Viscosity of concentrated suspensions and properties of porous media

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Viscosity of concentrated suspensions and properties of porous media

by

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A Doctoral Thesis

Submitted in partial fulfilment of the requirements
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ABSTRACT

In this study new theoretical method of calculations of effective properties of porous and dispersed materials is suggested. The new method takes into account cluster formation in colloidal suspensions/emulsions. This method is applied to calculations of dependence of effective properties of porous and dispersed materials on volume fraction of dispersed phase. Theoretical predictions are compared with available experimental data.

Chapter 1 presents a review of available theoretical methods for calculation of effective properties of dispersed and porous media.

Our new method is applied for calculation of effective diffusion coefficient in porous media in Chapter 2. The deduced dependency of the effective diffusion coefficient on the porosity shows the good agreement with available experimental data.

A new theoretical method of calculations of viscosity of concentrated suspensions is suggested in Chapter 3. The new method is based on the consideration of the influence of cluster formation on the viscosity of concentrated suspensions. The deduced theoretical dependency of the effective viscosity on the volume fraction of the dispersed particles is compared with available experimental measurements. The comparison shows the good agreement between the theory predictions and the experimental data.

In Chapter 4 the new method for calculation of the dependency of effective viscosity of emulsions on the volume fraction of droplets is suggested. The new theory takes into account flocculation of droplets. Theoretical dependencies of the effective viscosity on the volume fraction of droplets are deduced in two cases: developed flocculation and low flocculated emulsions. The comparison of the theory predictions with available experimental data shows the good agreement in both cases of developed and low flocculation.

Our new method is applied to calculations of the effective viscosity and permeability of porous media, illustrated in Chapter 5. Brinkman equations are frequently used for the description of the liquid flow in porous media. These equations include two semi-empirical parameters: effective viscosity and permeability. It is shown in Chapter 5 that these two dependencies on the particle volume fraction can not be determined independently. The system of two interconnected differential equations for the calculation of the effective viscosity and permeability is deduced and calculations are compared with available computed simulations of the flow inside porous media.
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In Chapters 6 and 7 the new method is applied for the calculations of elastic properties of different composite materials: rubber/polymer sheets with cracks, laminated composite materials, composite materials with more than one type of inclusions. In each case deduced theoretical dependencies are compared with available experimental data. In the case of rubber/polymer sheets with cracks this comparison, this shows the very good agreement with experimental data. In the case of concrete the comparison shows better agreement with the experimental data than the frequently used Mori-Tanaka method.

Keywords: averaging, effective, viscosity, diffusion, composite materials, mean field approximation, porous media
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VISCOITY OF CONCENTRATED SUSPENSIONS AND PROPERTIES OF POROUS MEDIA

Abstract
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Chapter 1 EFFECTIVE PROPERTIES OF POROUS AND DISPERSED MEDIA: REVIEW

1.1 Averaging methods

Multiphase systems dominate nearly every area of science and technology, and the method of volume averaging provides a foundation for the analysis of these systems. The development is based on classical continuum physics, and it provides both the spatially smoothed equations and a method of predicting the effective transport coefficients that appear in those equations. However, the averaging method in many cases does not allow calculation of these effective coefficients from the volume fraction of dispersed phase. These calculations can be carried out using a new version of mean field approximation method suggested in this thesis.

The determination of the average or macroscopic properties of porous materials is a longstanding problem of great interest, for instance (Thompson, et al., 1987), (Levich, 1962), (Lichter, Steefel, and Oelkers Editors, 1996), (Schraad, 2001). Application of the averaging method to the problem of porous catalyst has been done by (Whitaker, 1999) and in this section we present his derivation.

Boundary value problem of the diffusion and reaction in a porous catalyst can be expressed as

\[
\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{D} \nabla c, \quad \text{in the continuous phase, } \lambda, \tag{1.1.1}
\]

\[-n \cdot \mathbf{D} \nabla c = kc, \quad \text{at the boundary between two phases, } \Sigma_{\lambda}, \tag{1.1.2}
\]

\[c = \mathcal{S}(r,t), \quad \text{at the external boundary} \tag{1.1.3}
\]

in which \( \mathbf{D} \) is the diffusion coefficient, \( c \) is the concentration of molecules, which diffuse in the porous medium, \( n \) is normal vector and \( k \) is pseudo reaction rate constant.
It is sufficient to determine the *average concentration* and the *average rate of reaction* with the averaging volume for design purposes. The details of this averaging volume are presented in Figure 1.1 where the position vector $r_\lambda$ is used to locate any point in the $\lambda-$phase. The position vector $x$ locates the centre of the averaging volume that may lie

**Figure 1.1** Averaging volume for the $\lambda-s$ system
in either the $\lambda$-phase or the $s$-phase. The relative position vector $y_\lambda$ is used to locate points in the $\lambda$-phase relative to the centre of averaging volume.

The process of spatial smoothing begins by associating with every point in space an averaging volume which does not change with respect to time and space. For the two-phase system under consideration we can express the averaging volume $\mathcal{V}$ as

$$\mathcal{V} = V_\lambda(x) + V_s(x),$$

where $V_\lambda(x)$ represents the volume of the $\lambda$-phase containing within the averaging volume and the volume fraction of the $\lambda$-phase (identified as the porosity) is given by

$$\phi = V_\lambda(x)/\mathcal{V}.$$  \hspace{1cm} (1.1.4)

In the method of volume averaging the average of $c$ is expressed according to

$$\langle c \rangle^* = \frac{1}{\mathcal{V}} \int c dV.$$  \hspace{1cm} (1.1.5)

Thus integration of Eq. (1.1.1) and dividing by $\mathcal{V}$ results in

$$\frac{1}{\mathcal{V}} \int \frac{\partial c}{\partial t} dV = \frac{1}{\mathcal{V}} \int \nabla \cdot (\mathcal{D} \nabla c) dV.$$  \hspace{1cm} (1.1.6)

Since $V_\lambda$ is not a function of time, the general transport theorem (Whitaker, 1981) can be used to express the left side of this result as

$$\frac{1}{V_\lambda} \int \left. \frac{\partial c}{\partial t} \right|_{x+Y_\lambda} dV = \frac{d}{dt} \left( \frac{1}{V_\lambda} \int c dV \right) = \frac{d}{dt} \langle c \rangle^*_\lambda.$$  \hspace{1cm} (1.1.6)

Because the spherical average concentration is associated in the fixed point $x$, it is appropriate to make use of the partial derivative and express Eq. (1.1.6) as

$$\frac{\partial (c)^*}{\partial t} = \langle \nabla \cdot (\mathcal{D} \nabla c) \rangle^*.$$  \hspace{1cm} (1.1.7)

In Eq. (1.1.7) notation $\nabla \cdot$ means $\text{div}$ (and notation $\nabla$ means $\text{grad}$). It should be clear that it is necessary to interchange differentiation and integration on the right hand side of Eq. (1.1.7). Given some scalar $\Xi_\lambda$ associated within the $\lambda$-phase, the spatial averaging theorem for the $\lambda-s$ system can be expressed as
\[ \langle \nabla \xi \rangle^* = \nabla \langle \xi \rangle^* + \frac{1}{V} \int_{\Sigma_s} n \xi \, d\Sigma \] 

(1.1.8)

in which \( \Sigma_s \) represents the area of the \( \lambda - s \) interface contained within \( V \). This theorem represents a three-dimensional version of the Leibniz rule for interchanging differentiation and integration. Eq. (1.1.8) was derived independently by (Marle, 1967) in a study of single-phase flow in porous media, by (Anderson and Jacson, 1967) in a study of fluidised beds and by many other authors later. Derivation of Eq. (1.1.8) is especially simple in one-dimensional case.

