The Einstein coefficient of suspensions in generalized Newtonian liquids\textsuperscript{a)}

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Synopsis

A new, theoretically more satisfactory, definition for relative viscosities of suspensions in generalized Newtonian media is presented, which according to the viscosities of suspensions and pure liquids should be compared to equal averaged squared strain rates $\bar{\gamma}^2$ in the liquid phases. Comparison of this quantity ($\eta_0^f$) is made with two definitions currently in use, in which viscosities are compared either at equal macroscopic stresses $\tau$ or at equal macroscopic squared strain rates $\dot{\gamma}^2$. Interrelations between the three different relative viscosities have been derived in the case of dilute suspensions of particles of arbitrary shape in generalized Newtonian liquids. Values for limiting viscosity numbers (Einstein coefficients $K_E$) have been derived from experimental data on suspension viscosities both as obtained by the authors and as obtained from other sources. The data cover suspensions of spherical particles in liquids with power-law exponents $n$ between 0.07 and 1.0. According to the new definition the Einstein viscosity coefficient $K_E = \lim_{\gamma \to 0} (d \ln \eta)/(d\gamma)$ is constant with a value of 2.5 over the whole range of $n$. According to the other definitions, $K_E$ is 2.5 only for $n = 1$; with $n$ decreasing to zero, $K_E$ decreases linearly to 0.75 (under equal strain rate) or rises exponentially to $\infty$ (under equal strain stress). The values of $K_E$, as deduced from experiments, obey the theoretical interrelations derived. There are strong indications that the value of $n$ has no influence on the inhomogeneity in rate of strain in dilute suspensions.

I. INTRODUCTION

The rheology of suspensions in non-Newtonian media is, from a technological point of view, even more interesting than its counterpart

\textsuperscript{a)}Dedicated to Prof. Dr. H. Janeschitz-Kriegl on the occasion of his 67th birthday.

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with Newtonian media. Important industrial applications are in the processing of filled polymers, "technical ceramic" pastes, and drilling muds for oil recovery. Theoretical analyses, be it nonrigorous, of these flow problems are only available for high volume fractions, where particle-particle lubrication hydrodynamics dominate the particle-fluid interactions.

One of the major problems in developing such rigorous theories is the nonlinearity of the viscous contribution in the Navier-Stokes equation. Apparently research efforts in the area of suspension rheology at present are focused mainly in the rheology of highly filled suspensions in Newtonian media; rather accurate predictions are now available for simple shear flow of hard spheres both at high and low Peclet numbers (Pe). This complements the numerous publications on the rheology of dilute suspensions in Newtonian media. First, Einstein published his classical result: $K_E = 2.5$ with $K_E = \lim_{\phi \to 0} \left[ \eta_r - 1 \right] / \phi$, where $\eta_r$ is the relative viscosity and $\phi$ is the volume fraction of spherical particles as dispersed phase. In the last three decades many studies have been published on deviations of $K_E$ from 2.5, e.g., due to electrostatic interactions.

Experimental results of the suspension rheology with non-Newtonian media is mainly restricted to high Pe numbers, i.e., with (almost) negligible Brownian motion. This is due to the fact that in most industrial applications the particles are relatively large and because mixing of small particles (< 1 µm) with pseudoplastic liquids is impossible in most cases without degrading the liquid (excessive shear rates and viscous heating).

A difficulty in evaluating relative viscosities $\eta_r = \eta_{\text{susp}} / \eta_{\text{liq}}$ in such systems is in defining what circumstances in suspension and in pure liquid should be kept equal. Experimental data in this field are mainly interpreted in terms of relative viscosities while taking the macroscopic shear rates or shear stresses equal. We will denote these quantities with $\eta_r^p$ and $\eta_r^f$. The quantity $\eta_r^f$ was inspired by the time-temperature superposition method employed in polymer rheology when comparing data taken at different temperatures. In such a way these pseudoplastic viscosities can be better compared. A logical but until now unexploited method compares viscosities of suspension and pure liquid while their liquid phase viscosities are equal. This method will be evaluated in the present paper.

The precise definition of $\eta_r$ has a large influence on its value as is evident, e.g., from the value of the Einstein viscosity coefficient $K_E = \lim_{\phi \to 0} \left[ \eta_r - 1 \right] / \phi$, where $\phi$ is the volume fraction of the filler par.
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Published experimental results\(^{14-16}\) indicate that \(K'_E\) (i.e., \(K_E\) using \(\eta_r\)) is approximately \(\frac{3}{2}n\) where \(n = \frac{d(\ln r)}{d(\ln \varphi)}\); \(K'_E\) is equal or slightly larger than 2.5.

The Einstein coefficient is a tool for studying the effects of the definition of \(\eta_r\) on its quantitative value. A disadvantage of this tool is that experimental data are only useful if they are very accurate (see also Sec. IV). However, it has an important advantage as well, which is related to the difficulty in obtaining monosized particles of a size large enough both to neglect the influence of electrical double layers on the suspension viscosity and to be able to mix the particles into the fluid. The almost inevitable polydispersity of such particles has considerable influence on the suspension viscosity at high volume fractions of solids. However, it has no influence on the value of the Einstein coefficient, because particle interactions are absent under \(\varphi \rightarrow 0\) conditions and because \(K_E\) is, in principle, independent of the particle radius.

In Sec. II A we will propose a new definition of \(\eta_r\) which is much more satisfactory from a theoretical point of view than the former two. In Sec. II B we calculate the relationship between the macroscopically applied strain rate and the local one in the Newtonian liquid phase of a dilute suspension; we also derive to what extent the latter one is different from the strain rate in the pure liquid when evaluating \(\eta_r\) according to the three definitions. In Sec. II C we show how to calculate these three relative viscosities for dilute suspensions in generalized Newtonian media. In Sec. II D we indicate how to cross section a diagram of a collection of flow curves in order to calculate the three types of relative viscosity. We demonstrate the inhomogeneity of strain rates in the liquid phase of a dispersion to be independent of the degree of pseudoplasticity. Experimental results with suspension systems described in Sec. III and as taken from the literature are analyzed; Einstein coefficients according to the different definitions are evaluated in Sec. IV.

