SUSPENSIONS, EMULSIONS AND FOAMS

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Keywords: Einstein Viscosity, Krieger-Dougherty Viscosity, Normal Stresses, Single Drop Dynamics, Taylor Viscosity, Frankel and Acrivos Normal Stresses, Ellipsoidal Models, Palierne Equation, Breakup and Coalescence, Foam Ageing.

Contents

Summary

This chapter gives a survey on the rheology of multiphase systems. The topic is of the utmost practical relevance, as flows of multiphase systems, e.g., solids in liquid, liquid-liquid or gas-liquid systems are encountered in a very wide range of applications. It is then evident the difficult task of gathering together sparse results while also unifying concepts and interpretations. We were thus forced to make a severe selection of main topics, and to leave out many arguments which, though interesting, appear to be of less general relevance. We are fully aware that such a selection is certainly biased from our own interests and fields of expertise; although we apologize for this anisotropic point of view, we believe this is unavoidable in any review chapter.

The chapter opens with a section devoted to suspensions of solids in liquids. In order to maintain the discussion as simple as possible, we consider the case of identical solid spheres as inclusions, by neglecting inertia and buoyancy. The section progresses from dilute to “dense” suspensions. The second section reports on the rheology of liquid-liquid suspensions, i.e., emulsions. The relevance of the dynamic nature of the interface is stressed throughout, from the disperse to the co-continuous morphology. Deformability of the interface, together with breakup and coalescence phenomena play the central role under flow. The chapter then closes with a rather brief introduction to foams, i.e., the case of gas-liquid systems at very high gas fraction.

Whenever theoretical analysis can be profitably used to describe experimental evidences, it has been included in some detail. The reader will notice how theoretical understanding progressively fades out while reaching the end of the chapter, somehow reflecting both the *age* of the subjects here addressed, and their intrinsic difficulties. Although the topics covered in this chapter are widespread, a unifying tool is often used (if not explicitly reported) for the rheological description, namely, the celebrated stress averaging procedure formalized by Batchelor (1970). Useful limiting behaviors and scaling arguments are presented as well. In the cases where no clear cut understanding can be found, phenomenological arguments and practical rules of thumb are reported to guide the reader.

1. Suspensions

A suspension consists of discrete particles dispersed in a liquid matrix. As already mentioned in the Introduction, we will mainly consider monodisperse rigid spheres, in the inertialess case and buoyancy free. Even within these limitations, the multiphase system behavior is affected by several factors. Still at the level of solid/liquid interactions, surface properties may play a crucial role. For example, hydrophilic/hydrophobic particle characteristics with respect to the suspending liquid, surface charge density related to the matrix pH, possible adsorption of species (or even the presence of surfactants), and chemical stability of the particles can be of importance. Also particle/particle interactions, e. g., repulsions or attractions leading to flocculation, certainly have a profound influence on the suspension behavior. In what follows, however, we will present the rheology of the overall suspension as determined essentially by hydrodynamics, to keep the discussion as simple as possible.

1.1. Dilute Systems

Dilute systems are usually regarded as the simplest system to understand the effect of fillers on hydrodynamics. A suspension is defined to be dilute when, loosely speaking, particles do not interact at all, and hence the only effect of the addition of particles results in local distortions of the flow field. Since such distortions are completely unrelated with each other, the size of particles (and even their size distribution, if any) does not play any role, provided of course that sample size is much larger than particle dimensions. The undisturbed flow field is supposedly recovered at some distance from the inclusion. The region interested by distortion due to the particle has a characteristic dimension that scales with the only available length scale, i. e., the particle size. Thus, the actual particle dimension is irrelevant, and all macroscopic observables in the dilute case will only depend on the (low) solid volume fraction, ϕ, of the suspension.