This result with the right hand side of Eq. (1.1.7) can be used to obtain

\[ \langle \nabla \cdot (D\nabla c) \rangle^* = \nabla \cdot \langle D\nabla c \rangle^* + \frac{1}{V} \int_{\Sigma_s} n D\nabla c d\Sigma. \] 

(1.1.9)

Substitution of the boundary conditions (1.1.2) into Eq. (1.1.9) gives

\[ \frac{\partial \langle c \rangle^*}{\partial t} = \nabla \cdot \langle D\nabla c \rangle^* - \frac{1}{V} \int_{\Sigma_s} k c d\Sigma. \] 

(1.1.10)

Since concentration within the phase \( s \) in the reaction of porous catalyst is zero:

\[ \langle c \rangle^* = \phi \langle c \rangle^*_\lambda, \] 

(1.1.11)

where \( \langle . \rangle^*_\lambda \) means averaging on the phase \( \lambda \), \( \phi \) is porosity and

\[ \langle c \rangle^*_\lambda = \frac{1}{V \lambda} \int c dV. \] 

(1.1.12)

Substitution of the Eq. (1.1.11) into (1.1.10) results in

\[ \phi \frac{\partial \langle c \rangle^*_\lambda}{\partial t} = \nabla \cdot \langle D\nabla c \rangle^* - \frac{1}{V} \int_{\Sigma_s} k c d\Sigma. \] 

(1.1.13)

In Eq. (1.1.13) the first term \( \phi \frac{\partial \langle c \rangle^*_\lambda}{\partial t} \) means accumulation in phase \( \lambda \), the second term \( \nabla \cdot \langle D\nabla c \rangle^* \) means diffusion, and \( \frac{1}{V} \int_{\Sigma_s} k c d\Sigma \) means the decreasing of the concentration due to heterogeneous reaction. This form (1.1.13) illustrates a key aspect of the process.
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of spatial smoothing, i.e. the interfacial boundary conditions are joined to the governing equations for the multiphase transport phenomena.

Using notation for averaged value at interface $\langle \Xi \rangle_{\lambda s}$

$$\langle \Xi \rangle_{\lambda s} = \frac{1}{\Sigma_{\lambda s}} \int \Xi d\Sigma,$$

here $\Sigma_{\lambda s}$ represents the area of $\lambda - s$ interface. Eq. (1.1.13) can be simplified as

$$\phi \frac{\partial (c)_{\lambda}}{\partial t} = \nabla \cdot (D \nabla c)^* - \frac{\Sigma_{\lambda s}}{V} \langle kc \rangle_{\lambda s}.$$  (1.1.14)

Here $\Sigma_{\lambda s}$ is surface area between $\lambda$ and $s$ phases.

Eq. (1.1.14) and (1.1.8) give

$$\phi \frac{\partial (c)_{\lambda}}{\partial t} = \nabla \cdot \left[ D \left( \nabla (c)_{\lambda}^* + \frac{1}{V} \int n cd\Sigma \right) \right] - \frac{\Sigma_{\lambda s}}{V} \langle kc \rangle_{\lambda s}.\quad (1.1.15)$$

Eqs. (1.1.15) can be transformed using (1.1.11) in the following way

$$\phi \frac{\partial (c)_{\lambda}}{\partial t} = \nabla \cdot \left[ D \left( \phi \nabla (c)_{\lambda} + \langle c \rangle_{\lambda} \nabla \phi + \frac{1}{V} \int n \phi d\Sigma \right) \right] - \frac{\Sigma_{\lambda s}}{V} \langle kc \rangle_{\lambda s}.\quad (1.1.16)$$

Since the intrinsic average concentration is the quantity of interest, the point concentration is decomposed as

$$c = \langle c \rangle_{\lambda} + \tilde{c}_{\lambda}.\quad (1.1.17)$$

On substitution of Eq. (1.1.17) into Eq. (1.1.16):

$$\phi \frac{\partial (c)_{\lambda}}{\partial t} = \nabla \cdot \left[ D \left( \phi \nabla (c)_{\lambda} + \langle c \rangle_{\lambda} \nabla \phi + \frac{1}{V} \int n \phi d\Sigma + \frac{1}{V} \int n \tilde{c}_{\lambda} d\Sigma \right) \right] - \frac{\Sigma_{\lambda s}}{V} \langle k \rangle_{\lambda s}.\quad (1.1.18)$$

In order to remove the volume averaged concentration from the area integral in Eq. (1.1.18) a Taylor expansion is used about the centroid of the averaging volume to obtain

$$\langle c \rangle_{\lambda, y_{\lambda}} = \langle c \rangle_{\lambda} + y_{\lambda} \cdot \nabla \langle c \rangle_{\lambda} + \frac{1}{2} y_{\lambda} y_{\lambda} : \nabla \nabla \langle c \rangle_{\lambda} + ...$$  (1.1.19)
Substitution of the latest equation into surface integrals in Eq. (1.1.18) gives
\[ \frac{1}{V} \int_{\Sigma_u} n(c)_\lambda d\Sigma = \frac{1}{V} \int_{\Sigma_u} \langle c \rangle_{\lambda,xx} nd\Sigma + \frac{1}{V} \int_{\Sigma_u} \langle y_\lambda \cdot \nabla \langle c \rangle_{\lambda,xx} \rangle nd\Sigma + \frac{1}{V} \int_{\Sigma_u} \left[ \frac{1}{2} \langle y_\lambda y_\lambda \rangle : \nabla \nabla \langle c \rangle_{\lambda,xx} \right] nd\Sigma + \ldots \]

Since all terms evaluated at the centre can be removed from the integral, Whitaker arrived at
\[ \frac{1}{V} \int_{\Sigma_u} n(c)_\lambda d\Sigma = \left( \frac{1}{V} \int_{\Sigma_u} \langle c \rangle_{\lambda,xx} nd\Sigma \right) \nabla \langle c \rangle_{\lambda,xx} + \ldots \]
It is easy to see that
\[ \frac{1}{V} \int_{\Sigma_u} k dV = \phi. \quad (1.1.20) \]
This means that Eq. (1.1.20) leads to a well-known result given by
\[ \frac{1}{V} \int_{\Sigma_u} nd\Sigma = -\nabla \phi. \quad (1.1.30) \]
In the case of isotropic porous distribution $\nabla \phi$ is zero. Volume $V$ is sufficiently big comparable with porous size. All pores are distributed randomly and estimation shows so the integral $\frac{1}{V} \int_{\Sigma_u} nd\Sigma$ as well integral $\int_{\Sigma_u} y_\lambda - y_\lambda nd\Sigma$ are zero. Consequently, Eq. (1.1.18) is simplified in this case using the additional condition $\langle c \rangle_{\lambda,xx} = \langle c \rangle_\lambda$ resulting from estimation of value $\langle c \rangle_{\lambda,xx}$ as
\[ \phi \frac{\partial \langle c \rangle_\lambda}{\partial t} = \nabla \left( \frac{1}{V} \int_{\Sigma_u} \nabla \langle c \rangle_\lambda + \frac{1}{V} \int_{\Sigma_u} \nabla \langle c \rangle_\lambda d\Sigma \right) + \frac{1}{V} \int_{\Sigma_u} k \langle c \rangle_\lambda. \quad (1.1.31) \]
The solution of Eq. (1.1.31) is proposed in the form
\[ \vec{c}_\lambda = b_\lambda \nabla \langle c \rangle_{\lambda,xx} + f_\lambda \langle c \rangle_{\lambda,xx} + g_\lambda, \quad (1.1.32) \]
where $g_\lambda$ is an arbitrary function. Choosing the functions $b_\lambda$ and $f_\lambda$ in the following form:
Problem 1:
\[ \nabla^2 \mathbf{b}_\lambda = 0, \]
\[ \mathbf{n} \cdot \nabla \mathbf{b}_\lambda = \mathbf{n}, \text{ at } \Sigma_\lambda, \]
\[ \mathbf{b}_\lambda (r) = \mathbf{b}_\lambda (r), \quad i = 1, 2, 3 \quad \text{Periodicity conditions.} \]

Problem 2.
\[ \nabla^2 f_\lambda = -\frac{ak}{\phi \mathcal{D}_\lambda}, \]
\[ \mathbf{n} \cdot \nabla f_\lambda = \frac{k}{\mathcal{D}_\lambda} \text{ at } \Sigma_\lambda, \]
\[ f_\lambda (r + l_i) = f_\lambda (r), \quad i = 1, 2, 3 \quad \text{Periodicity conditions}. \]