II. THEORY OF THE RELATIVE VISCOITY OF SUSPENSIONS

A. General

For the derivation of Einstein's law of the relative viscosity of suspensions two approaches appear to exist in literature, the original one by Einstein (see also his book on this subject)\(^{17}\) and the one described by Landau and Lifshitz.\(^{18}\) The original one best suits our purpose.

The starting point of this section is the notion that a comparison of
the viscosities of a liquid and a suspension of that liquid can be made under circumstances that the liquid viscosity in both systems is the same.

In this study we describe suspensions of particles in non-Newtonian, nonelastic liquids ("generalized Newtonian liquids"\textsuperscript{19}). These liquids obey

\[ \tau = -\eta \dot{\gamma}, \quad (1) \]

where \(\tau\) and \(\dot{\gamma}\) are the deviatoric stress and the rate of strain tensors and where the viscosity function \(\eta\) is a function of the second invariant or the "magnitude" \(\dot{\gamma}\) of the rate of strain tensor only:

\[ \dot{\gamma}^2 = [\dot{\gamma} \cdot \dot{\gamma}] / 2, \quad (2) \]

where \(\dot{\gamma} = \nabla v + [\nabla v]^\dagger\), \(\nabla v\) being the dyadic product of the liquid velocity \(v\) and of \(\nabla = \sum_i (\partial / \partial x_i)\).

In this study we exclude special suspension flow effects arising from Brownian motion of the particles (inducing pseudoplasticity\textsuperscript{20}) and from a competition of hydrodynamic forces with long range repulsive forces on the particles (inducing viscosity dilatancy\textsuperscript{21}).

**B. Dilute suspensions in Newtonian media**

If one sphere (volume \(V^r\)) is placed in a very extended Newtonian liquid (total volume \(V\)) which is subjected to simple shear then the average rate of dissipation per volume of the dispersion \(\dot{\omega}\) will be

\[ \dot{\omega} = \gamma_{0,\infty}^2 \eta_0 \left[ 1 + \frac{V^r}{2V} \right], \quad (3) \]

where \(\gamma_{0,\infty}\) is the undisturbed shear rate (at infinite distance to the sphere) and \(\eta_0\) is the viscosity of the liquid phase. Because in very dilute suspensions the areas of flow disturbances of individual spheres are far apart, their effects on \(\dot{\omega}\) are additive, giving

\[ \dot{\omega} = \gamma_{0,\infty}^2 \eta_0 [1 + \phi / 2]. \quad (4) \]

For suspensions it is also possible to write

\[ \dot{\omega} = \eta_s \dot{\gamma}_m^2 \quad (5) \]

where \(\eta_s\) and \(\dot{\gamma}_m\) are the macroscopically measurable suspension viscosity and suspension strain rate, respectively.

It can be shown\textsuperscript{17} that
in which $\varphi$ denotes the volume fraction of the dispersed phase. Substitution of Eq. (6) into Eq. (4) and comparing the result with Eq. (5) gives Einstein's law for suspension viscosity (first order in $\varphi$):

$$\eta_s = \eta_0 = 1 + \frac{1}{2} \varphi.$$  

In reality dissipation in a suspension is confined to the volume occupied by the liquid, thus the intensity of the rate of dissipation $\dot{\omega}$, in a suspension volume $V$, can be written as

$$\dot{\omega} = \frac{\eta_0}{V} \int_{[1 - \varphi] V} \dot{\gamma}^2(r) dV(r) = \eta_0 [1 - \varphi] \dot{\gamma}^2_L,$$

where $\dot{\gamma}^2_L$ stands for the square of the strain rate as averaged over the liquid phase. Comparing Eqs. (8) and (5) and eliminating $\eta_s$ with the aid of Eq. (7) gives

$$\dot{\gamma}^2_L = \dot{\gamma}^2_m [1 + \frac{1}{2} \varphi].$$

Equation (9) indicates that the determination of $\eta_s$, while keeping the macroscopic strain rates in suspension ($s$) and in pure liquid ($p$) equal, involves different average liquid strain rates according to

$$\frac{\dot{\gamma}^2_L}{\dot{\gamma}^2_L} = 1 + \frac{1}{2} \varphi.$$  

The alternative, used by Kataoka et al.,$^{14}$ i.e., keeping the shear stresses equal in a determination of $\eta_s$, means that

$$\frac{\dot{\gamma}^2_L}{\dot{\gamma}^2_L} = 1 - \frac{1}{2} \varphi.$$  

In view of our starting point (Sec. II A) the latter method is debatable as an objective definition of $\eta_s$ of non-Newtonian suspensions.

C. Dilute suspensions in generalized Newtonian liquid media

1. Relative viscosity at equal averaged squared strain rates in the liquid phases

Also with generalized Newtonian liquids a single sphere in an extended liquid phase will disturb the local flow field increasing the averaged strain rate in the liquid phase, if the macroscopic deformation rate is kept constant. For a specific flow rate (indicated with index 1) in the dilute suspension in a generalized Newtonian liquid, we can in similarity to Eq. (4), formally write
\[ \dot{\omega} = \gamma_{m}^{2} \eta_{0}(\gamma^{2} = \gamma_{L,1}^{2}) [1 + f \varphi/2], \]

where \( [\gamma_{L,1}^{2}]^{1/2} \) is a specific average value of the strain rates in the liquid phase, the exact way of averaging to be defined later. Parentheses ( ) indicate that the quantity concerned, e.g., \( \eta_{0} \), is a function of the parameter concerned, e.g., \( \eta_{0}(\gamma^{2}) \). Note that \( \eta_{0} \) is the local viscosity of the liquid phase, its value being defined [see Eqs. (1) and (2)] by the local squared strain rate \( \gamma^{2} \). However, the viscosity of a suspension can be defined as a function of either of two types of squared strain rates: \( \gamma_{m}^{2} \) or \( \gamma_{L}^{2} \). We will use either of them, where appropriate.

In Eq. (12) any deviation of \( f \) from unity accounts for the fact that the flow profile around the sphere is different from that in the Newtonian liquid case as well as for the fact that the liquid viscosity is not \( \eta_{0}(\gamma_{L,1}^{2}) \) at any location. In the case of a power-law liquid we could write \( f(n) \) where \( n \) is the power-law exponent. The exact value of \( f \) will of course depend on how \( \gamma_{L,1}^{2} \) is averaged.