Some caution is required to proceed, however, as small volume fractions do not necessarily imply diluteness in the above stated sense. Indeed, a simple estimate of “particle crowding” in terms of volume fraction in the absence of any structuring of the suspension can be derived from a purely geometrical argument for the simple case of equally sized spherical inclusions. By calling *h* be the distance among first neighbors, and *R* the sphere radius, for the hypothetical case of simple cubic arrangement it is:

$$\frac{h}{R} = 2\left[\left(\frac{\pi}{6\phi}\right)^{\frac{1}{3}} - 1\right] \tag{1.1}$$

Equation (1.1) shows that *h* diverges for vanishing volume fraction, as it should be. Furthermore, the maximum packing fraction for simple cubic arrangement is found at $h = 0$, namely $\phi_{\mathrm{m}} = \pi / 6 \sim 0.52$. By inspection, one can note that even at low volume fractions, h / R can be a small number. For example, for $\phi = 0.1$, it is $h / R = 1.46$, i.e., particles are less than one-particle diameter apart. The volume fraction for which particles are exactly one-diameter apart is as low as $\phi = 0.06$. Similar conclusions hold in the more realistic case of so-called “randomly packed” spheres (Truskett et al. 2000). For such arrangement, Woodcock (1985) estimates that:

$$\frac{h}{R} = 2\left[\left(\frac{1}{3\pi\phi} + \frac{5}{6}\right)^{\frac{1}{2}} - 1\right] \tag{1.2}$$

In this case, the maximum packing fraction is $\phi_{\mathrm{m}} = 2 / \pi \sim 0.64$, and the condition for having spheres one-diameter apart is $\phi = 0.03$, even more restrictive than for the crystalline cubic arrangement. It is then apparent that dilute conditions in the sense of isolated particles can be practically attained at extremely low volume fractions (infinite dilution limit). Such a dilution might be hardly achievable in actual experiments, and, correspondingly, macroscopic effects might become barely measurable in such conditions. By increasing the volume fraction, hydrodynamic interactions between particles will become significant, and will in fact play a key role in semi dilute suspensions.

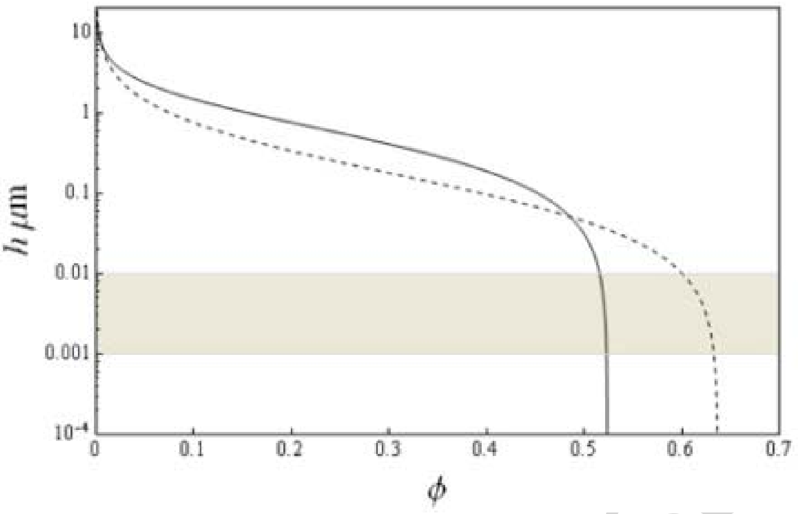

Figure 1. Packing functions: Solid line represents Eq.(1.1), dashed line represents Eq. (1.2), both for *R*=1μm. Shaded area indicates length scale range of colloidal forces.

To roughly characterize the influence of the other possible particle interactions (electric, interfacial etc.) of colloidal origin, one can still refer to Eqs.(1.1) and (1.2). Figure 1 shows the characteristic distance calculated from Eqs. (1.1) and (1.2) for spherical particles with *R*=1μm. The shaded area in the figure represents the typical scale length of colloidal forces, namely, around a few nanometers. It is thus confirmed that, for nonBrownian particles, colloidal forces are only relevant close to maximum packing. It can be concluded that one can identify three main concentration regions: 1) Infinite dilution, i.e., single particle effects; 2) Semidilute systems, with hydrodynamic interactions only; 3) Concentrated systems, where also colloidal interactions should be accounted for.

Under highly dilute conditions, rigorous hydrodynamic predictions are available, which can be used to determine rheological properties of the suspension as a whole. Indeed, in the infinite dilution limit single particle behavior only is relevant, and predictions of bulk properties can then be achieved through proper averaging. The phrasing "suspension "as a whole" and "bulk properties" point to the simple concept that the suspension, although microscopically a two-phase system, can be envisaged instead as a homogeneous liquid when observed at a macroscopic scale, where "proper averaging" cancels fine local details. Quite naturally, two different characteristic length scales have already emerged in the above discussion on concentration regimes, i.e., the sphere radius R , and the intersphere distance h : diluteness implies $R \ll h$. For the "macroscopic scale" of the averaging, L , it clearly must be $L \gg h$. In many cases, L is a linear dimension of the apparatus in which the rheological experiments are performed, for example the gap in a Couette cell. In view of the ordering $R \ll h \ll L$ of the length scales, the averaging over L implies the contribution of many particles, and each particle behaves individually. Thus, in dilute conditions bulk properties are averaging of single-particle results.