Substitution of Eq. (1.1.32) into (1.1.31) gives closed form of the governing differential equation for \( \langle c \rangle \). Since \( \langle c \rangle \) and \( \nabla \langle c \rangle \) are evaluated at the centroid of the representative unit cell, these terms can be removed from the area integral in Eq. (1.1.31) and this leads to
\[ \phi \frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot \left[ \mathcal{D} \left( \phi \nabla \langle c \rangle + \frac{1}{V} \int \mathbf{n} \mathbf{b}_\lambda d\Sigma \right) \right] + \nabla \cdot \left( \langle c \rangle \frac{\phi \mathcal{D}}{V} \int \mathbf{n} \mathbf{s}_\lambda d\Sigma \right) - \frac{\Sigma}{\phi V} k \langle c \rangle. \]

The effective diffusion tensor is defined by
\[ \mathcal{D}_{\text{eff}} = \mathcal{D}_\lambda \left( I + \frac{1}{V} \int \mathbf{n} \mathbf{b}_\lambda d\Sigma \right) \]

We represent the vector associated with the chemical reaction as
\[ \mathbf{u} = \frac{\phi \mathcal{D}_\lambda}{V} \int \mathbf{n} f_\lambda d\Sigma. \]

Substitution of these two definition (1.1.32) and (1.1.33) into equation (1.1.31) gives the following form the closed equation
\[ \phi \frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot \left[ \phi \mathcal{D}_{\text{eff}} \nabla \langle c \rangle \right] + \nabla \cdot \langle c \rangle \mathbf{u} - \frac{\Sigma}{\phi V} k \langle c \rangle. \]

The latter expression does not allow calculation dependency of effective coefficients as functions of the porosity of the porous medium. This derivation is presented to show that
the averaging method predicts only a general form of resulting effective equations, but is either unable to calculate the dependency of effective coefficients on the porosity or the volume fraction of dispersed phase in the explicit form or leads to very substantial problems in their calculations.

The averaging method has been applied for calculation effective diffusion coefficient in papers (Ryan, et al., 1981), (Chang, 1983) and (Quintard, et al., 1993, 1993a), (Ochoa-Tapia, del Río, and Whitaker, 1993), (Kim, Ochoa, and Whitaker, 1987), (Ochoa-Tapia, Stroeve, and Whitaker, 1994), (Barenblatt, Entov, and Ryzhik, 1990), (Bear, and Bachmat, 1990), (Bear, 1988).


Single-phase flow in heterogeneous porous media (membranes) is considered by averaging method in papers (Quintard, and Whitaker, 1987), (Plumb and Whitaker, 1988a, 1988b). Other approaches include references (Gross, and Osterle, 1968)

In all of the above papers effective differential equations have been deduced, however, effective coefficients either have not be explicitly calculated via porosity or a number of additional simplifications have been introduced.
The aim of our work is to use effective equations, which have been deduced according to the averaging or statistical method (see below), and to calculate dependence of effective coefficients on porosity or volume fraction of dispersed phase.

1.2 Statistical methods

The statistical reconstruction of real porous media is one of the basic engineering problems in the theory of porous structure and has a variety of applications in the study of transport, in mineral processing, and in material characterisation has been investigated by (Giona, and Adrover, 1996). The problem for consideration is about to obtaining porous medium equivalent to the original porous medium. The equivalence means that the real porous media and the reconstructed one should have the same porosity and the same pore-pore correlation function (correlation function of the second order). The reconstruction of porous media is a typical inverse problem.

Let us consider the experimental cross section of a porous medium as a two-dimensional image \( Y \). \( \mathcal{P} \) is the pore space, described by its characteristic function \( \chi_{\mathcal{P}}(x) \)

\[
\chi_{\mathcal{P}}(x) = \begin{cases} 
1 & x \in \mathcal{P} \\
0 & \text{elsewhere} 
\end{cases} 
\]  

(1.2.1)

The porosity is given by \( \phi = \langle \chi_{\mathcal{P}}(x) \rangle \), and the normalised pore- pore correlation function by

\[
C_{2x}(x) = \frac{\langle (\chi_{\mathcal{P}}(y) - \phi)(\chi_{\mathcal{P}}(y + x) - \phi) \rangle}{\phi - \phi^2} . 
\]  

(1.2.2)

Note that \( \langle \chi_{\mathcal{P}}(x) \rangle = \phi \) (\( \langle . \rangle \) includes statistical spatial average).

Under the assumption of isotropy, \( C_{2x}(x) \) is solely a function of \( |x| \) and the generic cross section of the material is representative of the entire three-dimensional structure. The statistical analysis is limited to the pore-pore correlation function, so that the lattice
structure to be generated must have the same porosity and the same pore-pore correlation function as the original image.

A simplest way to obtain this is to consider a continuous correlation random process (Giona, and Adrover, 1996):

\[ Y(x) = \sum_{r'} a(r') \xi(r' + x), \quad (1.2.3) \]

where \( \xi(x) \) is a normalised Gaussian random variable (with zero mean and unit variance), \( a(r) \) is the kernel of the linear filter, and the summation is extended over the value of \( r' \) belonging to the lattice representation of the periodic unit cell. Since \( Y \) is a linear superposition of Gaussian variables. The transformation from the \( Y \) process to the binary, (pore- pore matrix, 0/1) porous structure is given by a non-linear filter \( G \), depending on the function of distribution \( F_y \) of \( Y \) and on the porosity \( \phi \), for each point \( x \), the reconstructed porous structure \( Z(x) \) is given by

\[ Z(x) = G(Y(x), \phi) = \begin{cases} 1 & F_y(Y) < \phi \\ 0 & F_y(Y) > \phi \end{cases} \quad (1.2.4) \]

Eq. (1.2.4) statistically ensures that the reconstructed porous medium admits the porosity, \( \phi \), so that the only condition to be further imposed is that \( C_{2Z} = C_{2Y} \).

The correlation function \( C_{2Z}(x) \) is related to the corresponding correlation function \( C_{2Y}(x) \) through the relation

\[ C_{2Z} = \int dy_1 \int dy_2 \left( \frac{(G(y_1, \phi) - \phi)(G(y_2, \phi) - \phi)}{\phi - \phi^2} \right) p(y_1, y_2), \quad (1.2.5) \]

where

\[ p(y_1, y_2) = \frac{1}{2\pi(1 - C_{2Y})^2} \exp \left[ -\frac{y_1^2 + y_2^2 - 2C_{2Y}y_1y_2}{2(1 - C_{2Y})} \right], \quad (1.2.6) \]

The normalised correlation function \( C_{2Y}(x) \) for \( Y \) given by Eq. (1.2.5) reads as

\[ C_{2Y}(x) = \sum_{r'} a(r') a(r + x) / \sum_{r'} a^2(r'). \quad (1.2.7) \]
Figure 1.2 Statistical reconstruction of porous medium with $\phi = 0.5$ and different values of $\lambda$- parameter in Gaussian kernel (Giona, and Adrover, 1996):

A) $\lambda = 1$,
B) $\lambda = 0.1$;
C) $\lambda = 0.05$;
D) $\lambda = 0.01$
Therefore, for every $C_{2z}(x)$, the corresponding value of $C_{2y}(x)$ is evaluated through Eqs. (1.2.5-1.2.6). In papers (Quiblier, 1984), and (Adler, Jacquin, and Thovert, 1990), $C_{2z}$ is expressed as a power series of $C_{2y}$ by using an orthogonal expansion in terms of Hermite polynomials. This series expansion is computationally expensive and the convergence deteriorates for $C_{2y}$ tending towards unity. For this reason, it is convenient to integrate numerically Eq. (1.2.5) for the prescribed value of the porosity $\phi$. Starting from a set of values $\{C_{2y}\} \in [-1,1]$ the corresponding values $\{C_{2z}\}$ can be obtained in this way, and can be used as a calibration curve. From the knowledge of $C_{2y}(x)$, the coefficients of the linear filter $\{a(r')\}$ are then calculated starting from Eq. (1.2.7) by means of optimisation methods.