In an analogous way Eq. (6) can be adjusted to the present case:

\[ \dot{\gamma}_{m} = \dot{\gamma}_{\infty} [1 - g \varphi], \]

where \( g \) may be unequal to unity, accounting for the fact that Eq. (6) may be invalid in case of a non-Newtonian liquid medium. Additionally, Eq. (5) in the non-Newtonian case reads

\[ \dot{\omega} = \eta_{0}(\gamma_{m}^{2} = \gamma_{m,1}^{2}) \gamma_{m,1}^{2}. \]

Combination of Eqs. (12), (13), and (14) gives

\[ \frac{n_{s}(\gamma_{m}^{2} = \gamma_{m,1}^{2})}{\eta_{0}(\gamma^{2} = \gamma_{L,1}^{2})} = 1 + [2g + f/2] \varphi = 1 + h \varphi. \]

The left-hand side of Eq. (15) can be interpreted as the relative viscosity of a dilute suspension while keeping the strain rates in the liquid phases (averaged in a way still to be defined) equal:

\[ \eta_{r}^{L} = \frac{n_{s}(\gamma_{L}^{2} = \gamma_{L,1}^{2})}{\eta_{0}(\gamma^{2} = \gamma_{L,1}^{2})}, \]

\[ \eta_{r}^{L} = \frac{n_{s}(\gamma_{m}^{2} = \gamma_{m,1}^{2})}{\eta_{0}(\gamma^{2} = \gamma_{L,1}^{2})}. \]

Because in the remaining of the present paper \( f \) and \( g \) would appear always in the same combination we introduce \( h = [2g + f/2] \). The quantity \( h \) can be seen as the Einstein coefficient at that average squared liquid strain rate: \( K_{E}^{L} = h. \)
The dissipation is confined to the liquid phase. The intensity of dissipation as averaged over the whole suspension, can be written in analogy to Eq. (8):

$$\dot{\omega} = \frac{1}{V} \int_{[1-\varphi]V} \eta_0[I^2(r)] \dot{\gamma}^2(r) dV(r) = [1 - \varphi] \eta_0(I^2(L_1)) \dot{\gamma}^2(L_1).$$

(17)

where the bar indicates averaging over the liquid phase. In a way analogous to that employed by Fowler and Guggenheim in the description of strictly regular solutions we define $\gamma_L$ introduced in Eq. (12) according to

$$\eta_0(\gamma_L) \dot{\gamma}_L = \eta_0(\gamma_L^2) \dot{\gamma}_L^2.$$  

(18)

In this way Eq. (17) can be converted into

$$\dot{\omega} = [1 - \varphi] \eta_0(\gamma_L) \dot{\gamma}_L.$$  

(19)

Equating Eqs. (14) and (19), with $\eta_L$ defined in Eq. (16), we arrive at

$$\eta_L = [1 - \varphi] \frac{\dot{\gamma}_L}{\dot{\gamma}_{mL}}.$$  

(20)

Inspection of Eqs. (15) and (20) shows that calculation of the Einstein coefficient $K_E$ requires knowledge of $\dot{\gamma}_m$ in terms of $\dot{\gamma}_L$. For this purpose we define $n$ as the local slope of the non-Newtonian flow curve (log $\tau$ versus log $\dot{\gamma}$). We assume that $\tau(\dot{\gamma})$ is a continuous function of $\dot{\gamma}$, which can be differentiated to first order. This implies that the non-Newtonian behavior of the suspension can, in a small range of strain rates, be represented with a power-law behavior $\tau = k \dot{\gamma}^n$, where, in principle, the exponent $n$ may still be a function of $\varphi$ and of $\dot{\gamma}$. This linearization is allowed because in determining $K_E$ we are only interested in $\varphi - \dot{\gamma}$ at which only small variations in mean strain rates occur (i.e., $[\dot{\gamma}^2_{mL}/\dot{\gamma}^2_L] \rightarrow 1$).

In the Appendix we demonstrate that, provided the liquid medium is a power-law liquid, adding particles does not change the power-law exponent of the suspension (even at higher $\varphi$), but only its power-law index (the "consistency index"). This implies that, in case of a generalized Newtonian liquid medium, dilute suspensions have the same local flow curve slope $n(\dot{\gamma}) = d[\ln \tau(\dot{\gamma})]/d[\ln \dot{\gamma}]$ as the liquid medium has.
For dilute suspensions with "local" power-law behavior \( \eta(\dot{\gamma}_m^2) = k[\dot{\gamma}_m^2(n - 1)/2] \) we can evaluate the values of \( \eta \) at \( \dot{\gamma}_m^2 = \dot{\gamma}_{L,1}^2 \) and \( \dot{\gamma}_m^2 = \dot{\gamma}_{m,1}^2 \). Elimination of \( k \) in these expressions for \( \eta \) results in

\[
\frac{\dot{\gamma}_{L,1}^2}{\dot{\gamma}_{m,1}^2} = \left[ \frac{\eta_s(\dot{\gamma}_m^2 = \dot{\gamma}_{L,1}^2)}{\eta_s(\dot{\gamma}_m^2 = \dot{\gamma}_{m,1}^2)} \right]^{2/(n - 1)}.
\]

Elimination of \( \eta_s(\dot{\gamma}_m^2 = \dot{\gamma}_{m,1}^2) \) in Eqs. (20) and (21) gives

\[
\frac{\dot{\gamma}_{L,1}^2}{\dot{\gamma}_{m,1}^2} = \left[ \frac{\eta_s(\dot{\gamma}_m^2 = \dot{\gamma}_{L,1}^2)}{\eta_0(\dot{\gamma}_m^2 = \dot{\gamma}_{L,1}^2)[1 - \varphi]} \right]^{2/(n + 1)} \left( \frac{\eta_s(\dot{\gamma}_m^2 = \dot{\gamma}_{m,1}^2)}{[1 - \varphi]} \right)^{2/(n + 1)}.
\]

where \( \eta''_s \) is the relative viscosity at equal macroscopic strain rates.

