The Concept of hydrodynamic Amplification in filled Elastomers

Introduction

More than 100 years ago, in 1906, Albert Einstein computed in his dissertation [1] the change in viscosity of a dilute suspension of rigid spherical particles, the result was corrected a few years later in [2]. The outcome of this seminal work is that if one adds a small amount of rigid spherical particles with volume fraction \( \varphi \) to a Newtonian fluid with viscosity \( \eta_0 \), the viscosity of the suspension \( \eta \) is then given by [1,2]:

\[
X = \frac{\eta}{\eta_0} = 1 + 2.5\varphi. \tag{1}
\]

This equation is nowadays often called Einstein equation and \( X \) is referred to as the “hydrodynamic amplification factor”. Einstein’s equation (1) was later derived using various approaches, to name a few: Landau and Lifshitz [3], Happel and Brenner [4] and Batchelor [5].

For rigid spherical particles embedded in an incompressible linear elastic matrix Smallwood [6] obtained the same relation for the amplified shear modulus \( \mu \sim 0.07 \) as Einstein did for the viscosity in equation (1):

\[
X = \frac{\mu}{\mu_0} = 1 + 2.5\varphi. \tag{2}
\]

In the above relation \( \mu_0 \) is the shear modulus of the matrix. The fact that the results obtained by Einstein (eq. (1)) and Smallwood (eq. (2)) lead to the same mathematical expression can be traced back to a mathematical analogy between the problems the two authors considered. Smallwood [6] first realized this analogy, which we will discuss later.

The above equations (1) and (2) only hold in the dilute case, say for \( \varphi \leq 0.03 \) [7], and assume “a single sphere in an infinite matrix”. Furthermore, it is crucial to note that the relations (1) and (2) only hold in the linear case, i.e. assuming the matrix to be a Newtonian fluid or a linear elastic material (both incompressible). Based on these assumptions we will shortly explain in the next section how one obtains effective properties of the material, like those described by equations (1) and (2). In section „Analogy” the mentioned mathematical analogy between a Newtonian fluid and a linear elastic material will be discussed. Next, in section „Higher volume fractions”, higher volume fractions of particles will be considered. For that case we will revisit in section „Analogy revisited” the mathematical analogy between a suspension of rigid particles in a Newtonian fluid and a linear elastic solid. Last, in section 6, we will look at the strain amplification approach widely used in the rubber community.

Effective Properties

The computational determination of effective properties of composites is generally referred to as homogenization. A relatively new and complete treatment of this topic can be found, for example, in Torquato [8].

The main idea behind the calculations to obtain the relations (1) or (2) is the comparison of energy at two levels of observation, at the microscale where the particles are “visible” and the macroscale where the particles cannot be seen anymore. We will illustrate the homogenization procedure for the linear elastic solid. First one computes the average stored energy density in the “microscopic” system. This is in our case represented by the incompressible linear elastic matrix with embedded rigid particles. In the next step we define a new virtual “macroscopic” system, whereby we assume it does not have a microstructure. That is what we assume the new material to be homogeneous. We now require that the work done on the “macroscopic” system should be equal to the work done on the...
expressed as [13–15]. It has to be noted here that for active fillers in a soft rubber elastic matrix the factor \(X\) no longer depends on the simple filler volume fraction \(\varphi\) but on some effective volume fraction \(\varphi_{\text{eff}}\). This is due to the appearance of a localized rubber layer at the particle surface [14]. We further note that at higher loadings of particles, building disordered fractal-like aggregates, the strain amplification factor is predicted to scale according to a power law, where the scaling exponents are determined by fractal dimensions of the reinforcing clusters and their values differ in the two different regimes below or above the cluster overlap [13,14].

In equation (9), another frequently used value for \(b\) is 14.1 which is attributed to Guth and Gold [16]. First appearance of this equation is in Gold’s PhD thesis in 1936 [17]. However, it is hard to follow the derivation of this factor in the thesis. In his derivation Gold assumed a Newtonian matrix fluid. Gold’s final result has undergone a peculiar fate. The value 14.1 is extensively (if not exclusively) and uncritically adopted in the rubber community as a strain amplification factor without any proof of its validity. For Newtonian matrix fluids, one finds this value for the increase of viscosity in books on polymer processing, e.g. the book by Osswald and Hernández-Ortiz [18], and in books on hydrodynamics like the seminal work of Happel and Brenner [4]. On the other hand it appears that the rheology community has forgotten about this result as nowadays it cannot be found in recent books on rheology, like Macosko [7], Larson [19] or Mewis and Wagner [20].

**Analogy revisited**

In the calculations performed by Einstein/Smallwood to arrive at equations (1) and (2), respectively, only one single particle is considered. That is, it is assumed that the particles do not interact with each other, which corresponds to the limit of dilute suspensions.

As the particle concentration is increased the particles will inevitably interact with each other. The disturbance of approximation of the expansion of the amplification factor up to second order in the volume fraction

\[
X = 1 + 2.5\varphi + 5.0\varphi^2 = 1 + \frac{2.5\varphi}{1 - 2\varphi}
\]  

turned out to be a suitable expression for \(X\) [13–15].