A $d$-dimensional isotropic structures (see Figure 1.2) can be reconstructed in a slightly different way than in the previous subsection, by convoluting a Gaussian uncorrelated process with a Gaussian kernel,

$$\mathcal{Y}(x,\lambda) = \int_{E^d} a(u,\lambda)\xi_\lambda(u + x)du = \left(\frac{4\lambda}{\pi}\right)^{d/4} \int_{E^d} e^{-2\lambda \cdot \cdot \cdot} \xi_\lambda(u + x)du,$$  \hspace{1cm} (1.2.8)

where $E^d$ is the Euclidean $d$-dimensional space, $E^d = \{x | -\infty < x_i < \infty\}$, (i=1,...,d). The correlation function for the process given by Eq. (1.2.8) is Gaussian.

The problem of reproducing porous medium is also analysed in papers (Adler, et al, 1992), (Berryman, 1985), (Berryman, and Blair, 1986). Historical revue of development of porous media theory is given by (de Boer, 1996).

Another interesting contribution comes from the analysis and filtering of stochastic fluctuation by applying fractional Brownian motion models or multifractal methods (for an overview of various approaches see (Baldo, Norman, and Tricot, 1994), (Chandrasechar, 1997), (Bossas, and Brady, 1987, 1989, 1984), (Brady, 1993a), (Branka, and Heyes, 1999), (Kim, and Oppenheim, 1972), (Lodge, and Heyes, 1999a, 1999b), (Adrian, and Ronald, 2002), (Dutta, et al., 2001), (Kyunil, Chan, and Byung, 2002).
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(Buryachenko, 2001), (Dammak, Ltaif, Bulvestre, Pourcelly, and Auclair, 2001), (Edwards, and Grinev, 2001)

Some of the macroscopic transport properties of porous media can be derived by the method of multiple scales (Bensoussan, et al., 1978) and (Sanchez-Palencia, 1980).

We adopt however a different procedure in modelling of a porous structure, which is in a way, similar to that described above. We assume that the porous structure is built up of either single, randomly distributed particles, or by randomly distributed clusters of the single particles. Figure 1.2 clearly shows the presence of clusters in the case of porous media built up by individual single particles. There are also a number of direct experimental evidences (see below) that particles in suspensions as well as droplets in emulsions form clusters (doublets, triplets and so on. We apply our consideration below both to emulsions/suspensions and to porous media. In the case of suspensions/emulsions cluster size distribution depends on colloidal hydrodynamic conditions and should be determined in the self-consistent way. In the case of porous media cluster size distribution, it is predetermined by the way the porous media was formed.

1.3 Effective diffusion coefficient in porous media

Calculation of effective diffusion coefficient is presented in the following publication (Quintard, and Whitaker, 1994), (Rayleigh, 1982), (Weissberg, 1963), (Ryan, Carbonel, and Whitaker, 1981), (Bowen, et al., 2000), (Schwartz, et al., 1994).

The first attempt of a theoretical prediction of the effective diffusion coefficient was done by (Maxwell, 1881) (see Figure 1.3), who analyzed a dilute suspension of monodispersed spheres to obtain the result

$$\frac{D_{\text{eff}}}{D_0} = \frac{2}{3 - \phi}.$$  \hspace{1cm} (1.3.1)

The next step is presented by (Weissberg, 1963), which is in reasonably good agreement with the experimental data, and gives an upper bound of the diffusion coefficient
Figure 1.3 Dependency of effective diffusion coefficients on porosity. From (Whitaker, 1999).
(Wakao, and Smith, 1966) obtained the following relation

\[
\frac{D_{\text{eff}}}{D_0} = \phi.
\]  

(1.3.3)

Comparison of the different theoretical dependencies with experimental data is given in Figure 1.3.

Below we apply our modified mean field approximation method for calculation of the effective diffusion in porous media to show that our method gives very good agreement with experimental data.

### 1.4 Dielectric permeability of suspensions

In this section we follow (Dukhin, and Shilov, 1988).

Electrical induction $\mathbf{\bar{D}}$ in the absence of a distributed volume charge satisfies the following law

\[
\text{div} \mathbf{\bar{D}} = 0.
\]  

(1.4.1)

Effect of polarization in dielectric results in interrelation between electrical induction and electric field intensity, $\mathbf{\bar{E}}$

\[
\mathbf{\bar{D}} = \varepsilon \mathbf{\bar{E}}.
\]  

(1.4.2)

In a homogeneous dielectrics vector, $\mathbf{\bar{D}}$ has the same direction as vector $\mathbf{\bar{E}}$. Dielectric permeability $\varepsilon$ becomes a scalar.
The work expended in moving a charge along any closed path in an electrostatic field is zero. According to Stokes' theorem, this yields the second differential equation of electrostatics:

\[
\text{rot } \vec{E} = 0. \tag{1.4.3}
\]

This expression indicates that \( \vec{E} \) is a potential vector, in which case a scalar potential \( \Psi \) of an electrostatic field can be introduced:

\[
\vec{E} = -\text{grad } \Psi. \tag{1.4.4}
\]

At any surface \( \Sigma \) the following boundary conditions should be satisfied:

\[
\left[ \vec{D} \vec{n} \right]_{\Sigma} = 0, \tag{1.4.5}
\]

\[
\left[ \Psi \right]_{\Sigma} = 0. \tag{1.4.6}
\]

where \( \vec{n} \) is normal vector to the surface \( \Sigma \) and square brackets mean the difference of a function in square brackets on crossing the surface \( \Sigma \).

Application of the cell method to the boundary problem (1.4.1)-(1.4.6) gives

\[
\varepsilon_{\text{eff}} = \frac{\varepsilon^m \left( \varepsilon^P + 2\varepsilon^m + \gamma \left( 2\varepsilon^P - 2\varepsilon^m \right) \right)}{(1 - \gamma)\varepsilon^P + \gamma\varepsilon^m + 2\varepsilon^m}. \tag{1.4.7}
\]

where \( \gamma = \left( a/R \right)^3 \) is the volume fraction of particles. Eq. (1.4.7) is Wagner's equation (see (Dukhin, and Shilov, 1988) for details).

1.5 Mean field approximation (Bruggeman's method)

Wagner's equation has been substantially improved by Bruggeman using the mean field approximation method. This approach results in Bruggeman's equation (Bruggeman, 1935).

\[
\frac{\varepsilon^P - \varepsilon_{\text{eff}}}{\varepsilon^P - \varepsilon^m} \left( \frac{\varepsilon^m}{\varepsilon_{\text{eff}}} \right)^{1/3} = 1 - \gamma. \tag{1.5.1}
\]
Figure 1.4 Dielectric constant of water-in-oil emulsion on the disperse phase volume fraction from (Dukhin, and Shilov, 1988). Experimental data (Hanai, at al. 1968).

Theoretical curves:
1) Rayleigh;
2) Böttcher;
3) Bruggeman (Eq. (1.5.1));
4) Kubo Nikamura;
5) Wiener.
Figure 1.5 High-frequency limit of the dielectric constant of an oil-in-water emulsion on volume fraction from (Dukhin, and Shilov, 1988). Experimental data (Hanai, et al. 1959). Theoretical curves:
1) Rayleigh (Rayleigh, L, 1982);
2) Böttcher;
3) Bruggeman (Eq. (1.5.1));
4) Kubo Nikamura;
5) Wiener.
Comparison of dependence of effective dielectric permeability on the volume fraction of particles calculated according to Eq. (1.5.1) (Bruggeman, 1935) with experimental data and other theoretical curves is presented in Figures 1.4, 1.5.

This method has been applied for solution of different problems: viscosity of suspensions, where particles do not form clusters (Roscoe, 1952, 1973), (Brinkman, 1952); elastic properties of composite materials with only one type of inclusions (McLaughlin, 1977), (Christensen, 1990); viscosity of non-flocculated emulsions (Phan-Thien, and Pham, 1997). However, in all these papers a mathematical derivation of the Bruggeman method is not presented. Below is presented such derivation in our thesis.