We are now able to determine the relative viscosity at constant strain rates in the liquid phases. From flow curves (e.g., measured), at a specific strain rate \( [\dot{\gamma}_{L,1}]^{1/2} \) in the liquid phase, the value of \( \eta''_s \) in Eq. (22) can be evaluated from the distance AB in Fig. 1. At point B the slope of the curve equals \( [1 - n] \), thus Eq. (22) can be solved for \( \dot{\gamma}_{m,1}^2 \). Now the suspension viscosity in Eq. (15) can be evaluated (point C). Thus the Einstein coefficient \( K_E^L = h \) can be calculated.

2. **Relative viscosity at equal macroscopic strain rates**

The relative viscosity under constant macroscopic strain rate conditions can easily be related to the Einstein coefficient \( K_E^L \) by elimination of the strain rates and \( \eta_s(\dot{\gamma}_{L,1}^2) \) in Eqs. (15), (20), and (21). The solution, to first order in \( \varphi \), is

\[
\eta''(\dot{\gamma}_m^2) = 1 + K_E^L \varphi = 1 + \left[ \frac{n - 1}{2} + \frac{n + 1}{2} K_E^L \right] \varphi.
\]

Generally speaking, \( K_E^L \) will be a function of \( n \). For \( n = 1 \), we have \( K_E^L = 5/2 \). Later on we will show experimental evidence of \( K_E^L \approx 5/2 \), independent of \( n \). This implies \( K_E^L(n = 0) \approx 3/4 \).

3. **Relative viscosity at equal macroscopic shear stresses**

In order to calculate the relative viscosity at constant shear stress, from Eq. (23) we derive an equation for the shear stress \( \tau \) in a dilute suspension at a macroscopic simple shear rate \( \dot{\gamma}_1 \):
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FIG. 1. Possible viscous behavior of a suspension in a non-Newtonian liquid. For explanation, see the text.

\[
\tau_s(\dot{\gamma}_m^2 - \dot{\gamma}_1^2) - \{1 + K_E^n\} \tau_0(\dot{\gamma}_1^2),
\]

where \(\tau_0\) represents the shear stress in pure liquid.

In order to modify Eq. (24) into an equation which contains \(\eta_\infty\), the quantity \(\tau_s(\dot{\gamma}_m)\) must be at a shear rate at which \(\tau_s\) is equal to \(\tau_0(\dot{\gamma}_1^2)\). Therefore we seek a shear rate \(\dot{\gamma}_2\) which holds for

\[
\tau_s(\dot{\gamma}_m^2 = \dot{\gamma}_2^2) = \tau_s(\dot{\gamma}_m^2 = \dot{\gamma}_1^2)/\{1 + K_E^n\}.
\]

Because \(\varphi \to 0\), the ratio \(\dot{\gamma}_1/\dot{\gamma}_2 \to 1\); thus a generalized Newtonian liquid medium can in a small range around \(\dot{\gamma}_1\) and \(\dot{\gamma}_2\) be described as a power-law liquid \(\tau = k(\dot{\gamma}^2)^n/2\). Substitution of the latter expression in Eq. (25) gives

\[
\dot{\gamma}_2^2 = \dot{\gamma}_1^2[1 + K_E^n\]^{2/n}.
\]

In analogy to Eq. (21) it can be derived that
By substitution of Eq. (27) in Eq. (26), \( \gamma_2/\gamma_1 \) can be eliminated:

\[
\frac{\eta_s(\gamma_m=\gamma_2)}{\eta_s(\gamma_m=\gamma_1)} = \frac{\gamma_2^{n-1/2}}{\gamma_1^{n-1/2}} = \left[ \frac{\gamma_2}{\gamma_1} \right]^{(n-1)/2}.
\] (27)

With Eq. (28) we can, to first order in \( \varphi \), modify Eq. (24) into an expression for the relative viscosity \( \eta^r \) at constant shear stress:

\[
\eta^r_s = \left[ 1 + K_E^m \varphi \right]^{1/n} = 1 + \left[ \frac{n - 1}{n} + \frac{n + 1}{2n} K_E^L \right] \varphi.
\] (29)

Thus, from Eqs. (23) and (29) we learn the Einstein coefficient at constant stress conditions:

\[
nK_E^r = K_E^m.
\] (30)

Note the similarity of Eq. (30) with equivalent relationships for other viscosity parameters in case of power-law liquids. For the temperature and pressure dependencies of the viscosities of polymer melts (\( \alpha \) and \( \beta \), respectively) identical relationships hold in good approximation:\[^23\]

\[
n\alpha_T = \alpha_m \quad \text{and} \quad n\beta_T = \beta_m.
\] (31)

D. The strain rates

1. How to cross section a diagram of flow curves when evaluating relative viscosities of suspensions in generalized Newtonian media

The condition \( \tau = \) constant of a collection of suspensions with varying \( \varphi \) defines a line with slope \(-1\) in a flow curve diagram (\( \log \eta \) versus \( \log \gamma_m \)). For the case \( n = 1 \) this is shown in Fig. 2.

The case where \( \gamma_m \) is constant is trivial: in a flow curve diagram it represents a vertical cross section.

The slope of the cross section in case of the condition \( \gamma_2^2 = \) constant can, for dilute suspensions, be calculated with the aid of Eqs. (15) and (20):
In the case of non-Newtonian liquids, the slope of the $\dot{\gamma}_L = \text{const}$ line can, at the present state of science, not be calculated on theoretical grounds. However, below we will give experimental evidence that, for a wide range of power exponents ($0.1 < n < 1.0$), the quantity $K_E^L$ is con-
stant with value 2.5, implying the initial (at $\phi \to 0$) slope calculated in
Eq. (32) to have a value of $-10/7$, independent of the power-law
exponent.

2. Local variations of strain rates in dilute suspensions

We will estimate if and to what extent the degree of pseudoplasticity
influences the inhomogeneity in local strain rates in the liquid phase of
a dilute suspension. Generally speaking, the degree to which different
moments of an averaged quantity deviate from each other is an indica-
tion of the inhomogeneity of that quantity (cf. the use of $M_w/M_n$ in
characterizing the polydispersity of a polymer). In a similar way
the quantity $R$ defined by $R + 1 = \frac{\gamma_{L,12}^2}{\gamma_{L,12}}$ is a measure for the inho-
mogeneity of strain rates. Here $\gamma_{L,12}$ is the component of the liquid-
phase rate of strain tensor in the main shear direction. If $\gamma_{L,12}$ is uni-
form (i.e., at $\phi = 0$), then $R = 0$; otherwise $R > 0$.