Now one equates the microscopic energy density (eq. (3)) with the macroscopic energy density (eq. (5)) to obtain the effective shear modulus:

\[
\mu = \frac{\langle \sigma \cdot \varepsilon \rangle}{2\varepsilon_0 \varepsilon_0}
\]  

where \(\varepsilon_0\) is the applied strain, that is assumed to be homogeneous, \(\mu\) is the macroscopic (effective) shear modulus. In equation (5) we assume that the material behaviour is isotropic and incompressible.

Thus, given the same boundary conditions, equations (7) and (8) provide the same numerical results.

Due to the discussed mathematical analogy it becomes obvious why Einstein and Smallwood obtained analogous results. In section “Analogy revisited” we will revisit this analogy, as there are differences, when higher volume fractions of particles are considered. This analogy is also the reason why many authors refer to the amplification in elastic solids as hydrodynamic amplification even though there are no hydrodynamics in a solid.

**Higher volume fractions**

If one adds “more than just a few” particles to a Newtonian fluid or a linear elastic solid the problems to solve become more complex and will lead to different results. While in the dilute case the validity of the Einstein/Smallwood equation is considered almost a fact, this is not the case for higher volume fractions. For moderate loadings of particles, say \(\varphi \leq 0.10...0.15\), a quadratic term appears in the equation for the amplification factor \(X\):

\[
X = 1 + 2.5\varphi + b\varphi^2.
\]  

The value of the factor \(b\) in equation (9) turns out to depend on the matrix material (fluid or solid) and also on the applied deformation (at least for fluids) and, curiously, on the research community.

Let us start with the work of Batchelor and Green [10] who calculated for \(b\) a value of 7.6 in the case of a Newtonian fluid in an elongational flow. For an incompressible linear elastic solid they derived for the shear modulus the value \(b = 5.2 \pm 0.03\). Later Batchelor [11] obtained for a Newtonian fluid in a shear flow \(h = 6.2\), here the particles are subjected to Brownian motion. Chen and Acrivos [12] refined the result of Batchelor and Green for an incompressible elastic solid and obtained the value \(b = 5.01\) which is within the estimated error range given by Batchelor and Green [10]. Interestingly, in this case a corresponding Padé approximation of the expansion of the amplification factor up to second order in the volume fraction

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\]
the flow/displacement field due to the presence of one particle will influence the disturbance of the flow/displacement field around another particle in the vicinity. At this point the difference between a fluid and a solid becomes important, as in a fluid the particles can move freely in the flow field and thereby change their relative positions to each other. In a linear elastic solid the change of relative positions of the particles is negligible [12]. This is also the argument given by Batchelor and Green [10] in the derivation for the factor \( b \) for a Newtonian fluid and linear elastic solid mentioned above. The movement of the particles with the flow field can even lead to non-Newtonian behaviour [19].

Thus, while the mathematical analogy is valid for the case of Einstein/Smallwood, it is generally not valid for higher volume fractions of filler particles as the particles can move freely in the flow field of a fluid but they will not in a solid.

These considerations immediately raise the question whether the Guth-Gold equation, namely

\[
X = 1 + 2.5p + 1.4p^2 \tag{11}
\]

is valid at all for solids since it was originally computed for fluids.

**Strain amplification**

If it comes to elastomers there exist many non-linear constitutive models to describe the dependency of the stress on the strain. To account for the presence of filler particles one often tries to modify these equations by introducing amplification factors. A first suggestion for the strain amplification factor is due to Mullins and Tobin who proposed in their paper [16] to use, a priori, the amplification factor \( X \) as the strain amplification for rubber in the form:

\[
\lambda = 1 + X \varepsilon_p = 1 + X (\lambda_m - 1) \tag{12}
\]

with \( \lambda \) the amplified stretch and \( \varepsilon_p \) the applied strain. It should be noted that this approach was only proposed for uniaxial extension but later on used for other deformations too.

To the authors’ knowledge, the first critical review of strain amplification approach by Mullins and Tobin was given by Schikowsky [21]. He used arguments based on the equivalence of energy (see section „Effective properties“) and derived the effective stretch as

\[
\lambda = 1 + \frac{X}{1-\psi}(\lambda_m - 1). \tag{13}
\]

Schikowsky’s argument is fairly straightforward: we know from the works of Einstein/Smallwood that the energy in the composite increases according to Einstein or a similar relation, thus we should define the strain amplification factor such that, when inserted into the energy, the correct increase of the energy is obtained. We will illustrate the arguments of Schikowsky for an isotropic incompressible linear elastic solid. The strain energy for such a solid is given by [9]

\[
W = \mu \varepsilon : \varepsilon. \tag{14}
\]

For simplicity, let us consider a uniaxial extensional deformation with elongation \( \varepsilon \). In this case the tensor is given by

\[
\varepsilon = \begin{pmatrix}
\varepsilon & 0 & 0 \\
0 & -0.5\varepsilon & 0 \\
0 & 0 & -0.5\varepsilon
\end{pmatrix}. \tag{15}
\]