The latter comparison shows that the Bruggeman equation gives the best agreement with experimental data. These figures show that this method gives amazingly good agreement with experimental data, that is, deserves further developments.

Unfortunately neither in the original paper (Bruggeman, 1935) nor in subsequent publications was a mathematical derivation of his method presented (instead it was a wordy description). Below in our thesis we present a new derivation of the Bruggeman method, which allows us its application to a number of different problems.

1.6 Effective viscosity of suspensions

The steady shear viscosity of suspension should obey the state equation (Gerald, and Krieger, 1986)

$$\frac{\eta^{\text{eff}}}{\eta_0} = f(\gamma, \sigma_c),$$

(1.6.1)

where $\eta^{\text{eff}}$ is the effective viscosity of suspensions, $\eta_0$ is the viscosity of the dispersion medium, $\gamma$ is the volume fraction of particles and $\sigma_c$ is dimensionless shear stress
\[ \sigma_c = \frac{\sigma a^3}{kT}, \]  

where \( \sigma \) is the actual shear stress, \( a \) is the particle radius, \( k \) is the Boltzman’s constant, and \( T \) is the absolute temperature. Reducing the ionic strength in aqueous systems increases the low-shear limiting viscosity dramatically, and eventually produces an apparent yield stress (Choi, and Krieger, 1986a).

Viscosity- volume fraction relationship has been suggested by Krieger- Dougherty (Choi, and Krieger, 1986a)

\[ \frac{\eta^\eta}{\eta_0} = \left(1 - \frac{\gamma}{\gamma_m}\right)^{\gamma_m[n]} \]  

(1.6.3)

The fitting parameters \([\eta]\) and \( \gamma_m \) are used with Eq. (1.6.3) to interpolate the relative viscosity, \( \eta^\eta/\eta_0 \), at the other volume fractions keeping the shear rate unchanged.

Eq. (1.6.3) can be applied in a wide range of shear rates, however, fitting parameters \([\eta]\) and \( \gamma_m \) change with shear rate.

Shear rate dependency of the effective viscosity in Newtonian flow behaviour has been suggested for use in the following form (Krieger, 1986)

\[ \frac{\eta^\eta - \eta_l}{\eta_2 - \eta_l} = \left(1 + \frac{\sigma}{\sigma_c}\right)^{-1}. \]  

(1.6.4)

Eq. (1.6.4) can be converted to the dimensionless form as

\[ \frac{\eta^\eta/\eta_0 - \eta_{lr}}{\eta_{2r} - \eta_{lr}} = \left(1 + \frac{\sigma}{\sigma_c}\right)^{-1}, \]  

(1.6.5)

here \( \eta_{2r} \) and \( \eta_{lr} \) are two new fitting parameters, the low- and high-shear limiting viscosity.

Krieger- Dougherty Eq. (1.6.3) is widely used for description of the dependence of the effective viscosity of suspension on the volume fraction of suspensions. It is necessary to
notice that the derivation of this equation is rather semi-empirical and does not reveal a physical meaning of fitting parameters $[\eta]$ and $\gamma_m$. This equation (as well as a number of other approaches) does not take into account formation of cluster (doublets, triplets and so on) in suspensions. Clustering is a result of colloidal and hydrodynamic interaction and is taken into account within this thesis.

The phenomenon of shear-thickening (or dilatancy) has been considered by Barnes (Barnes, 1989). He concludes, at a high Reynold's (high shear rate) number the viscosity of suspensions increases with applied shear rate. We hope that our method will give us in the future a possibility of explaining this phenomenon based on the consideration of cluster formation. Influence of cluster formation on viscosity of suspension and dilatancy have also been investigated by (Quemada, 1998a, 1998b, 1998c), (Quemada & Berli, 2002).

1.7 Viscosity of emulsions

The relative viscosity of a emulsion, $\eta_{\text{eff}} / \eta_0$, having negligible colloidal interactions can be expressed in the form of a rheological equation of state (Choi, and Krieger, 1986b)

$$\frac{\eta_{\text{eff}}}{\eta_0} = f\left( \frac{\eta_d}{\eta_0}, \gamma, Ca, Re \right).$$  \hspace{1cm} (1.7.1)

where $\eta_{\text{eff}}$ is effective viscosity of emulsion, $\eta_0$ is viscosity of dispersion medium, $\eta_d$ is viscosity of the liquid inside droplets. $Ca$ and $Re$ are dimension capillary and particle Reynolds number defined as

$$Ca = \frac{\eta_d r_d}{\mu},$$
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\[ \text{Re} = \frac{\rho_o \tau a^2}{\eta_0}, \]

where \( \tau \) is the shear rate, \( a \) is the droplet radius, \( \gamma \) is the interfacial tension, and \( \rho_o \) is the continuous-phase density.

At low capillary numbers \( \text{Ca} \rightarrow 0 \) and under creeping flow conditions \( \text{Re} \rightarrow 0 \), the relative viscosity of unflocculated/unaggregated emulsion can be written (Choi, and Krieger, 1986b)

\[ \frac{\eta^{\text{eff}}}{\eta_0} = f \left( \frac{\eta_d}{\eta_0}, \gamma \right) \quad (1.7.2) \]

At small particle volume fraction a particular form of Eq. (1.7.2) has been suggested by (Taylor, 1932) as

\[ \frac{\eta^{\text{eff}}}{\eta_0} = 1 + \frac{5 \eta_d + 2}{\eta_0} \frac{\eta_d}{\eta_0} \gamma. \quad (1.7.3) \]

To take into account the hydrodynamic interaction between the neighbouring droplets (Choi, and Schowalter, 1975) derived the following equation

\[ \frac{\eta^{\text{eff}}}{\eta_0} = 1 + \frac{2 \left[ 5 \frac{\eta_d + 2}{\eta_0} - \left( \frac{\eta_d - 1}{\eta_0} \right)^2 \gamma^2 \right]}{4 \left( \frac{\eta_d}{\eta_0} + 1 \right) - 5 \left( \frac{\eta_d}{\eta_0} + 2 \right) \gamma + 42 \frac{\eta_d}{\eta_0} \gamma^2 - 5 \left( \frac{\eta_d - 2}{\eta_0} \right) \gamma^3 + 4 \left( \frac{\eta_d - 1}{\eta_0} \right) \gamma^4} \gamma, \quad (1.7.4) \]

(Yaron, and Gal-Or, 1972) used the cell model and arrived to the following equation

\[ \frac{\eta^{\text{eff}}}{\eta_0} = 1 + \frac{5.5 \left[ \frac{7}{4} \gamma^3 + 10 - \frac{84}{11} \gamma^2 + 4 \frac{\eta_0}{\eta_d} \left( 1 - \gamma^3 \right) \right]}{10 \left( 1 - \gamma^3 \right) - 25 \gamma \left( 1 - \gamma^2 \right) + 10 \frac{\eta_0}{\eta_d} \left( 1 - \gamma \right) \left( 1 - \gamma^3 \right)} \gamma, \quad (1.7.5) \]
Starting from Taylor’s Eq. (1.7.3) and using the mean field approximation (Phan-Thien, and Pham, 1997) have developed an equation for the effective viscosity of unflocculated/unaggregated emulsions

\[ \left( \frac{\eta_{\text{eff}}}{\eta_0} \right)^{2/5} \left[ \frac{2 \eta_{\text{eff}} + 5 \eta_d}{\eta_0} \right]^{3/5} \] = \frac{1}{1 - \gamma}. \]  

Previous dependencies (1.7.3)-(1.7.6) agree reasonably well with available experimental data at low volume fraction of droplets and deviate substantially at intermediate and high volume fractions.

As it has been mentioned, all the equations above do not take into account flocculation, which is responsible for the most part for the effective viscosity of concentrated emulsion, as shown below in this thesis. Below is suggested a new method which allows us to take the influence of flocculation on the effective viscosity of emulsions.

**1.8 Permeability of porous media**

Permeability, heat conductivity and diffusion of porous and dispersed media are very important parameters for the design of chemical reactors and a number of applications of these processes. Permeability is an essential parameter for processes of filtration of liquids and gases.