For a flow field with local flow disturbances (with length scale $l$) the
strain rate $\gamma_{ij}$ on a length scale $\gg l$ is given by

$$\gamma_{ij} = \frac{1}{V} \int_V \gamma_{ij}(r) dV(r).$$

(33)

Applied to suspensions this gives

$$\gamma_{ij} = \frac{1}{V} \int_{[1-\phi)V} \gamma_{ij}(r) dV(r) = [1-\phi] \gamma_{L,ij}.$$  

(34)

where the strain rate average on the right-hand side is the strain rate as
averaged over the liquid phase. Thus we arrive at

$$\gamma_{m} = [1-\phi] \gamma_{L,12}.$$  

(35)

Substitution of Eq. (35) in Eq. (22) leads to

$$R + 1 = \frac{\gamma_{L,12}^2}{\gamma_{L,12}^2} = [(1-\phi)^n \eta_r^{\eta_r}]^{2/(n+1)}.$$  

(36)

Substitution of $\eta_r^{\eta_r}$ from Eq. (23) into Eq. (36) results, to first order in
$\phi$, in

$$R = [K_2^F - 1] \phi.$$  

(37)

With a value $K_2^F = h = 2.5$, independent of $n$, this leads to $dR/dn = 0$.
According to this measure the inhomogeneity of flow rates in a suspen-
TABLE I. Survey of suspension systems analyzed.

<table>
<thead>
<tr>
<th>Suspension system</th>
<th>Liquid phase</th>
<th>Glass spheres diameter/µm</th>
<th>Symbol in Figs. 7–9</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol/water (87/13)</td>
<td>30; 22</td>
<td>△</td>
<td>Laven et al.</td>
<td></td>
</tr>
<tr>
<td>2% PAA/water</td>
<td>36 &lt; d &lt; 50 (80% of vol.)</td>
<td>+</td>
<td>Laven et al.</td>
<td></td>
</tr>
<tr>
<td>2% PEO/water (2 systems)</td>
<td>36 &lt; d &lt; 50 (80% of vol.)</td>
<td>♦ •</td>
<td>Laven et al.</td>
<td></td>
</tr>
<tr>
<td>6.6% PEO/water</td>
<td>4 &lt; d &lt; 44</td>
<td>□</td>
<td>Nicodemo et al.²</td>
<td></td>
</tr>
<tr>
<td>3% SCMC/water (pH = 10.9)</td>
<td>4 &lt; d &lt; 44</td>
<td>+</td>
<td>Nicodemo et al.²</td>
<td></td>
</tr>
<tr>
<td>4.3% PIB/decalin</td>
<td>4 &lt; d &lt; 44</td>
<td>▲</td>
<td>Nicodemo et al.²</td>
<td></td>
</tr>
<tr>
<td>Carbopol 941/water (pH = 7)</td>
<td>53 &lt; d &lt; 65</td>
<td>◊</td>
<td>Jurgens et al.⁵</td>
<td></td>
</tr>
<tr>
<td>Liquid detergents A, B, C, D</td>
<td>53 &lt; d &lt; 65</td>
<td>□ • ▼ ●</td>
<td>Jurgens⁵</td>
<td></td>
</tr>
</tbody>
</table>

*aReference 28.  
*Reference 16.  
*Reference 35.

Dilute shear thinning suspension is only a function of the volume fraction φ and not of the degree of pseudoplasticity of the suspending liquid.

III. EXPERIMENTAL

Three types of suspensions were prepared. In all cases sieved fractions of glass beads were employed. The density of the glass beads used with a glycerol/water mixture and with polyethylene oxide (PEO) solutions was 2.81 x 10³ kg/m³; those used with polyacrylamide (PAA) solutions had a density of 2.83 x 10³ kg/m³. These densities were measured with a Quantachrome Stereopycnometer instrument. Details on the particle sizes are given in Table I.

Three types of liquid media were employed:

(i) A mixture of glycerol ("reinst," ex Merck) and distilled water in a mass ratio 87:13.

(ii) A solution of 2% (mass) PEO (M₆₅ = 5 x 10⁶, ex Janssen Chimica) in distilled water. Solutions were prepared by filling a glass container with very thin layers (less than 1 mm) alternating of PEO powder and of water. This "sandwich" structure was allowed to stand for two days. Subsequent mild stirring resulted in a homogeneous solution. A similar system was prepared again one year later in order to prove that our procedures for the preparation of suspensions and for the
measurement of suspension viscosities are reproducible. Because results with the latter system closely resemble those of the first, only its $K_E$ values will be presented.

(iii) A solution of 2% PAA (Separan AP30-E, ex Dow Chemical) was added to distilled water which was being stirred intensively. Thereafter, the vessel containing the mixture was closed and mildly stirred during 3 h. Finally, the pH was adjusted to $pH = 10$ using KOH; at that pH the viscosity is not sensitive to changes in pH.

All viscosities were measured with a Contraves Rheomat 115 rheometer, equipped with a concentric cylinders geometry (DIN 145).

IV. RESULTS AND DISCUSSION

A. Selection of experimental data

Flow curves of the suspensions outlined in Sec. III are shown in Figs. 3–5. All viscosities have been corrected for inhomogeneity of shear rates in a concentric cylinders geometry. Einstein coefficients have been evaluated both from the results obtained by the authors (Figs. 3–5) and
FIG. 4. Viscosities of suspensions of glass spheres in a 2% solution of PEO in water for a range of volume fractions of the glass particles. The temperature was kept at 293.2 K.

FIG. 5. Viscosities of suspensions of glass spheres in a 2% solution of PAA in water for a range of volume fractions of the glass particles. The temperature was kept at 293.2 K.
evaluated from both the results obtained by the authors (Figs. 3–5) and from a number of published studies that provide data accurate enough for the present purpose. Table I summarizes the suspension systems analyzed. The Einstein coefficients have been calculated under conditions of constant shear stress, constant macroscopic shear rate, and constant averaged squared rate of strain in the liquid phases. Before presenting the results of these evaluations an outline is given of how these results have been obtained and of the considerations involved.

