FUNDAMENTAL CONSIDERATIONS ON SUSPENSION RHEOLOGY

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The basic assumptions of suspension rheology (existence of a unique viscosity and dependence of the effective viscosity on the solids volume fraction) are discussed from the viewpoint of rational mechanics and micromechanics. The most important effective viscosity formulae are presented in a new way, which clarifies the status of these formulae and makes a clear distinction between exponential (Mooney-type) relations and power-law (Krieger-type) relations. Based on a functional equation approach, a tentative explanation is given why the latter are more successful. The Frankel-Acrivos relation is modified to exhibit correct behavior in the dilute limit.

INTRODUCTION

The mathematical formulation of rheology, the science of fluid flow in general, is essentially an achievement of the 18th century, related to the names of Daniel Bernoulli, Euler and Lagrange. During the second half of the 20th century, the Truesdell-Noll school of rational mechanics performed a critical revision of the non-linear theories of mechanics [1] and summarized virtually all that was known and correct about the non-linear theory of rheology and the corresponding experimental issues [1-8]. From the viewpoint of rational theory, Newtonian fluids (Navier-Stokes-Poisson fluids) appear as a very special case of far more general materials models (non-Newtonian fluids). The possibilities and the outcome of experimental work, however, depend widely on the equipment available. E.g. when a capillary or rotational viscometer is the only equipment available the shear stress at a certain shear rate, in other words the apparent viscosity, is usually the only quantity directly accessible to measurement. In this case it is necessary, for pragmatic reasons, to introduce the concept of generalized Newtonian fluids to interpret the measured data. In this paper, this concept is recalled and it is emphasized that, inspite of this, suspension rheology is based on the assumption of the existence of a (unique) Newtonian viscosity.

Suspension rheology as a special subject in its own right, is about 100 years old. Except for Arrhenius' empirical exponential relation dating back to 1887 [9,10], Einstein's inaugural dissertation of 1906 [11] can be considered as the starting point of suspension rheology (and of micromechanics in general). Einstein's work has launched an immense amount of theoretical and experimental work on suspension rheology during the 20th century. In particular, there have been many efforts to extend the Einstein relation, which can be valid only for dilute suspensions, to non-dilute systems. Apart from the theoretical interest, there is a strong practical aim behind this line of research: suspensions are important in materials processing technology. E.g. ceramic technology relies widely on the shaping of slurries and pastes. In this case a prediction of the effective viscosity for a certain solids volume fraction can be very useful for process control. Nevertheless, it seems that in the literature there exists some confusion about the status and applicability of effective viscosity formulae. This paper should clarify some of these points. The most important effective viscosity formulae are presented in a new way which clarifies the status of these formulae and makes a clear distinction between exponential (Mooney-type) relations and power-law (Krieger-type) relations. Based on a functional equation approach, a tentative explanation is given why power-law relations are usually more successful than exponential relations. The so-called Robinson relation is rediscovered from oblivion and the reader is reminded of the fact that the Eilers relation is identical with the Maron-Pierce relation. The latter can be recommended for rough prediction purposes in cases where measured data are scarce and microstructural input information is lacking. Finally, a modified version of the so-called Frankel-Acrivos relation is proposed which, in contrast to the original formula, exhibits correct behavior in the dilute limit.

VISCOSITY FROM THE VIEWPOINT OF RATIONAL MECHANICS

From the macroscopic point of view suspensions can be considered as continuous media. Within the framework of rational thermomechanics (continuum mechanics and thermodynamics) [1-8] viscous fluids are characterized by a constitutive equation of the form

$$\mathbf{T} = \mathbf{T}(\rho, T, \mathbf{D}) \qquad (1)$$

where $\mathbf{T}$ is the Cauchy stress tensor (in the case of suspensions the effective Cauchy stress tensor), ρ the density (in the case of suspensions the effective density), T the absolute temperature (assumed to be the same for all constituents or phases) and $\mathbf{D}$ the (effective) deformation rate tensor defined as the symmetric part of the velocity gradient $\mathbf{v}$,

$$\mathbf{D} \equiv \tfrac{1}{2}\,(\nabla\mathbf{v} + \nabla\mathbf{v}^{T}) \qquad (2)$$