Different models are used for the calculation of the permeability of porous media. The most frequently used model is the Darcy model (Scheidegger, 1974), (Darcy, 1856). This model is based on the following equation

\[ U = -\frac{kD}{\eta_0} \nabla p, \]  

(1.8.1)
where $\eta_0$ is the viscosity of the liquid, $U$ is the velocity of the liquid in the porous medium, $p$ is the pressure, $k_D$ is the permeability.

Various models are used to calculate the permeability dependency on the porous medium properties (Wong, 1984, 1994). According to (Koponen, Kataja, and Timonen, 1997) the porous medium is envisaged as a layer of solid material with straight parallel tubes of fixed cross-sectional shape intersecting the sample. Within this model the permeability is given as

$$k_D = \frac{\phi^3}{cS^3}, \quad (1.8.2)$$

where $c$ is the Kozeny coefficient which depends on the cross section of the capillaries, $\phi$ is the porosity, $S$ is the specific surface area, which gives the ratio of the total internal interfacial area to the total volume. In the case of straight cylindrical capillaries $c = 2$.

A common characteristic of any material transported in porous media is that the actual path followed by the transport material is microscopically very complicated or "tortuous" (Carman, 1937, 1956), (Scheidegger, 1974), (Bear, 1972), (Dullien, 1979). The simplest way to introduce the tortuosity in the capillary model is to allow the tubes to be inclined in such a way that the axes of each capillary form a fixed angle $\theta$ with the normal of the surface of the material (while the angles, $\theta$, of the capillaries are randomly distributed (Koponen, Kataja, and Timonen, 1997). In this case the permeability becomes

$$k_D = \frac{\phi^3}{cS^2\zeta^2}, \quad (1.8.3)$$

where $\zeta = 1/\cos \theta$ is the tortuosity of the porous medium.
According to the Carman-Kozeny model (Koponen, Kataja, and Timonen, 1997) the permeability $k_D$ expresses as a function of the hydraulic radius $m$ and the total porosity $\phi$:

$$k_D = \frac{\phi m^2}{k_{koz}},$$  \hspace{1cm} (1.8.4)

where $\phi = 1 - \gamma$. Here $k_{koz}$ is the Kozeny constant.

(Kats, and Thompson, 1986) proposed a simple relationship between the permeability and the conductivity $s$ starting from percolation concepts:

$$k_D = c_1 l_c^2 \frac{s}{s_0},$$  \hspace{1cm} (1.8.5)

where $s$ is the conductivity of the rock saturated with a brine solution of conductivity $s_0$ (the ratio $F = s_0/s$ is also called the formation factor).

In the formulation in (Katz and Thompson, 1986), $l_c$ is a unique transport length scale related to the threshold pressure in a mercury injection experiment in a porous medium with a broad pore size distribution. However, $l_c$ is well defined only when the porous medium can be modeled as a distribution of cylindrical pores.

(Johnson, Koplic, and Schwartz, 1986) introduced a new geometrical parameter $\Lambda$, related to dynamically connected pore sizes and was measured as an effective pore volume-surface area ratio defined in terms of the electrical potential of the steady current flow.

The parameter $\Lambda$ introduced by (Johnson, Koplic, and Dashen, 1987) has been used to describe the effects of an internal boundary layer on a variety of processes, including Stokes flow and Darcy permeability.
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\[ k_D = C \frac{A^2 s}{8 s_0}, \]  

(1.8.6)

where \( C \) is a constant. This constant is equal to one in the case of an array of non-intersecting capillaries.

In (Saeger, Scriven, and Davis, 1991) also pointed out that neither the rotational velocity field inside a porous medium nor any integral quantity related to the velocity can be accurately derived from the solution of the Laplace equation for current flow in static field.

In (Hilfer, 1991, 1992, 1996) an attempt was made to give a theoretical explanation of the relation between the permeability and the formation factor through the introduction of the statistical characterisation of pore size geometry in terms of local percolation probability. Once again he stressed the formal similarity between the permeability and the conductivity.

Extensive literature has been developed on the subject of flow through packed beds. For packed beds of uniform spheres (Happel, and Brener, 1965) deduced the following dependency of the effective permeability on radius of particles \( a \) and porosity \( \phi \):

\[ k_D = \frac{2}{9} \frac{3 - 9 (1 - \phi)^{1/3} + 2 (1 - \phi)^{5/3} - 3 (1 - \phi)^2}{3 + 2 (1 - \phi)^{5/3}} \cdot \frac{a^2}{1 - \phi}. \]  

(1.8.7)

The Kozeny equation may be rewritten in the case of packed beds of the uniform spheres as (Happel, and Brenner, 1965)

\[ k_D = \frac{\phi^3 a^2}{8 (1 - \phi)^3 k_{loc}}. \]  

(1.8.8)
Darcy equations are of the first order, however, Navier-Stokes equations are of the second order. The latter means that the flow inside and outside the porous medium cannot be matched on their interface (Vasin, Starov, and Fillipov, 1996). The Brinkman equations have been introduced (Brinkman, 1952) to overcome this problem. These equations are introduced for the description of the flow in porous media. According to this model

\[-\nabla p + \eta_B \Delta U - \frac{\eta_0}{k_B} U = 0,\]

(1.8.9)

where $\eta_B$ is the effective viscosity of the liquid in the porous medium, $k_B$ is the permeability. The Eq. (1.8.1) or (1.8.4) should be coupled with the continuity equation:

\[\text{div} U = 0.\]

(1.8.10)

Brinkman Eqs. (1.8.9) are of the second order, but a new semi-empirical coefficient the effective viscosity, $\eta_B$, has been introduced.

It is suggested that average viscosity of the liquid in the porous structure differs from viscosity of the pure liquid (Brinkman, 1947). It has been deduced in (Koplik, and Levine, 1983) that the effective viscosity, $\eta_B$, is lower than the viscosity of the liquid outside the porous media.

Our consideration shows that at the moment there is no agreement even on the value of the effective viscosity in Brinkman Eqs. (1.8.4). We suggest below in our thesis a new method of calculation of both permeability and effective viscosity in porous media. It is shown that both these dependences can be determined in a self-consistent way and cannot be determined separately.

1.9 Elastic properties of composite materials
Various methods have been proposed to derive the macroscopic properties of composite materials such as rocks (Watt, Davies, and O'Connel, 1976), (Thorpe, and Jasiuk, 1992), (Orozco, Gan, and Hewen, 2002). In (Cleary, Chen, and Lee, 1980) different applications of self-consistent approximation method are summarised. In (Kantor, and Webman, 1984) elastic properties of randomly percolated system have been investigated. Chapmen and Higdon (Chapman, and Higdon, 1994) have recently deduced elastic properties of a composite material built up by a three-dimensional array of overlapping spheres using the collocation method based on Kelvin's general solution of the elasticity equations. Day et al. (Day, et al., 1992) calculated the elastic properties of a porous medium built up by circular holes using a discretised-spring scheme.

Effective elastic and viscoelastic properties of composite materials have been investigated in (Christensen, 1979) using the cell method. The cell contains the same volume fraction of inclusions as the non-homogenous medium around. According to the cell model the non-homogenous medium outside the cell is substituted by an effective homogeneous medium with effective properties to be determined. Effective properties can be obtained as the result of solution of the boundary problem with the boundary conditions imposed at the boundary of the cell.

Effective elastic properties of composite materials have been investigated in (Pobedria, 1984) as follows. Equations of elasticity have been solved exactly for cases when all non-homogeneity varies in only one direction (lamellar materials and material with spherical symmetry).

Effective modules of composite materials at low volume fraction of inclusions have been calculated by (Russel, and Acrivos, 1972).