The classical result of Einstein (1906, 1911) on the viscosity of a dilute suspension of buouancy-free rigid spheres can then be attained as follows. A single sphere is immersed in an incompressible Newtonian liquid for which the stress tensor $\mathbf{T}$ is:

$$\mathbf{T} = -p\mathbf{I} + \eta_0\left(\nabla\mathbf{v} + \nabla\mathbf{v}^{\mathrm{T}}\right) = -p\mathbf{I} + 2\eta_0\mathbf{D} \tag{1.3}$$

where p is the pressure, η_0 is the viscosity, $\mathbf{I}$ is the unit tensor, $\mathbf{v}$ is the local velocity field, and $\mathbf{D}$ is the rate of deformation tensor. A linear flow field is imposed far away from the sphere (i.e., with a constant velocity gradient “at infinity”), and the full hydrodynamic problem is solved (in the absence of inertia), with no-slip conditions at the sphere surface. Once this single particle problem is solved, the local stress fields are available and can be used in an averaging procedure involving both the liquid and the sphere. In principle, to perform the averaging of the stress, also the stress inside the particle would be required, which is undetermined, however, because of the rigidity constraint. To overcome this difficulty, the volume integral over the sphere is transformed to a surface integral over the sphere surface A_s, where local stresses are instead known. Summing over the n spheres contained in the averaging volume L^3, one eventually obtains the average (i.e., bulk) deviatoric stress:

$$\bar{\mathbf{T}} = 2\eta_0\bar{\mathbf{D}} + \frac{n}{L^3}\int_{A_s}\mathbf{T}\cdot\mathbf{nn}\,dA \tag{1.4}$$

with $\mathbf{n}$ being the unit outward normal to the sphere surface, and the overbar denotes L^3 volume averaging. Upon integration, the famous Einstein formula for the bulk viscosity of the suspension is finally obtained:

$$\bar{\eta} = \eta_0\left(1 + \frac{5}{2}\phi\right) \tag{1.5}$$

the volume fraction being of course $\phi = \left(n\dfrac{4\pi R^3}{3}\right)\Big/L^3$. In passing, notice that no effects other than such viscosity modification occurs, i.e., the suspension as a whole remains a Newtonian liquid for which the intensity of the flow field does not affect the viscosity. This simplicity is due to diluteness. Indeed, as it will be shown in a subsequent section, concentrated suspensions in a Newtonian medium show an overall non-Newtonian behavior.

Equation (1.5) is a very robust result. It is worth noting that Einstein original derivation was quite different from that followed here, as it was based on a calculation of dissipation in the single sphere problem. On the other hand, the deduction of the constitutive relation (Eq.(1.5)) by averaging can be made in several ways. Here, a volume averaging was chosen (e. g., Landau and Lifshitz, 1958; Batchelor, 1970). Other choices refer to ensemble averaging or homogenization techniques together with asymptotic analysis (Brenner, 1972; Hinch, 1977). Convergence of all these methods to the same result is then certainly remarkable. Another interesting feature of Eq.(1.5) is that it is applicable to Brownian suspensions of spheres as well. Once again, this feature was indeed exploited with a great understatement by Einstein himself to derive his famous relationship for the diffusivity in suspensions or solutions. In fact, Eq.(1.5) was later adopted in the procedure for obtaining molecular weight of polymers through viscosity measurements of their dilute solutions (e.g., Flory, 1953).

From a purely rheological point of view the Einstein equation provides a limiting behavior. Dilute suspension theory indeed covers the range below at most 5-10% volume fraction. Nearly all systems of practical interest, however, are well beyond that range, hence utility of Eq.(1.5) is limited. The experimental assessment of the validity of the Einstein equation is not a trivial issue. When dealing with large spherical particles particle inertia, settling, and migration can cause serious problems. In the case of submicron particles, preparation of homogeneous samples could be difficult for agglomeration due to colloidal forces. Careful experiments carried out in the semidilute regime (to be examined later on, see Figure 3) show the correct Einstein limiting behavior when approaching very low dilution.