Note that internal friction (viscosity) can only be modeled when the deformation rate tensor $\mathbf{D}$ is included in the set of independent variables. Otherwise only inviscid fluids, i.e. ideal gases, are included in equation (1). On the other hand, viscoelastic behavior is not included in the material model described by equation (1). It is usual to decompose the stress tensor $\mathbf{T}$ into a so-called spherical part - $p\mathbf{1}$, containing the pressure p, and a deviatoric part $\boldsymbol{\tau}$ (shear stress tensor), responsible for dissipation due to internal friction. While for compressible fluids (gases) the spherical part corresponds to the thermodynamic pressure $p\,(\rho, T)$ (determined by an equation of state, e.g. the ideal gas equation $p\rho^{-1} = RT$), for incompressible fluids (liquids) the spherical part corresponds to an indeterminate hydrostatic pressure $p(= \text{constant})$, which can be arbitrarily assigned from the exterior.

Due to the so-called Cayley-Hamilton theorem and the representation theorem for (symmetric) isotropic tensor functions with (symmetric) second-order tensor arguments [1-8], the constitutive equation for isotropic viscous liquids can be written as

$$\boldsymbol{\tau} = \mathbf{T} + p\,\mathbf{1} = \psi_0\,\mathbf{1} + \psi_1\,\mathbf{D} + \psi_2\,\mathbf{D}^2 \qquad (3)$$

In this equation, the scalar coefficients ψ_i ($i = 0, 1, 2$) are functions of ρ, T and three scalar invariants of the deformation-rate tensor $\mathbf{D}$, e.g. the invariants tr $\mathbf{D}$, tr $(\mathbf{D}^2)$ and tr $(\mathbf{D}^3)$ or the so-called principal invariants

$$\begin{aligned} I_D &\equiv \text{tr}\,\mathbf{D}, \\ II_D &\equiv \tfrac{1}{2}[(\text{tr}\,\mathbf{D})^2 - \text{tr}\,(\mathbf{D}^2)], \\ III_D &\equiv \det \mathbf{D}. \end{aligned} \qquad (4)$$

Note that the nonlinear constitutive equation (3) follows directly from equation (1) for the special case of isotropic symmetry, without further assumptions. The class of non-Newtonian fluids described by equation (3) is called Reiner-Rivlin fluids.

For reasons of convenience let us ignore the temperature dependence in the following, i.e. although not explicitly written, the temperature dependence is understood automatically.

For incompressible fluids ρ is constant and can therefore be omitted from the set of independent variables (i.e. as arguments in the coefficients ψ_i). Further, the first invariant reduces to zero because of mass conservation ($I_D = \text{tr}\,\mathbf{D} = 0$) and the first r.h.s. term of equation (3) can be included into the indeterminate hydrostatic pressure term on the l.h.s. When, additionally, normal stress effects are neglected (i.e. geometrical singularities are avoided during flow) and only viscometric flow is considered (i.e. flow types equivalent to simple shear flow), the third r.h.s. term of equation (3) can be ignored and the third invariant reduces to zero ($III_D = \det \mathbf{D} = 0$). Taking into account the fact that the second invariant is also simplified due to incompressibility, the resulting constitutive equation for the shear stress tensor $\boldsymbol{\tau}$ is

$$\boldsymbol{\tau} = 2\eta\,[\text{tr}(\mathbf{D}^2)]\mathbf{D} \qquad (5)$$

where η is the shear viscosity. This is the constitutive equation of so-called generalized Newtonian fluids (liquids), which is the basic constitutive equation assumed for viscometric measurements. For one-dimensional flow geometry, the constitutive equation of generalized Newtonian liquids can be written as

$$\tau = \eta\,(\gamma^2) \qquad (6)$$

where τ is the shear stress and γ the shear rate. For Newtonian liquids the shear viscosity η is a constant, while for non-Newtonian liquids the shear viscosity is a (even) function of the shear rate, cf. equation (6). In other words, the flow curve of Newtonian liquids is linear, while for non-Newtonian liquids it is nonlinear. In the case of a nonlinear flow curve, equation (6) defines the so-called apparent (shear) viscosity as the ratio of shear stress and shear rate at a certain shear rate, i.e.

$$\eta \equiv \left(\frac{\tau}{\gamma}\right)_{\gamma\,fix} \qquad (7)$$

Of course, the constitutive equation of Newtonian fluids can also be obtained directly by linearizing equation (3), i.e.