Inserting equation (15) into (14) results in the strain energy for uniaxial extension

\[
W = \frac{3}{2} \mu \varepsilon^2. \tag{16}
\]

For a linear elastic solid filled with rigid particles the energy in the composite can be written as

\[
W' = \frac{3}{2} \mu \varepsilon_p^2 \tag{17}
\]

with \( \varepsilon_p \) the applied elongation. The energy in the filled material can also be written as

\[
W' = (1-\psi)W_m + \psi W_p \tag{18}
\]

with \( W_m \) the stored energy inside the matrix and \( W_p \) the stored energy inside the particles, whereby \( W_p = 0 \) as we assume that the particles are rigid. In the matrix material alone the energy is thus given by

\[
W_m = \frac{3X}{2(1-\psi)} \mu \varepsilon_p^2. \tag{19}
\]

If we compare (16) with (19) we can also “put” the amplification factor into the strain

\[
\varepsilon_m = \frac{X}{1-\psi} \varepsilon_p. \tag{20}
\]

so that

\[
W_m = \frac{3}{2} \mu \varepsilon_m^2. \tag{21}
\]

In other words the strain enters squared into the energy and thus we should take the square root of the amplification factor in (20). The factor \((1-\psi)^{-1}\) enters because we only consider the matrix volume, excluding the rigid particles.

Similar arguments to those of Schikowsky [21] can be found in Suquet [22]. Both authors introduce the strain amplification factor in such a way that the correct increase of stored energy inside the composite is obtained.

The stress in the composite material can be calculated by

\[
\sigma = \frac{\partial W'}{\partial \varepsilon_p} = (1-\psi)\frac{\partial W_m}{\partial \varepsilon_p} =
\]

\[
\frac{\partial}{\partial \varepsilon_p} \frac{3}{2} \mu (1-\psi) \left( \frac{X}{1-\psi} \varepsilon_p \right)^2. \tag{22}
\]

Evaluating the derivative in equation (22) gives the stress as

\[
\sigma = 3X \mu \varepsilon_p = X E \varepsilon_p \tag{23}
\]

with \( E = 3 \mu \) the Young’s modulus. From equation (23) it can be seen that for a linear elastic material there is no difference between using the strain amplification factor introduced in (20) or simply multiplying the modulus by the factor \( X \). However, if the relation between the stress and the strain becomes non-linear the results will differ. On the other hand, if we would have used the strain amplification factor as proposed by Mullins and Tobin the amplification factor \( X \) would enter squared into the stored energy and thus into stress and one would strongly overestimate the additional work to be done.

It is also possible to directly compute the average strain in the matrix phase. For a linear elastic solid one obtains for the average strain in the matrix [23,24]

\[
\langle \varepsilon \rangle = \frac{1}{1-\psi} \varepsilon_p. \tag{24}
\]

The above equation for the average strain in the matrix gives much lower values for the strain amplification as equation (20). It was shown in [25] that using this relation fairly well agreement could be achieved with direct experimen-
tal observations of the microscopic strain enhancement in reinforced polymer networks, when performing small-angle neutron scattering (SANS) on special designed model systems [26].

For non-linear elastic solids, like rubber, that are generally subjected to large deformations the strain amplification factor cannot easily be computed, e.g. for the Green-Lagrange strain. The only available general result for an amplification factor in the case of large deformations is given by Govindjee and Simo [27,28]. They showed that the deformation gradient is amplified as

\[
(F^n)_{m} = \frac{1}{1 - \varphi} R_n (U^n - \varphi I) = \frac{1}{1 - \varphi} (F^n - \varphi R_n)
\]

(25)

if the particles move affine. Here \(R_n\) is the applied rotation tensor and \(U^n\) is the applied right stretch tensor. The above relation for the average deformation gradient in the matrix was also compared with local strain measurements from NMR experiments [29].

Conclusions

We showed that the analogy for the hydrodynamic amplification factor \(\chi\) between a fluid and a solid is only valid in the dilute case, as here the two problems are mathematically identical. For higher volume fractions this mathematical analogy is not valid anymore, since in a fluid the particles can move freely in the flow field while in a solid they cannot move freely. As the rubber community almost exclusively uses the Guth-Gold equation (11), one has to ask the question if the Guth-Gold equation is valid for rubbers at all, as it was computed for a fluid suspension.

We showed that the approach by Mulins and Tobin is wrong if one considers conservation of energy, as here the strain amplification factor enters squared into the energy.

We further introduced two different types of strain amplification factors in equations (20) and (24)/(25). These different factors result from different arguments. To obtain (20) we required that the average energy in the filled system must be \(\chi\) times higher than in the unfilled system and introduced the strain amplification factor such that if it is inserted in the strain we obtain that the energy is about \(\chi\) times higher. For equations (24) and (25) the average of the strain in the matrix is computed directly. The approach taken in equation (20) appears to be favorable if one attempts to modify constitutive relations [22,30]. On the other hand the direct averages given in equations (24) and (25) are useful if one is able to measure local strains like Westermann et al. [25,26] and Pérez-Aparicio et al. [29].

References