The Einstein prediction applies to “hard spheres”, while the case of “soft spheres” has to be considered when either one or more of the following conditions are encountered: (a) a significant electrical double layer is present on the particle surface; (b) the thickness of the adsorbed stabilizing layer (surfactant layer) is significant with respect to particle size; (c) the solvation or hydration of particles is significant (solvation or hydration refers to a phenomenon whereby the continuous-phase liquid becomes immobilized at the particle surface). The presence of an electrical double layer on the surface of the particles results in an increase of the viscosity. This phenomenon is referred to as electroviscous effect (Krieger, 1972). In the case of dilute suspensions, the electroviscous effect is associated with the distortion of electrical double layer from spherical symmetry due to the shear field. The stresses generated by asymmetric electric fields around the particle tend to restore the symmetry of double layer, thereby opposing the flow. This results in extra dissipation of energy, hence, an increase in viscosity. In the case (b) or (c) listed above, the presence of a thick adsorbed layer of surfactant or continuous-phase liquid at the particle surface also results in an increase in the viscosity of the dispersion.

The effects of viscoelasticity of the suspending fluid are relevant in many systems of practical interest, e.g., filled polymer melts or filled worm-like surfactant systems (“living polymers”). Of course, a wealth of non-Newtonian fluids encompassing a wide range of rheological properties exists, thus preventing a simple unifying description of their constitutive equations. Thus, even in the simplest case of dilute suspension of spherical particles, general common features are hardly found. To maintain the highest possible generality, the so-called "Second Order Fluid" (SOF) constitutive equation can be considered for the suspending fluid. The SOF stress tensor is the asymptote of an extremely ample class of viscoelastic constitutive equations, in the limiting conditions of slow and slowly varying flows (Truesdell and Noll, 1965). It is:

$$\mathbf{T} = 2\eta_0\mathbf{D} + \alpha_0\mathbf{A} + \beta_0\mathbf{D}\cdot\mathbf{D} \tag{1.6}$$

where $\mathbf{A}$ is the second Rivlin-Ericksen tensor, and the coefficients α_0 and β_0 are constant constitutive parameters that account for elastic properties of the fluid. These coefficients are linked to the first and second normal stress coefficients in shear flow,

Ψ_1 and Ψ_2 respectively, through the well known relationships: $\alpha_0 = -\Psi_1/2,\ \beta_0 = 4(\Psi_1 + \Psi_2)$. The SOF constitutive equation is the most general properly invariant stress tensor quadratic in the velocity gradient.

Some analytical results for dilute suspensions have been presented in the past based on Eq.(1.6), and on proper averaging of the stress field from single-sphere results, akin to that of Eq. (1.4). Because of the mathematical complexities of the calculations, however, those results were at variance with each other. Quite recently, the analytic problem has been re-tackled again and convergence (though not yet identity) in the obtained formulae has been gained (Greco et al, 2005, 2007; Koch and Subramanian 2006). Non-Brownian rigid spheres in a SOF is then shown to be itself a SOF, with the overall elastic constitutive coefficient $\bar{\alpha}$ given by

$$\bar{\alpha} = \alpha_0 \left(1 + \frac{5}{2}\phi \right) \tag{1.7}$$

and the viscosity always given by Eq.(1.5).The $\bar{\beta}$ coefficient is slightly different in Greco et al. (2005, 2007) and Koch and Subramanian (2006). Even more than for the Einstein equation, the experimental assessment of the validity of Eq. (1.7) is not an easy task. Indeed, as mentioned above, coefficients α and β are linked to normal stresses, and the error on normal stress difference measurements is often substantial. A peculiar prediction from these recent calculations should be signaled, however: The presence of suspended spheres should lead to the appearance of a second normal stress difference $\bar{N}_2$ in shear even in fluids which, when unfilled, do not present such normal stresses.