$$\boldsymbol{\tau} = \mathbf{T} + p\,\mathbf{1} = \lambda\,(\text{tr}\,\mathbf{D}) + 2\,\eta\,\mathbf{D} \qquad (8)$$

where the viscosities γ and η are constants. In the case of incompressible fluids (liquids) this equation reduces to

$$\boldsymbol{\tau} = 2\,\eta\,\mathbf{D} \qquad (9)$$

in 3D geometry and to

$$\tau = \eta\,\gamma \qquad (10)$$

in 1D geometry. We remind the reader that it is understood, although not explicitly written in equations (5)

through (10), that the shear viscosity η is also a function of temperature. Note that only for Newtonian liquids there is a uniquely defined shear viscosity. Most real suspensions, however, exhibit non-Newtonian behavior, i.e. usually nonlinear flow curves are measured in viscometric flow experiments. Some suspensions, however, exhibit approximately Newtonian behavior (i.e. linear parts of flow curves) at very low or very high shear rates. Sometimes it is recommended to consider these regions to compare the effective viscosities for different solids volume fractions. But it should be kept in mind that this approach suffers from a fundamental disadvantage: the quasi-Newtonian (i.e. linear) regions of the flow curves are usually attained at different shear rates for different concentrations. This indicates a fundamental problem of suspension rheology in general, which has not been paid due attention to in the literature so far.

CONCENTRATION DEPENDENCE OF VISCOSITY FROM THE VIEWPOINT OF MICROMECHANICS

In the preceding section, the existence of the shear viscosity was discussed within the framework of rational mechanics, i.e. from the viewpoint of classical continuum mechanics. This is a valid approach for suspensions. As long as the suspensions are considered from a macroscopic length scale, i.e. in processes (e.g. viscometric flow experiments) in which the external characteristic length (e.g. the viscometer gap or capillary diameter) is much larger than the intrinsic characteristic length of the microscopic heterogeneities (e.g. the size of the suspended particles), suspensions can be treated in complete analogy to one-phase continua. This is important to know, in particular because a rigorous treatment of suspensions by rational mixture theory is still a non-trivial and highly disputable subject of research, cf. e.g. [12-15].

Nevertheless, it is possible to include a certain degree of microstructural information by adopting a micromechanical viewpoint [16,17]. In micromechanics, suspensions are considered as multiphase (usually two-phase) mixtures or, equivalently, as fluids (liquids) with microstructure. Micromechanics defines so-called effective material properties for the mixture (e.g. effective suspension viscosity) as a whole, which depend in principle on all details of the microstructure. Complete microstructural characterization is of course impossible. It would require e.g. an infinite set of so-called correlation functions [16-19]. Therefore one attempts to use the minimum of microstructural information necessary, i.e. the lowest-order correlation functions. These are the volume fractions. For a two-phase system (e.g. a suspension, which can be considered as a solid-liquid mixture) one of the volume fractions is sufficient, usually

the volume fraction ϕ of the solid phase. Thus, from the viewpoint of micromechanics, the effective viscosity of a suspension is assumed to be a function of the solids volume fraction,

$$\eta = \eta(\phi) \qquad (11)$$

This is the basic equation of suspension rheology. As before, it is understood, although not explicitly written in equation (11), that the effective viscosity is also a function of temperature. The principal problem with this assumption, i.e. with the fundament of suspension rheology itself, is that it cannot be valid in general. The effective viscosity of a solid-liquid mixture cannot be a unique function of volume fraction alone. E.g. a suspension with 50 vol.% of alumina powder and 50 vol.% water is easy to prepare and has a certain (finite) effective viscosity. It is also thinkable, however, to prepare a solid skeleton of alumina ceramic material with 50 vol.% open porosity and to infiltrate the pore space with 50 vol.% water. In both cases the solids volume fraction is $\phi = 0.5$, but in the latter the viscosity would be infinitely high or is simply not defined. Therefore, in abstract terms, equation (11) should be formulated as

$$\eta = \eta(\phi, \text{ all other details of microstructure}) \qquad (12)$$

Since, however, the second argument is hard to quantify by appropriate measures and even harder to determine experimentally (in porous solids e.g. second-order and third-order correlation functions can only be determined by intricate microscopic image analysis, tomography, NMR, diffraction techniques or, for model microstructures, by simulation methods [16,17,20]), one usually adopts the oversimplified version (11), as the fundamental assumption of suspension rheology. Often the only specification of the type of microstructure is a qualitative one: a suspension is considered as a solid-liquid mixture of matrix-inclusion type, i.e. with isolated solid particles in a liquid matrix. One has to keep in mind, however, that in doing so, other microstructural information, which would be included in a correlation-function approach, is a priori ignored (e.g. particle size distribution, particle shape, degree of particle orientation, structural type of particle arrangement).