Methods of calculation of the effective elastic coefficients of the composite material using statistical technique have been developed in (Shermergor, 1977), (Khoroshun,
Maslov, Shikulda, and Nasarenko, 1993). According to this approach, elasticity coefficients, \( C_{\mu\nu} \), are considered as random functions of co-ordinates. Below we follow (Shermogor, 1977) and (Khoroshun, Maslov, Shikulda, and Nasarenko, 1993). Elastic Green functions, \( G_{mk} \), are determined by the following differential equation

\[
\sum_{j=1}^{3} \sum_{n=1}^{3} \sum_{m=1}^{3} C_{\mu\nu} \frac{\partial G_{mk}}{\partial x_j \partial x_n} (x^{(1)}_j - x^{(2)}_j) + \delta (x^{(1)}_i - x^{(2)}_i) \delta_{ik} = 0 .
\]

Eq. (1.9.1) can be transformed using equations of Betti (Pobedria, 1995) to the stochastic integral equations with respect to fluctuation of deformation, \( \varepsilon^0 \) (where \( \varepsilon^0 = \varepsilon - \langle \varepsilon \rangle \)),

\[
\varepsilon^{(1)} = K (x^{(1)} - x^{(2)}) \cdot (C^{(2)} - C^{m}) \cdot \langle \varepsilon \rangle + \varepsilon^{(2)} ,
\]

(1.9.2)

where \( K \) is an integral operator, \( \langle \cdot \rangle = \frac{1}{V} \int \cdots \cdot dv \). Superscripts (1) and (2) show that the corresponding values are taken in points 1 and 2, respectively. Superscript \( m \) shows that the corresponding value is taken in the matrix (not in the inclusion). The most frequently used method of solution of the resulting equations is so-called “linearization method”. Smallness of the difference \( C^{(2)} - C^{m} \) is assumed according to the “linearization method”.

Thus,

\[
C^{(2)} - C^{m} = \zeta \Lambda^{(2)} ,
\]

(1.9.3)

where \( \zeta \) is a small fixed parameter. The solution can be represented as a sum

\[
\varepsilon^{(0)} = \sum_{n=0}^{\infty} \zeta^* \varepsilon_n .
\]

(1.9.4)

Substitution of Eqs. (1.9.3), (1.9.4) into Eq. (1.9.2) and equating coefficients with the same power of \( \zeta \) gives the sequence of linear equations:

\[
\varepsilon^{(0)} = 0 ; \; \varepsilon^{(1)} = K (x^{(1)} - x^{(2)}) \Lambda^{(2)} (\langle \varepsilon \rangle + \varepsilon^{(0)}),
\]

\[
\varepsilon^{(2)} = K (x^{(1)} - x^{(2)}) \Lambda^{(2)} \varepsilon^{(1)} , \ldots , \varepsilon^{(n)} = K (x^{(1)} - x^{(2)}) \Lambda^{(2)} \varepsilon^{(n-1)} , \ldots
\]

(1.9.5)

Using Eqs. (1.9.4), (1.9.5) the following equation can be deduced
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Expression for macro-stresses can be now written as

\[ \langle \sigma \rangle = \langle C^{(0)} \varepsilon^{(0)} \rangle = \langle C \rangle \langle \varepsilon \rangle + \langle (C^{(0)} - \langle C \rangle) (\varepsilon^{(0)} - \langle \varepsilon \rangle) \rangle. \]  

(1.9.7)

Substitution Eq. (1.9.5) into Eq. (1.9.7) gives an expression for tensor of effective elastic modules

\[ C^{(n)} = (C) + \sum_{m=2}^{n} K(x^{(0)} - x^{(2)}). K(x^{(2)} - x^{(0)}). K(x^{(n-1)} - x^{(n)}) \langle (C^{(0)} - \langle C \rangle) (C^{(2)} - \langle C \rangle) (C^{(n)} - \langle C \rangle) \rangle. \]

The latter expression shows that in this case under consideration (as in the averaging method) the latter method cannot give explicit dependency of effective coefficients on the volume fraction of inclusions.


Below, we apply our new method to the calculation of the effective elastic properties of composite materials. The resulting equations give better agreement with experimental data than the Mori-Tanaka method.

1.10 Discussion

Averaging and statistical methods give the possibility to deduce average equations, which describe transport process in porous and dispersed media. Resulting differential equations include one or more effective coefficients, whose dependency is on volume fraction of the dispersed phase to be determined. Unfortunately, neither of these methods gives the
direct possibility to calculate dependences of effective coefficients on the volume fraction of dispersed phase: other methods should be involved.

It is shown above that the Bruggeman method (Bruggeman, 1935) is the most promising method for the calculation of the dependencies of the effective coefficients. Unfortunately neither Bruggeman himself in the original paper (Shemergerog, 1977) nor in the subsequent publications presents direct mathematical derivation of this. That is, it was always doubtful if any result deduced using Bruggeman methods are physically meaningful and if ‘yes’ how this method can be extended to other more complex situations.

Below we suggest the proper mathematical derivation of the Bruggeman method, which is applied to various problems and compared with available experimental data.

In the case of suspensions and emulsions our modified method is coupled with a completely new idea: consideration of cluster formation (flocculation) in suspensions/emulsions. It is shown that in the case of suspensions our method gives a modification of the well-known Dougherty- Krieger equation. In the case of emulsions our method results in new theory of the effective viscosity of emulsions.
Chapter 2 EFFECTIVE DIFFUSION IN POROUS MEDIA

2.1 Introduction

The Bruggeman's method (referred also as the differential method, which is essentially a version of a mean field approximation) has been successfully applied to calculation of the effective dielectric constants of the suspensions and emulsions (Dukhin, and Shilov, 1974). The comparison of the different theoretical methods is given in Figure 2.1 (from (Dukhin, and Shilov, 1974)). The curve 3 In Figure 2.1 according to the Bruggeman equation (Bruggeman, 1935) shows the best agreement with the available experimental data. Unfortunately, neither in the original paper of (Bruggeman, 1935) nor in the subsequent papers (see for example (Christensen, 1990)) clear mathematical base of this method has not been presented, that did not allow a further application of this very promising method.

The properly modified version of Bruggeman's method free of the mentioned above disadvantage is presented below in this section. The new version of the Bruggeman method is applied to the calculation of the dielectric permeability of suspensions/emulsions, which gives the equation identical to that deduced by Bruggeman (Bruggeman, 1935).

This derivation gives us the possibility to be sure that (1) our modified method gives the same result in the case of the calculation of dielectric permeability of suspensions/emulsions, (2) can be applied to other problems. The first of them is the calculation of the effective diffusion coefficient in porous media.

The idea of the modified Bruggeman's method is illustrated below using the calculation of the dependency of an effective dielectric constant of emulsions/suspensions on the volume fraction of the dispersed phase, $\gamma$ (Figure 2.2). This example shows that the application of our modified method results in exactly the same Bruggeman equation. Below we consider the case of emulsion though the same consideration can be applied to suspensions.

Let $\varepsilon^m$, $\varepsilon^p$ are the dielectric constants of the dispersion phase and droplets, respectively; $\varepsilon^{eff}(\varepsilon^m, \varepsilon^p, \gamma)$ is the dependency of the effective dielectric constants on the dielectric constants of droplets, the dispersion phase and the volume fraction of droplets. Let us mark
randomly a small number $\delta n$ of droplets (top part A on Figure 2.2). The rest of emulsion containing non-marked droplets is replaced by the effective medium having the effective dielectric constant $\varepsilon^\text{eff}(\varepsilon^e, \varepsilon^p, \gamma - \delta \gamma)$. Let the volume fraction of the marked droplets in the new emulsion (bottom part B on Figure 2.2) be $\delta \theta$. This volume fraction is obviously different from $\delta \gamma$ (see Appendix 2 for details). The latter means that the dielectric constant of the emulsion B (Figure 2.2) is $\varepsilon^\text{eff}(\varepsilon^e, \varepsilon^p, \gamma - \delta \gamma, \varepsilon^p, \delta \theta)$. Obviously, the dielectric constant does not depend on the way of its calculation, i.e. the dielectric constants of emulsions A and B are equal. It yields the following equation for the determination of the dependency of the effective dielectric constants of the emulsion on the volume fraction of droplets.

$$
\varepsilon^\text{eff}(\varepsilon^e, \varepsilon^p, \gamma) = \varepsilon^\text{eff}(\varepsilon^e, \varepsilon^p, \gamma - \delta \gamma, \varepsilon^p, \delta \theta).
$$

The Taylor's series expansion of the right hand side of the latter equation and known solution for the dependency of the dielectric constant on the volume fraction of droplets in the case of small volume fraction (see Appendix 1 for details) results in a differential equation for $\varepsilon^\text{eff}(\varepsilon^e, \varepsilon^p, \gamma)$ determination. Solution of this equation coincides with the Bruggeman equation (1.5.1) for the dependency of the dielectric constants on the volume fraction of droplets.