Experimental data of a flow curve may contain systematic errors. Often such errors are most pronounced at one (the lower end) or at both extremes of the range of the variable parameter. In our case the measured shear stress at the lowest shear rates may contain a nonnegligible contribution from an imperfect zero setting of the torque detection system; at high shear rates viscous heating, secondary flow (especially with cone/plate geometry), partial detachment from the test cell wall may lead to systematic errors. In view of these arguments, extreme parameter values were avoided in the final calculations for obtaining relative viscosities: we focused on intermediate values of the variable parameters. In all cases we took the logarithmic value of any specific parameter in such a way that the distance to the low extreme is 3/4 of the available full range (e.g., with shear rates between 0.1 and 1000 s$^{-1}$ the $K_E$ was calculated at 100 s$^{-1}$).

In the selection of viscosity data from the literature the arguments given before appeared to be rather restrictive. The often cited data provided by Kataoka, Kitano, Sasahara, and Nishijima, although being qualified for the application by those authors (relative viscosities at higher volume fractions), were not accurate enough for our purpose (as judged from the scatter of individual points in a $\eta_r$ versus $\varphi$ plot). For a similar reason data from several other sources were not useful to our purpose (e.g., Faulkner and Schmidt; Kitano, Kataoka, and Shirota). With the results by Kataoka et al. an additional problem with some of their suspension systems was that the number of volume fractions investigated was too small for our purpose. For the same reason data from several other sources were not useful (e.g., Sundstrom, Atkins). Insufficient number of volume fractions was also the reason for analyzing only the very accurate data of three of the six suspension systems investigated by Nicodemo, Nicolais, and Landel.

The viscosity law of Einstein holds only for $\varphi$ lower than $\approx 0.05$. The method used to assess the $K_E$ is to employ viscosities of dispersions over a wider range of $\varphi$ and analyzing the slopes at $\varphi = 0$ in $\eta_r$ versus $\varphi$ plots.
B. Data reduction

Drawing the best (curved) line through data points in a plot automatically induces some sort of weighing of the different points, depending on the axes used. In the case of suspension viscosities, there is some evidence that measured viscosities of highly filled suspensions have less relative accuracy than those of low volume fraction suspensions. In view of this and because we focus on low \( \phi \) data, a \( \log(\eta_r) \) or an \( \eta_r^{-1} \) scale along the \( y \) axis in an \( \eta-r \) plot is much better than an \( \eta_r \) scale. This was confirmed by the quality of the fits of curves to the data points. The \( \eta_r^{-1} \) scale appeared to be slightly better than the \( \log(\eta_r) \) scale, except with almost plastic liquid phases where the \( \log(\eta_r) \) scale was slightly better. We will present results obtained with both scales. An additional advantage of both scales but especially of the \( \eta_r^{-1} \) scaling is that the curvature of the \( \eta-\phi \) curves becomes relatively small. This leads to more reliable estimations of the slopes at \( \phi = 0 \).

For fitting a curve to the data points several empirically and theoretically based mathematical descriptions (e.g., Dougherty-Krieger,\(^{29}\) Mooney,\(^{30}\) Maron and Pierce\(^{31}\)) are available which, with suspensions in Newtonian liquids, coincide fairly well with experimental viscosity data points in the higher, but not extremely high \( (\phi > 0.45) \) volume fraction range.\(^{14,15,32}\) Note that possible differences between these relationships at high volume fractions have only a minor influence on our results of \( K_E \) because differences between large \( \eta_r \) values will become small [with \( \log(\eta_r) \) versus \( \phi \) plots] or almost negligible (with \( \eta_r^{-1} \) versus \( \phi \) plots). The results to be presented here were obtained with the Dougherty-Krieger relationship. These results did show a consistency with experiments comparable to what results obtained with the Mooney equation did but slightly better than results obtained with the equation \( \eta_r = a_0 + a_1\phi + a_2\phi^2 \) did.

With a specific suspension system the calculations were carried out in the following way. First, when appropriate, “true” viscosities and shear rates were derived from “apparent” values.\(^{19}\) In order to calculate a viscosity at a prescribed value of, e.g., the shear stress (for evaluating \( K_E \)), the true double logarithmic flow curve involved was linearized locally, using the four closest data points. In that way \( \eta_r-\phi \) data were obtained for the already discussed intermediate values of the parameters \( \tau, \dot{\gamma}_m \) and \( \dot{\gamma}_L \). As an example, in Fig. 6 the three sets of data obtained for the suspensions in PIB/decalin are given.

Having obtained such a set of values [e.g., a set of \( (\phi, \eta_r^T) \)], a specific function [e.g., the Krieger–Dougherty equation \( \eta_r^{-1} = a_0 \) (1
FIG. 6. Logarithmic values of the relative viscosities of suspensions in PIB/decalin as function of the volume fraction of particles at fixed "intermediate" values of \( \tau, \gamma_m \) and \( \gamma_0 \). The curves are fits of the logarithmic Dougherty–Krieger equation to the experimental data.

\( \varphi/a_1, \eta^\circ \) [is fitted to the data, using a downhill-simplex method for nonlinear functions. As an example in Fig. 6 the three fitted Dougherty–Krieger curves are shown. Usually, the quality of such fits was adequate. Note that the data point \((\varphi = 0, \eta_r = 1)\) should, in the calculations, not be taken as a point through which the function \( f \) must pass (which would imply \( a_0 = 1 \) in the function given as an example), irrespective of the quality of the fit; that data point has an experimental uncertainty comparable with those of the other points.

The Einstein coefficient concerned (e.g., \( K_\circ \)) can now simply be derived as \((d\eta_r/d\varphi)_{\varphi=0}\)/\(\eta_r(\varphi = 0)\). The power-law exponent involved was deduced from the local linearization of the flow curve of \( \varphi = 0 \).
C. Discussion of analysis results

The three different Einstein coefficients $K_E$ are given in Figs. 7–9, for all suspension systems investigated. They were calculated both with log $(\eta_r)$ and with $1/\eta_r$ scaling; in cases where the scaling method had considerable effect, the $1/\eta_r$ scaling always led to the higher values of $K_E$.