EFFECTIVE VISCOSITY FORMULAE

Dilute approximation, second-order expressions and differential scheme approach

The dilute (i.e. non-interaction) approximation for the dependence of the effective suspension viscosity on the solids volume fraction is given by the Einstein rela-

tion [11]. According to Einstein, the effective viscosity of a dilute suspension of rigid, non-interacting spherical particles is

$$\eta = \eta_0 (1 + 2.5\phi) \qquad (13)$$

irrespective of (absolute) size and (relative) size distribution. In this equation, η denotes the effective (i.e. macroscopic) suspension viscosity and η_0 the viscosity of the suspending medium (pure liquid). In order to simplify notation in the following text, we introduce the relative viscosity η_r, i.e. ratio of the effective viscosity η and the viscosity of the suspending medium η_0. The Einstein relation, equation (13), is the cornerstone of suspension rheology. Note that in the limit $\phi \to 0$ it is an exact result for suspensions of spherical particles. Therefore all extensions to non-dilute rigid-sphere suspensions should reduce to the Einstein relation in the dilute limit. The Einstein relation has been extended to non-rigid (deformable) particles by Taylor [21] and to non-spherical (spheroidal) particles by Jeffery [22]. In this paper we confine ourselves to the discussion of rigid-sphere suspensions.

Early efforts to extend the validity of effective viscosity formulae to non-dilute systems resulted in second-order expressions of the type

$$\eta_r = 1 + 2.5\phi + A\phi^2 \qquad (14)$$

Interactions have to be taken into account in order to calculate the second-order coefficient A. Values that can be found in the literature range from 4.375 [23, 24] to 14.1 [25], but Batchelor's value of 6.2, based on a rigorous calculations of pair interactions for the case of strong Brownian motion [26], seems to be the most reliable. Note, however, that all second-order polynomial expressions of this type suffer from the serious drawback that the relative viscosity does not go to infinity ($\eta \to 0$) as the volume fraction approaches unity ($\phi \to 1$). Therefore second-order expressions are almost useless from a practical point of view, both for prediction and for fitting purposes. Note also that second-order expressions of the elastic constants (Coble-Kingery formulae) do not exhibit this principal disadvantage [27-31].

The first application of the so-called differential scheme approach to effective suspension viscosity is due to Roscoe [23] and Brinkman [24]. The basic idea is as follows [23, 24, 32, 33]: When an infinitesimally small volume fraction ϕ^* of (large) spheres is added to a suspension with original volume fraction ϕ, corresponding to a differential increase in concentration of

$$d\phi = \phi^*(1 - \phi) \qquad (15)$$

then the corresponding differential increase in effective viscosity is

$$d\eta = 2.5\eta\phi^* \qquad (16)$$

This leads to the differential equation

$$\frac{d\eta}{d\phi} = \frac{2.5\eta}{1 - \phi} \qquad (17)$$

which has the solution (Roscoe-Brinkman relation)

$$\eta_r = (1 - \phi)^{-2.5} \qquad (18)$$

For moderately small volume fractions this relation can be approximated by

$$\eta_r = \frac{1}{1 - 2.5\phi} \qquad (19)$$

which has a series expansion of the form

$$\eta_r = 1 + 2.5\phi + 6.25\phi^2 + \dots \qquad (20)$$

Equation (19) is but an alternative representation of Ford's [34] proposal, based on empirical findings, to describe the fluidity (i.e. the reciprocal viscosity) by a linear Einstein-type relation with negative coefficient, cf. [10]. We will therefore call it Ford's relation. Interestingly, the second-order coefficient in this case (6.25) is in remarkably close agreement with Batchelor's value mentioned above (6.2). Note in passing that the Ford relation predicts a locking phenomenon (percolation threshold) at a critical volume fraction of $\phi_c = 0.4$, at which $\eta_r \to \infty$. The Roscoe-Brinkman relation is a candidate for a relation potentially capable of fitting effective viscosity data in the whole concentration range from zero to unity. It exhibits the correct limit behavior, i.e. the relative viscosity relation reduces to the Einstein relation for $\phi \to 0$ and goes to infinity, $\eta_r \to \infty$, as the volume fraction approaches unity $\phi \to 1$. Another possiblility to derive the Roscoe-Brinkman relation (via the functional equation approach) will be given below.

