the arms overlap and build a semi-dilute solution, often called the sea of blobs, where the inner parts of the actual stars are embedded and where the polymer concentration of the sea of blobs levels off (see Fig. 3). The stars embedded in the sea of blobs occupy a volume fraction $\phi$ and the sea of blobs the remaining fraction $1 - \phi$. Above the overlapping concentration $c^*$, the values of the polymer concentration in the sea of blobs $c_p$, of the fraction occupied by the stars $\phi$, and of the radius of the embedded stars $R_{sd}$ can be calculated from mass conservation [24]:

$$\phi = k_1 \left( \frac{c^*}{c} \right)^{5/4} ,$$  \hspace{1cm} (7)

$$c_p \simeq c ,$$  \hspace{1cm} (8)

and

$$R_{sd} = R k_2 \left( \frac{c^*}{c} \right)^{3/4} .$$  \hspace{1cm} (9)

The constant $k_1$ can be obtained from continuity of the volume fraction at $\phi = \phi_{RCP} = 0.637$ from Eqs. (6) and (7) to get $k_1 = 0.3625$, while the constant $k_2$ is obtained by continuity from Eqs. (6) and (9) since $R_{sd} = R$ at the same point, to get $k_2 = 0.7130$. Notice that an increase of the polymer concentration $c$ leads to an increase of the fraction of space occupied by the sea of blobs and a shrinkage of the inner star dimensions. Additionally, the stars are embedded in a solvent with viscosity $\eta_{sb}$ formed by the sea of blobs and from Eqs. (9) and (10) the intrinsic viscosity of the embedded stars is

$$[\eta] = \frac{5}{2} \left[ \frac{a}{b} k_2^{-1} \left( \frac{c}{c^*} \right)^{3/4} \right]^3 .$$  \hspace{1cm} (10)
The sea of blobs exerts a strong opposition to flow because movement proceeds through a disentanglement of the stars from their neighbors \[25\] and since they consist of a semi-dilute polymer suspension we suggest to model the viscosity of the sea of blobs using the scaling relation

$$\eta_{sb} = \eta_{sb}^0 \left( \frac{c}{c^*} \right) \gamma,$$  \hspace{1cm} (11)

where \(\eta_{sb}^0\) and \(\gamma\) are additional fitting constants that allow to model the large viscosity of the sea of blobs.

Finally, substituting Eqs. (7) and (10) and replacing the viscosity of the solvent \(\eta_0\) in Eq. (2) with the viscosity of the sea of blobs \(\eta_{sb}\), we obtain the viscosity for \(c \) above \(c^*\).

Using this approach we can reproduce the viscosity-concentration curve of the star with \(f = 32\) above \(c^*\) as shown in Fig. 2(c). Notice that in this regime, the volume fraction occupied by the stars decreases with concentration and this effect alone would produce a decrease of the viscosity with concentration. However, this decrease is offset by the increase of the viscosity of the sea of blobs with concentration. The parameters \(\alpha\) and \(\beta\) used in this region are the ones obtained in the dilute regime and \(\eta_{sb}^0\) and \(\gamma\) are also shown in Table 1.

Finally, in panel (d) we show the case of a diblock copolymer star with 64 arms, an inner core composed of polybutadiene arms with \(N_{inner} = 20000\) and an outer shell of polystyrene arms with \(N_{outer} = 10000\). The viscosity data were collected in toluene which is a good solvent for both blocks. Again, two different regions are apparent and additionally a shoulder appears at a concentration near \(c^*\). Surprisingly, our model reproduces correctly this shoulder. Therefore, our model suggests that the origin of this feature is an intrinsic feature of the softness of the particles. The semi-dilute region is again well described by the Daoud-Cotton picture. Notice that in all the cases considered the thickness of the porous layer is very small as compared to the core size (see the values of the parameter \(a/b\) in Table 1). In other words, for any practical purpose, the star polymers behave as non porous particles and the value \(\eta^* = 5/2\) can be used.

Summarizing, in this work we have presented a simple model for the calculation of the concentration dependence of the viscosity for suspensions of soft spherical particles consisting of a hard core of radius \(a\) covered with a porous shell of thickness \(\delta = b - a\). The model contains three main ingredients, the first one consists in using an accurate model for the viscosity originally developed for rigid particles, Eq. (2). Secondly, we use a simple expression for the intrinsic viscosity of permeable core-shell particles, Eq. (4) to allow the possibility that the outer region of the particle is solvent permeable. Third and most importantly, we incorporated in a very simple way the effects of the softness of the particles through Eq. (5). Using this model we were able to reproduce the experimental results for the viscosity of star-branched polymers and explained the appearance of a shoulder seen in the viscosity concentration curves of the diblock star near the overlap concentration. We conclude that this peculiar behavior is an intrinsic feature of the softness of the particles and there is not need to invoke alternative mechanisms as a shrinking of the polybutadiene block \[15\] when the
total polymer concentration increases. Additionally, in the semi-dilute regime \( c/c^* > 1 \), the suspension is modeled using the Daoud-Cotton picture which completes the description of the viscosity in the whole concentration regime. We have tested our model comparing with experimental results finding an excellent agreement in spite of the numerous simplifications used in the obtention of our model.

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| System             | 128 arms | 64 arms | 32 arms | Diblock star 64 arms |
|--------------------|----------|---------|---------|----------------------|
| \(a/b\)           | 0.988    | 0.989   | 0.993   | 0.984                |
| \(\alpha\)        | 1.90     | 1.60    | 1.74    | 1.50                 |
| \(\beta\)         | 0.244    | 0.580   | 0.966   | 0.662                |
| \(\eta_{sh}^{\text{i}}\) | -        | -       | 9.28    | 17.4                 |
| \(\gamma\)        | -        | -       | 2.67    | 2.88                 |

Table 1: Fitting parameters of the model for the systems of Fig. 2.

**Figure Captions**

Fig. 1. Schematics of a model for a suspension of core-shell spheres. A hard core of radius \(a\) covered by a porous layer of thickness \(\delta\). The total radius of the particle is \(b = a + \delta\).

Fig. 2. Relative viscosity \(\eta(\phi)/\eta_0\) as a function of the particle volume fraction \(\phi\) for star polymers with (a) 128, (b) 64, and (c) 32 arms and (d) diblock copolymer micelle with 64 arms in the good solvent toluene. Experimental data taken from Ref. [15].

Fig. 3. Daoud and Cotton model for a semi-dilute suspension of star polymers.
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