For the system with power-law exponent $n = 1$ (the liquid medium is a mixture of glycerol and water) all experimental Einstein coefficients are close to the theoretical value 2.5. With pseudoplastic liquid media, the three Einstein coefficients deviate from each other. Within experimental accuracy $K_E$ is independent of the power-law exponent. The
value of $K_E'$ decreases linearly with decreasing $n$, but remains slightly positive ($\sim 0.75$) at $n = 0$. The quantity $k_E'$ remains almost constant at $n$ values down to $\sim 0.5$. However, below $n = 0.5$ its value increases asymptotically with $n$ decreasing to zero.

In order to indicate how the values of $K_E'$ depend on the decision (see Sec. IV A) that $K_E$ should be calculated at intermediate values of $\tau$, $\dot{\gamma}_m$, or $\dot{\gamma}_L$, for three suspension systems results at other values of these parameters are shown as examples in Fig. 10. For all usable values of $\tau$, $\dot{\gamma}_m$, and $\dot{\gamma}_L$, values of $K_E$ are plotted as functions of the "local" power-law exponent. It can be seen, their magnitudes reflect the main trends of Figs. 7-9. The systems with the higher $n$ values show slopes corresponding to those of Figs. 7-9. However, the systems with low $n$ values show

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**FIG. 8.** Einstein coefficients under constant shear stress conditions for all suspension systems, plotted as a function of the power-law exponent. Results for both log($\eta_p$) and $1/\eta_p$ scaling are shown.
slopes different from those of Figs. 7–9, presumably due to the experimental difficulties discussed in Sec. IV A. The unexpected shapes of the curves of the PAA/water suspensions in Fig. 10 possibly are due to the S-shaped flow curves of these suspensions (see Fig. 5). No other systems investigated by us showed either such $K_E - n$ behavior or any S-shaped flow curve.

Equation (29) indicates how the $K_E$ according to the different definitions should depend on $n$ and $h$. The quantity $h$ may itself be a function of $n$. However, Fig. 9 indicates $h = K_E^b$ to be 2.5, independent of $n$ in the range $0.1 < n < 1$. With this value for $h$, in Figs. 7–9 curves are drawn for the theoretical predictions of $K_E$. Within experimental accuracy the experimental data obey the theoretical predictions.
FIG. 10. Curves of Einstein coefficients $K_E$ (high), $K_E$ (middle), and $K_E$ (low) for suspensions in liquid detergent C (left), PAA/water (middle), and PIB/decalin (right); plotted as functions of the "local" power-law exponent. The $K_E$ have been calculated for all attainable values of $\eta$, $\gamma_m$, and $\gamma_L$. The dots on the curve indicate the high shear-rate ends. The dashed curves have been copied from Figs. 7-9.

D. General discussion

In order to be able to handle the subject, we supposed generalized Newtonian behavior, thus neglecting any effect of liquid elasticity. A justification for this may be the experience that many (pseudo) elastic liquids under steady shear flow behave as generalized Newtonian liquids, and that the suspensions were also tested under macroscopically steady conditions (note that this argument is not exact as material elements of the liquid are not under steady flow condition).

Our conclusions about the behavior of $K_E$ and $K_E$ seem to deviate from those of Kataoka et al.\textsuperscript{14} and Jurgens et al.\textsuperscript{16} However, differences can be understood, taking into account that those publications were
focused on the description of the viscosity over a wide range in \( \varphi \) but not at \( \varphi \rightarrow 0 \). Kataoka et al. claim that the \( \varphi \) dependence of \( \eta^\text{e} \) for all their data together can be described both with the equation of Dougherty-Krieger (with initial slope 2.5) and that of Maron-Pierce (with adjusted initial slope 3.1), which would suggest the corresponding \( K_E^\tau \) values to be on an average somewhat higher than 2.5. As the power-law exponents in those cases were between \( \sim 0.45 \) and \( \sim 0.7 \), their finding is not contradictory to our conclusion. Additionally, careful inspection of their data indicates considerable scatter in \( K_E^\tau \) values for the individual suspension systems; this reduces the value of those results as an independent check of our conclusions. Jurgens et al.\(^{16} \) found a modified Krieger-Dougherty equation for \( \eta^m \), adapted to the pseudoplastic nature of the liquid, from which can be derived \( \lim_{\varphi \rightarrow 0}(K_E^\tau) = 0 \). This is slightly different from our finding that \( \lim_{\varphi \rightarrow 0}(K_E^\tau) = 0.75 \). However their Fig. 2 indicates that they tested their model mainly with the viscosity behavior of suspensions at larger volume fractions; thus the conclusion about \( K_E^\tau \) as drawn from their results should only be seen as a rough estimate.

A rigorous theoretical treatment of suspensions in non-Newtonian liquids seems not to exist. Existing, less rigorous, treatments are not applicable in the \( \varphi \rightarrow 0 \) region. Kawase and Ulbrecht\(^{2} \) showed that cell models like the free surface model for non-Newtonian liquids by Happel\(^{134} \) never reduce to the Einstein solution at \( \varphi \rightarrow 0 \). They developed a modified version of that model in which they assumed that the particles are arranged in closely packed layers, the distance between the layers being controlled by \( \varphi \). They found \( K_E^\tau(n = 1) = 2.48 \) and concluded that, for \( n = 1 \), their model reduces to Einstein’s equation at low \( \varphi \). We give two arguments to show that their agreement with Einstein’s solution is accidental. First, a model in which the arrangement between the particles is critical cannot be identical to Einstein’s case in which the interparticle distance plays no role. Also from another argument the supposed agreement can be shown to be accidental: from their model for non-Newtonian suspensions only finite \( K_E^\tau \) values can be derived for \( n = 1 \) and \( n = 0 \) (2.48 and 1.24, respectively). For the range \( 0 < n < 1 \) we calculated, using their model, approximate values of \( K_E^\tau \):

\[
K_E^m(\text{approx}) = \left[ \eta(\varphi, \gamma_m) - \eta(0, \gamma_m) \right] / \left[ \varphi \cdot \eta(0, \gamma_m) \right]
\]

with \( \varphi = 10^{-3}, 10^{-4}, 10^{-5}, \) and \( 10^{-6} \). These values decrease steadily with \( \varphi \) approaching zero, by a constant difference per decade in \( \varphi \) (at a given value of \( n \)). This behavior is also reflected in Fig. 11 in
FIG. 11. Relative viscosities of suspensions in power-law liquids vs volume fraction, according to the model of Kawase and Ulbrecht, for various values of the power-law exponent.

which these relative viscosities are plotted versus \( \phi \). Only the \( n = 0 \) and the \( n = 1 \) curves have constant slopes at the low \( \phi \) end. Also not mentioned by Kawase and Ulbrecht for \( 0 < n < 1 \) is that \( K_0^n \rightarrow \infty \) and that \( \eta_{\text{eff}} < 1 \) over a considerable range of \( \phi \) in contradiction to all experimental evidence.