Functional equation approach

The so-called functional equation approach consists in the following: The total solids volume fraction ϕ in the suspension (liquid-solid mixture) is subdivided, in a thought experiment, into two partial volume fractions, ϕ_1 and ϕ_2, not necessarily small, which are (one after the other) added to the suspending medium (pure liquid). These two virtual partial volume fractions are

$$\phi_1 = \frac{V_1}{V_0 + V_1 + V_2} \qquad (21)$$

and

$$\phi_2 = \frac{V_2}{V_0 + V_1 + V_2} \qquad (22)$$

where V_0, V_1 and V_2 are the partial volumes of the suspending medium, the first virtual partial volume of particles and the second virtual partial volume of particles,

respectively. Thus the total volume fraction of solid particles is

$$\phi = \phi_1 + \phi_2 = \frac{V_1 + V_2}{V_0 + V_1 + V_2} \qquad (23)$$

as required. Since it is evident that the relative viscosity cannot be an additive function of the partial volume fractions[1],

$$\eta_r = \eta_r(\phi) = \eta_r(\phi_1 + \phi_2) = \eta_r(\phi_1) + \eta_r(\phi_2) \qquad (24)$$

it is reasonable to assume a multiplicative decomposition,

$$\eta_r = \eta_r(\phi) = \eta_r(\phi_1 + \phi_2) = \eta_r(\phi_1) \cdot \eta_r(\phi_2) \qquad (25)$$

which tantamounts to a additive decomposition of the logarithms, i.e.

$$\ln \eta_r = \ln \eta_r(\phi) = \ln \eta_r(\phi_1 + \phi_2) = \ln \eta_r(\phi_1) + \ln \eta_r(\phi_2) \qquad (26)$$

This is the functional equation of an exponential function [35]. Its solution is the Arrhenius relation [9]

$$\eta_r = e^{B\phi} \qquad (27)$$

The Arrhenius relation, although potentially capable of predicting the correct behavior in the dilute limit (i.e. for $\phi \to 0$) by choosing e.g. $B = 2.5$ for spheres, has again the serious disadvantage that in the high-concentration limit (i.e. for $\phi \to 1$) the relative viscosity does not approach infinity ($\eta_r \to \infty$) as required. In the following we will show, how the simple exponential relation can be modified in order to exhibit correct behavior in the high-concentration limit. For this purpose we refine the thought experiment introduced above to allow for the fact that, when the first virtual fraction ϕ_1 is to be given by equation (21) after mixing (i.e. when the second fraction is already present), then the actual first fraction, corresponding to the amount to be added, is

$$\phi_{12} = \frac{\phi_1}{1 - \phi_2} = \frac{V_1}{V_0 + V_1} \qquad (28)$$

i.e. more than ϕ_1. Similarly, if the second virtual fraction ϕ_2 is to be given by equation (22) after mixing, then the actual second fraction, corresponding to the amount to be added, is

$$\phi_{21} = \frac{\phi_2}{1 - \phi_1} = \frac{V_2}{V_0 + V_2} \qquad (29)$$

i.e. more than ϕ_2. The reason is simply that the presence of the one fraction already present reduces the relative content of the fraction added in the mixture as a whole. From this point onwards, however, two lines of argumentation are thinkable. Both occur in the literature.

1. It may be argued that, what holds true for the first fraction, must be valid simultaneously for the second fraction. This line of argumentation leads to Mooney-type exponential relations [36]. The corresponding functional equation is

$$\eta_r = (\phi_1 + \phi_2) = \eta_r(\phi_{12}) \cdot \eta_r(\phi_{21}) \qquad (30)$$

and it can easily be verified that the exponential expression

$$\eta_r = \exp \frac{B\phi}{1 - \phi} \qquad (31)$$

is a solution of this functional equation.