Another nice conclusion from both Eqs. (1.5) and (1.7), amenable to ready validation from steady shear experiments, is obtained by looking at normal stress data in terms of the overall tangential shear stress $\bar{T}_{xy}$, rather than in terms of the imposed shear rate, following the original suggestion by Highgate and Whorlow (1970). By considering, for example, the first normal stress difference $\bar{N}_1$, it is found:

$$\bar{N}_1 = -2\frac{\alpha_0}{\eta_0^2}\left(1 - \frac{5}{2}\phi \right)\bar{T}_{xy}^2 \tag{1.8}$$

Thus, at any fixed shear stress, the first normal stress difference decreases with ϕ (recall that α_0 is a negative quantity). This feature is in qualitative agreement with experimental data, although those data are regularly taken at volume fractions not actually in the dilute regime (see Figure 6). This kind of success is in fact a rather typical feature of “infinite dilution” results, namely, that the predicted trends from single-particle calculations turn out (somehow surprisingly) to be qualitatively correct even well beyond the $\phi \to 0$ limit.

Finally, by using Eq.(1.6) for the suspending liquid, also the linear viscoelastic behavior of the nonBrownian dilute suspension can be calculated, e.g., the response of the suspension to small shearing oscillations. Results do in fact coincide with those obtained as a special case (for solid particles) from the well-known Palierne theory for emulsions (see next section, Eqs.(2.8)). The storage and loss moduli of the suspension are always increased by filler addition, and the effect is the same for G' and G'', through the shift factor $\left(1+\frac{5}{2}\phi\right)$ (see Eqs.(1.5),(1.7)). Also in this case, the experimental assessment of such prediction is not easily made, because of the high dilution in principle required for the suspension. Finite dilution results, up to high concentration, show a vertical shift of both moduli, but the effect of the filler is not always the same for G' and G'' (Barnes, 2003). Quite often, other effects are observed, with the appearance of a low-frequency plateau in the storage modulus, usually from a pseudo-network arrangement between flocs or chains of particles.

Abandoning the SOF limit for the suspending liquid, non-Newtonian rheological properties depending on flow rate and/or time have to be described such as, for example, the well-known “thinning” of viscosity or normal stresses with the shear rate, or the “strain-rate hardening” during time evolution of the elongational viscosity. Many non-Newtonian constitutive equations for the stress tensor have been proposed to this aim, all of them containing a characteristic relaxation time τ (at least) as a yardstick of the slowness in the time response of the given fluid. In nondimensional terms, this leads to the introduction of the Deborah number De, as the ratio between the characteristic time of the material and that of the imposed flow. In shear, for example, it is $De = \tau\dot{\gamma}$, with $\dot{\gamma}$ the shear rate. Notice that, in fact, for the Newtonian suspending fluid it is $De = 0$, whereas the asymptotic SOF is linear in De, with $\tau = -\alpha_0/\eta_0$.

All the rheological phenomena of a dilute suspension in a non-Newtonian fluid become then in principle dependent on De, as well as on ϕ, and diverse nonlinear behavior is shown with different suspending fluids. For dilute suspensions in steady shear, experiments generally show (Han, 1981; Metzner, 1985; Barnes, 2003) that the viscosity, the first and (magnitude of) the second normal stress differences all increase with respect to the corresponding quantities for the pure suspending fluid, at any De. In general, it is also found that a simple vertical shift of the flow curves will not describe the effect of added particles at all shear rates. In other words, with increasing De, the difference between suspension and pure fluid rheological quantities progressively decreases. As an example, Figure 2 shows the viscosity of a suspension as a function of the shear rate, with the volume fraction of beads increasing, even well beyond the dilute limit.