In the present study assumptions about the shape of the particles have only been made in Sec. II B in which Einstein's result for suspensions of spheres was mentioned. With aspherical particles in Newtonian media the relationships between rheological parameters in Eqs. (3)-(6) and (8)-(11) may change. However, the principle of additivity of the effect of the particles is still valid, in the \( \phi \to 0 \) limit. This implies that Eqs. (3)-(6) and (8)-(11) should be changed in the sense that the coefficient \( c \) in the factor \( [1 + c\phi] \) now become unknown. With non-Newtonian media (Sec. III C) we had a similar problem which was solved by the introduction of the parameters \( f \), \( g \), and \( h \). Because the particle asphericity also affects the equations only via the parameters \( f \), \( g \), and \( h \) we can conclude that the theoretical analysis given for suspensions of spheres in non-Newtonian media is applicable to suspensions of aspherical particles as well. Also in that case our new definition of \( \eta_{\text{eff}} \),
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should be preferred. However the value of $h$ and its dependence on $n$ may be different, depending on the particle shape.

An interesting point is whether our results are applicable also to emulsions. In many cases the interfaces between droplets and the continuous liquid are fairly rigid. In such cases emulsions behave like suspensions and our equations are applicable. In the case of "ideal" emulsions with the two liquids in direct contact with each other, the situation is different. Equation (12) is not valid any more; a term accounting for the internal flow in the droplets should be added. Additionally, the boundary condition at the droplet surface (e.g., expressed as ratio of shear rates on both sides) is only shear rate independent if the power-law exponents of both liquids involved are equal. Only in that case is $f$ a unique function of $n$ of the continuous phase. Otherwise, it also depends on the actual shear rate and on the value of $n$ of the dispersed liquid; then our relationships between the different $K_E$ values are not applicable.

Our results are interesting for the rheology of filled plastic materials. We are not aware of the existence of any theoretical answer to the question whether and to what extent rigid particles change the yield value of a purely plastic material. The experimental evidence available from the science of plastic deformations (obscured by the coexistence of fracture and yield) directs toward a slight increase in yield value. We predict $\eta^\infty = 1 + \frac{\varphi}{2}$. On the other hand, it seems reasonable to expect a weakening effect on the yield value due to the presence of rigid particles around which stress concentrations occur. These stress concentrations lead to local yield at macroscopic stresses below the yield value of the pure-liquid phase. If at such a stress level the particle concentration is large enough for the local yield areas to overlap each other, macroscopic yield can be expected, implying yield weakening in contradiction to our experimental results and to experimental evidence with filled plastics. More research is needed to solve this discrepancy.

V. CONCLUSIONS

A new definition for the relative viscosity of suspensions in generalized Newtonian liquid media is introduced according to which viscosities should be compared at equal mean squared strain rates in the liquid phases ($\eta^\infty$). This definition is theoretically more satisfactory and also useful in practice. For dilute suspensions a theoretical analysis shows how its value relates to $\eta^\infty$ (relative viscosity at equal macroscopic
shear rates) and to \( \eta^* \) (relative viscosity at equal macroscopic shear stresses). The corresponding Einstein coefficients \( K_E \) are interrelated according to

\[
K_E^m = nK_E^p = [n + 1]K_E^f/2 + [n - 1]/2,
\]

where

\[
n = d\ln[r(\dot{\gamma})]/d[\ln(\dot{\gamma})].
\]

These relationships are valid irrespective of the shape of the particles; however, the values of the various \( K_E \) may vary with particle shape.

If the liquid medium is a power-law liquid \( (\tau = k\dot{\gamma}^n) \) then a suspension in such a liquid also exhibits that behavior with the same \( n \) but a higher value of \( k \). This holds for nondilute suspensions as well.

Experimental data (as supplied by the authors and from other sources) for suspensions of spheres were analyzed. The newly defined Einstein coefficient \( K_E^p \) appeared to be constant \( (= 2.5) \), over a wide range of \( n \). \( 0.07 < n < 1 \). \( K_E^p \) varies linearly between 0.75 at \( n \to 0 \) to 2.5 at \( n = 1 \). Also \( K_E^p(n = 1) = 2.5 \) but shows asymptotic behavior \( (\to \infty) \) at low \( n \) values. The values of the various \( K_E \) interrelate according to the theoretical predictions.

There are strong indications that the value of \( n \) has no influence on the inhomogeneity in rate of strain in dilute suspensions.

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**APPENDIX**

The power-law exponent of suspensions in power-law liquids

Let the liquid phase of a suspension of hard spheres be described by

\[
\tau = -\eta\dot{\gamma} \quad \text{with} \quad \eta = k[\dot{\gamma}]^{(n-1)/2},
\]

\( n \) being a fixed value. We consider a specific distribution of dispersed particles in the suspension. Suppose that for a given macroscopic shear rate \( \dot{\gamma}_m \) the solutions for the local shear rates and shear stresses are given by \( \dot{\gamma}^1(r) \) and \( \tau^1(r) \). Then, at a macroscopic shear rate \( \lambda \dot{\gamma}_m \) the solutions for the local shear rates and shear stresses are \( \lambda \dot{\gamma}^1(r) \) and \( \lambda\tau^1(r) \) as can be shown by substitution of all terms \( \dot{\gamma}^1(r) \) and \( \tau^1(r) \) in Eq.
Because all stresses scale with $\lambda^n$ this must also be true for the macroscopic shear stress in the suspension, leading to the conclusion that the power-law exponent of the suspension equals that of the pure liquid.

References

35. A. Jurgens (private communication).