2. Alternatively, it may be argued that the modification holds only for one of the volume fractions at one time. This line of argumentation leads to Krieger-type power law relations [37]. The corresponding functional equation is

$$\eta_r = (\phi_1 + \phi_2) = \eta_r(\phi_1) \cdot \eta_r(\phi_{21}) = \eta_r(\phi_{12}) \cdot \eta_r(\phi_2) \qquad (32)$$

and it can easily be verified that the power-law expression

$$\eta_r = (1 - \phi)^{-B} \qquad (33)$$

is a solution of this functional equation.

For both types of relation agreement with the Einstein relation in the dilute limit can be achieved by choosing $B = 2.5$ for spheres. Both types of relation avoid the serious drawback of the Arrhenius relation, i.e. they make sure that $\eta_r \to \infty$ for $\phi \to 1$. Both types of relations are frequently used. Nevertheless, we think there is one reason to prefer (Krieger-type) power law relations to (Mooney-type) exponential relations. This reason is as follows: It is evident that in the derivation of the Arrhenius relation above the sum of the virtual partial volume fractions used is

$$\frac{V_1}{V_0 + V_1 + V_2} + \frac{V_2}{V_0 + V_1 + V_2} = \frac{V_1 + V_2}{V_0 + V_1 + V_2} \qquad (34)$$

i.e. corresponds exactly to the actual total volume fraction in the suspension. This is not the case in the derivation leading to the Mooney-type relation and the Krieger-type relation. In these cases we have

$$\frac{V_1}{V_0 + V_1} + \frac{V_2}{V_0 + V_2} = \frac{V_0 V_1 + V_0 V_2 + 2 V_1 V_2}{V_0^2 + V_0 V_1 + V_0 V_2 + V_1 V_2} \qquad (35)$$

and

$$\frac{V_1}{V_0 + V_1 + V_2} + \frac{V_2}{V_0 + V_2} = \frac{V_0 V_1 + V_0 V_2 + 2 V_1 V_2 + V_2^2}{V_0^2 + V_0 V_1 + 2 V_0 V_2 + V_1 V_2 + V_2^2} \qquad (36)$$

for the Mooney-approach and the Krieger-approach, respectively. In order to compare the individual sums of volume fractions we consider the limits $\phi \to 0$ and $\phi \to 1$ or, more precisely, the limits $V_1, V_2 << V_0$ and $V_1, V_2 >> V_0$, respectively.

We obtain

$$\phi_1 + \phi_2 \approx 0$$
$$\phi_{12} + \phi_{21} \approx 0$$
$$\phi_1 + \phi_{21} \approx 0 \qquad (37)$$

in the limit $V_1, V_2 << V_0$ and

$$\phi_1 + \phi_2 \approx 1$$
$$\phi_{12} + \phi_{21} \approx 2$$
$$1 \le \phi_1 + \phi_{21} \le 2 \qquad (38)$$

in the limit $V_1, V_2 >> V_0$ for the Arrhenius relation, the Mooney-type relation and the Krieger-type relation, respectively. It can be seen that the argumentation leading to the Mooney-type relation is based on a virtual decomposition of the volume fractions which in the high-concentration limit leads in any case to the unphysical result that the total volume fraction ϕ is 2, while the Krieger-type relation is based on a decomposition, which at least allows the total volume fraction to be approx. 1 (viz. in the case $V_2 >> V_1$). The value of $\phi = 1$ is of course the maximum value admissible on physical grounds. This should be a principal reason to prefer Krieger-type relations for prediction and fitting purposes.

Effective viscosity relations with critical volume fraction

Experience shows, that solid volume fractions approaching unity ($\phi \approx 1$) are never attained in real suspensions. The reason is that for rigid particles there exists a critical volume fraction ϕ_C (also called maximum packing fraction or filling factor), which cannot be exceeded. That means, when this factor is attained, a suspension looses the capability of flow (locking phenomenon). In terms of percolation theory [38] the critical volume fraction can be interpreted as a percolation threshold. The exact value of this critical volume fraction ϕ_C depends on the particle shape, the degree of polydispersity (i.e. the width of the size distribution) and on the structural type of particle arrangement. For monodisperse spheres the value of ϕ_C is bounded from below by the filling factor of simple cubic (SC) packing ($\phi_C = 0.524$) and from above by the filling factor of face centered cubic (FCC) packing or hexagonal closest packing (HCP), for which $\phi_C = 0.741$. Traditionally, a filling factor of $\phi_C = 0.637$ has been assumed for so-called random close packing (RCP) [39]. According to newer research [40] this value seems to be slightly higher, viz. $\phi_C = 0.644$, but for most purposes $\phi_C = 0.64$ should give a sufficiently precise estimate for the critical volume fraction of monodisperse spheres. Note that the maximum packing fraction can be significantly higher for anisometric particles. E.g. ordered stacks of monodisperse penny-shaped particles (i.e. circular discs) can attain a value as high as $\phi_C = 0.907$. With increasing polydispersity (i.e. growing width of the size distribution) the maximum packing fraction is always higher than for monodisperse systems.