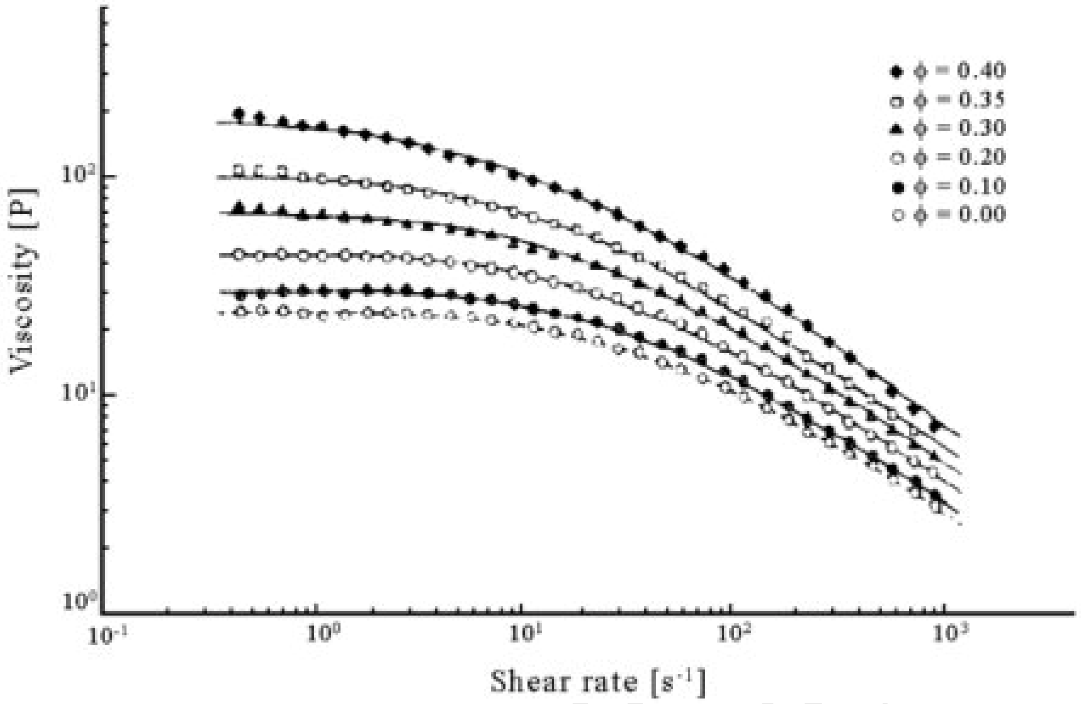

Figure 2. Viscosity-shear rate curves for glass beads suspended in polyisobutylene decalin solutions. (Reproduced from Nicodemo et al. 1974, with permission)

The latter observation can perhaps be rationalized as follows. For a suspension, the undisturbed shear flow in a cone-and-plate apparatus, say, with a constant shear rate changes to a situation where locally, in the neighborhood of a particle, there is an increase of the shear rate. (The obvious appearance of extensional components in the local flow around the particle is here neglected, for simplicity of argument.) As a consequence, for a thinning non-Newtonian suspending liquid, the local viscosity (or normal stresses) will be lower than that pertaining to the unfilled liquid at the same externally imposed shear rate, the more so the larger De. Such a thinning-induced decrease in the local (and hence in the overall) viscosity of the continuous phase somehow counteracts the increase in the suspension viscosity due to the presence of particles, and the effect of added particles is therefore smaller at high De, as observed. At present, no calculation of such a feature is however available in the literature, not even in the dilute limit (order ϕ).

In the case of elongational flow, essentially no experiments are available for dilute suspensions of spheres. The only available theoretical predictions (Greco et al. 2005; Koch and Subramanian, 2006), for the uniaxial elongational viscosity of a Newtonian and a SOF non-Brownian suspension, show quite small effects of non-Newtonianness on the Trouton ratio. Large effects of added particles on the elongational behavior of the suspension are observed instead for nondilute suspensions with non-Newtonian suspending fluids (see next section), or for rather dilute suspensions with elongated particles.

In the latter case, the effect of nonsphericity might be evaluated by considering uniaxial ellipsoidal particles, i.e., ellipsoids of revolution (semi-axes a, b and b). The aspect ratio of such particle is $r = a/b$. For $r > 1$, this is a prolate ellipsoid (rods) with the two equal axes being shorter than the larger axis, while for $r < 1$ this is an oblate ellipsoid (disks) with the two equal axes being longer. The nonspherical particle can be oriented by the flow field. In the case of extensional flows the anisotropic particles reach a steady state conditions: in the case of rod-like particles the major axis orients in the stretching direction, while in the case of disk-like particle the axis of symmetry orient along the compression direction. The extensional viscosity is then given by (see e.g., Petrie 1999):

$$\begin{aligned} \bar{\eta}_{\mathrm{el}} &= \eta_0\left[1+\phi\frac{r^2}{3\left(\log 2r - 3/2\right)}\right] \quad r \gg 1 \\ \bar{\eta}_{\mathrm{el}} &= \eta_0\left[1+\phi\frac{10}{3\pi r}\right] \qquad r \ll 1 \end{aligned} \tag{1.9}$$

Comparison of Eq.(1.9) with the case of spherical inclusions shows that a small amount of anisotropic particles gives rise to a strong increase of the extensional viscosity.

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FOAMS

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