In order to account for the maximum packing fraction it is useful to include the critical volume fraction ϕ_C into the Mooney- and Krieger-type relations. Mooney and Krieger did this already in their original papers [36,37]. Using the functional equation approach explained above with the newly defined quantities

$$\phi_{12}' = \frac{\phi_1}{1 - \phi_2/\phi_C} \qquad (39)$$

and

$$\phi_{21}' = \frac{\phi_2}{1 - \phi_1/\phi_C} \qquad (40)$$

one obtains the Mooney relation [36]

$$\eta_r = \exp\left(\frac{B\phi}{1 - \phi/\phi_C}\right) \qquad (41)$$

and the Krieger relation [37]

$$\eta_r = (1 - \phi/\phi_C)^{-B\phi_C} \qquad (42)$$

As the case may be, these two relations can be considered as model equations for the prediction of the effective viscosity of suspensions with monodisperse spheres (in this case set $B = 2.5$ and $\phi_C = 0.64$) or as fit equations with one (ϕ_C) or two (ϕ_C and B) fit parameters. Both the Mooney relation and the Krieger relation exhibit correct limit behavior, i.e. the relative viscosity relation reduces to the Einstein relation for $\phi \to 0$ and goes to infinity, $\eta_r \to \infty$, as the volume fraction approaches $\phi \to \phi_C$, as required.

It can now be asked what is the simplest model (or fit equation) allowing for a critical volume fraction (or percolation threshold) ϕ_C. It is the Robinson relation [41]

$$\eta_r = 1 + B\left(\frac{\phi}{1 - \phi/\phi_C}\right) \qquad (43)$$

which can be recognized as the linear (first-order) approximation to the Mooney relation (i.e. a truncated series expansion of the Mooney relation). In this connection the well-known Eilers relation [42]

$$\eta_r = \left[1 + \tfrac{1}{2} B\left(\frac{\phi}{1 - \phi/\phi_C}\right)\right]^2 \qquad (44)$$

can be considered as a binomial reducing to the Robinson relation for moderately small ϕ. Note that the Eilers relation is at the same time identical with the so-called Maron-Pierce relation [43],

$$\eta_r = (1 - \phi/\phi_C)^{-2} \qquad (45)$$

which can be considered as a special case of the Krieger relation, when we set $B\phi_C = 2$. In practice the Maron-Pierce relation, i.e. the Eilers relation, can be used for

fitting purposes instead of the Krieger relation when a two-parameter fit is to be avoided and the parameter B is not known (for non-spherical particles). Kitano et al. [44] used the Maron-Pierce relation for data fitting. Based on experiments concerning polymer melts filled with fibers they found an approximately linear relation between ϕ_C and the fiber aspect ratio R (relevant range of R : 6-27):

$$\phi_C = 0.54 - 0.0125 \cdot R \qquad (46)$$

Although this is a purely empirical finding, it is often used and seems to serve quite well for prediction purposes, when a rough estimate of the effective viscosity of fiber suspensions is required and an alternative is not in sight. Similar to the relations of Mooney and Krieger, also the relations due to Robinson and Eilers (or Maron-Pierce) exhibit correct limit behavior, i.e. the relative viscosity relation reduces to the Einstein relation for $\phi \to 0$ and goes to infinity, $\eta_r \to \infty$, as the volume fraction approaches $\phi \to \phi_C$.

This is not the case for the Frankel-Acrivos relation [45], here in the amended version proposed by van den Brule and Jongschaap [46]:

$$\eta_r = 1 + (9/8)\,\phi_C\left(\frac{(\phi/\phi_C)^{1/3}}{1 - (\phi/\phi_C)^{1/3}}\right) \qquad (47)$$

This relation, although it has the advantage of being rigorously derived for the high-concentration region (close to the critical volume fraction ϕ_C), and containing only one adjustable parameter (ϕ_C) when used as a fit equation, has the drawback, that it does not reduce to the Einstein equation in the dilute limit. To overcome this drawback the Frankel-Acrivos relation for rigid-sphere suspensions can be modified as follows:

$$\eta_r = 1 + [\,\phi/\phi_C + (20/9) \cdot (1 - \phi/\phi_C) \cdot (\phi/\phi_C)^{2/3}\,] \cdot$$
$$\cdot (9/8) \cdot \phi_C\left(\frac{(\phi/\phi_C)^{1/3}}{1 - (\phi/\phi_C)^{1/3}}\right) \qquad (48)$$

This modified version of the Frankel-Acrivos relation does reduce to the Einstein relation in the dilute limit and can thus potentially be used in the whole concentration range from $\phi = 0$ to $\phi = \phi_C$.

assumptions are often not fulfilled. But in the absense of a better alternative, these assumptions are often adopted. Naturally, the violation of these fundamental assumptions has less severe consequences when the relations of suspension rheology (effective viscosity formulae) are used for fitting purposes only. Although a certain qualitative specification of the type of microstructure is given by the fact that suspensions are mixtures with matrix-inclusion type microstructure (solid particles in a liquid medium), it is clear that the solids volume fraction alone is not a sufficient microstructural measure. But even in cases when microstructural features other than the volume fraction come into play (e.g. particle size distribution, particle shape, structural type of particle arrangement), the relations of suspension rheology can be useful. In a primitive way e.g., particle shape information is contained in the Einstein coefficient, which is 2.5 for spheres but attains other values for anisometric particles. Similarly, some rudimentary information on particle size distribution and / or arrangement is contained in the critical volume fraction ϕ_C.

In this paper, the most important effective viscosity formulae for rigid-sphere suspensions (Einstein relation, second-order expressions, Roscoe-Brinkman relation, Ford relation, Arrhenius relation, Mooney relation, Krieger relation, Robinson relation, Eilers or Maron-Pierce relation, Frankel-Acrivos relation) are presented in a unified way, which clarifies their mathematical status and corrects certain misunderstandings prevailing in the literature. It has been shown that the Einstein relation must be used as a benchmark test for the dilute limit (i.e. all relation are required to reduce to the Einstein relation when $\phi \to 0$) and in the high concentration limit it must be required that $\eta_r \to \infty$ as the volume fraction approaches unity ($\phi \to 1$) or a critical volume fraction (percolation threshold) ($\phi \to \phi_C$). Exponential and power law relations have been derived by the functional equation approach. An argument has been provided why the Krieger relation is to be preferred to the Mooney relation for principal reasons. The so-called Frankel-Acrivos relation has been appropriately modified and amended in order to be potentially usable in the whole concentration range from $\phi = 0$ to $\phi = \phi_C$.

CONCLUSIONS

The basic assumptions of suspension rheology (existence of Newtonian viscosity, sufficience of the volume fraction as a microstructural measure, uniqueness of the volume fraction dependence of effective viscosity) have been scrutinized and discussed from the viewpoint of rational mechanics and micromechanics. It must be admitted that for real suspensions these

Notation:

[1] If this was true, the relative viscosity of a suspension (mixture), in which only negligible amounts of particles have been added (i.e. $\phi_1 \approx 0$ and $\phi_2 \approx 0$) would be 2, which is a contradiction in itself.

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ÚVAHY O ZÁKLADECH REOLOGIE SUSPENZÍ

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V této práci jsou základní předpoklady reologie suspenzí (existence Newtonské viskozity a závislost efektivní viskozity na objemové frakce pevné fáze) diskutovány z hlediska racionální mechaniky a mikromechaniky. Nejdůležitější vztahy pro popis závislosti efektivní viskozity na objemové frakci pevné fáze jsou zde prezentovány novým způsobem, který objasňuje jejich matematickou podstatu a ukazuje na formální souvislosti těchto vztahů. Jasně jsou rozlišeny exponenciální a mocninové vztahy, které jsou zde odvozeny z tzv. funcionálních rovnic. Práce poskytuje argument, proč by se měly mocninové vztahy preferovat z principiálního hlediska. Pro vztah Frankela a Acrivose je navržena modifikace, která odstraňuje nedostatek původního vztahu a je aplikovatelná i v případě zředěných suspenzí.