### 2.2 Calculation of the dependency of the effective diffusion coefficient on porosity

Figure 2.3 presents a porous medium built up by impermeable spherical particles with a liquid (or a gas) in between. Molecular diffusion takes place in the space between particles. It has been mentioned above, that for an application of the modified Bruggeman's method the dependency of the effective diffusion coefficient on the volume fraction of particles at low volume fraction of particles is required (high porosity in the case under consideration). The effective coefficient of the molecular diffusion in the porous medium built up by impermeable spherical particles in the case of high porosity is calculated below using the cell model (Figure 2.4).
The unit cell of radius $R$ is presented in Figure 2.4. It includes an impermeable spherical particle of radius $a$ in the centre and the dispersion medium around. The cell is surrounded by the effective medium with unknown effective diffusion coefficient, $D_{\text{eff}}$. The radius of the cell, $R$, is given by the following condition:

$$y = \frac{4\pi a^3}{3} / \frac{4\pi R^3}{3} = \left(\frac{a}{R}\right)^3, \quad R = \frac{a}{\gamma^{1/3}},$$

where $\varphi = 1 - \gamma$ is the porosity, $\gamma$ is the volume fraction of the particles. The volume fraction and the flux of the molecular substance (which is diffusing between particles) should be continuous on the boundary of the cell. On the boundary of the particle the flux in the direction perpendicular to the boundary of particle should be zero (impermeable particle). The concentration profile both inside the cell and outside obeys the Laplace equation. The solutions of the corresponding problem (see Appendix 1) results in the Maxwell equation (Maxwell J.C., 1954).

$$D_{\text{eff}} = \left[1 - \frac{3\gamma}{\gamma+2}\right] D^m, \quad (2.2.1)$$

where $D^m$ is the diffusion coefficient in the interparticle space, $D_{\text{eff}}$ is the effective diffusion coefficient in the porous medium.

In the case of the very low volume fraction of particles ($\delta \gamma << 1$) Eq. (2.2.1) becomes:

$$D_{\text{eff}} = D^m + A_{\text{diffusion}}(D^m) \delta \gamma, \quad (2.2.2)$$

where

$$A_{\text{diffusion}}(D^m) = -1.5 D^m. \quad (2.2.3)$$

Below a modification of the Bruggeman's method briefly described in 2.1 Introduction is presented in more details.

Let us mark randomly some small number of particles in the porous medium (with volume fraction $\delta \theta << 1$). The porous medium can now be considered as the mixture of the small number of the marked particles surrounded by the effective porous medium built up by the non-marked particles and the liquid (or the gas). Thus, the effective diffusion coefficient can be expressed using two different ways:(i) using equation

$$D_{\text{eff}} = D(D^m, \gamma), \quad (2.2.4)$$
where $D(D^m, \gamma)$ is the dependency to be determined and (ii) using “the marked particles” with volume fraction $\delta \gamma$, surrounded by the effective porous medium with “not marked particles” with volume fraction $\gamma - \delta \gamma$. Diffusion coefficient inside this effective porous medium is $D(D^m, \gamma - \delta \gamma)$. The latter two definitions should give the same dependency of the effective diffusion coefficient. It yields the following equation for calculation of $D(D^m, \gamma)$:

$$D(D^m, \gamma) = D(D(D^m, \gamma - \delta \gamma), \delta \theta).$$  

(2.2.5)

Geometrical consideration (see Appendix 2) gives $\delta \theta = \frac{\delta \gamma}{1 - \gamma}$. Substitution of the latter expression into Eq. (2.2.5) and using first two terms of the Taylor series in the right hand side (small parameters $\delta \gamma$ and $\delta \theta$) results in the following differential equation (see, Appendix 2 for details):

$$\frac{dD_{eff}}{d\gamma} = A_{diffusion}\left(\frac{D_{eff}}{1 - \gamma}\right)$$  

(2.2.6)

with the boundary conditions

$$D_{eff}\bigg|_{\gamma=0} = D^m.$$  

(2.2.7)

The problem (2.2.3), (2.2.6), (2.2.7) has the following solution:

$$D_{eff} = D^m(1 - \gamma)^{1/2}.$$  

(2.2.8)

The comparison of the latter dependency (2.2.8) (dashed curve) with the known theoretical relations (continuous lines) and available experimental data (Whitaker., 1999) is presented in Figure 2.5. Comparison shows that the relation (2.2.8) gives the very good approximation of the experimental data.
2.3 Appendix 1

**Calculation of the effective diffusion coefficient using cell method**

Let us consider a porous medium built up by the spherical impermeable particles (Figure 3) filled with a liquid (or gas). The effective coefficient of the molecular diffusion in this porous medium is calculated below using the cell model. The unit cell of radius $R$ is presented in Figure 4. It includes an impermeable spherical particle of radius $a$ in the centre and the dispersion medium around. The cell is surrounded by the effective medium with unknown effective diffusion coefficient, $D_{\text{eff}}$. The radius of the cell, $R$, is given by the following condition:

$\frac{4\pi}{3} a^3 / \frac{4\pi}{3} R^3 = \left( \frac{a}{R} \right)^3 = \frac{a}{R^3}$, where $\varphi = 1 - \gamma$ is the porosity, $\gamma$ is the volume fraction of the particles.

Diffusion of some admixture is taken place in the space between particles, which are impermeable for this admixture. Far from the cell the gradient of concentration of the admixture is constant (see condition (2.3.7)). On the boundary of the cell the concentration and the flux of the admixture are continuous. On the boundary of the particle the flow in the direction perpendicular to the boundary of the particle is zero (impermeability condition).

The field of concentration outside and inside of the cell obeys to the Laplace equation:

\[
\Delta C_{\text{eff}} = 0, \quad r > R. \\
\Delta C_{m} = 0, \quad r < R.
\]

The boundary condition on the boundary of the particle of radius $a$ is

\[
\mathbf{n} \nabla C_{m} \bigg|_{r=a} = 0.
\]

The boundary condition on the boundary of the cell of radius $R$ are

\[
C_{m} \bigg|_{r=R} = C_{\text{eff}} \bigg|_{r=R} \tag{2.3.4}
\]

and

\[
D_{m} \nabla C_{m} \bigg|_{r=R} = D_{\text{eff}} \nabla C_{\text{eff}} \bigg|_{r=R} \tag{2.3.5}
\]

where $D_{m}$ is the diffusion coefficient in the dispersion medium, $D_{\text{eff}}$ is the effective diffusion coefficient to be determined.
The solution of the Eq. (2.3.1) can be presented in the following form:

$$C^{eff} = g(r) \cos \theta, \quad r > R.$$  \hspace{1cm} (2.3.6)

Far from the cell the constant gradient of admixture concentration is imposed:

$$C^{eff} = C^{\infty} r \cos \theta, \quad r < R,$$  \hspace{1cm} (2.3.7)

here $C^{\infty}$ is the constant describing concentration field far from the cell. Comparison of the latter two equations shows: $g(r) = C^{\infty}$.

The solution of Eq. (2.3.2) can be presented in the same form as (2.3.6):

$$C_{m} = f(r) \cos \theta, \quad r < R,$$

Substitution of the latter expression in Eq. (2.3.2) gives:

$$C_{m} = \left( G r + \frac{Q}{r^2} \right) \cos \theta.$$  \hspace{1cm} (2.3.8)

here $G$ and $Q$ are integration constants. The unknown effective diffusion coefficient $D^{eff}$ can be calculated using three boundary conditions (2.3.3)-(2.3.5). Indeed, the concentration profiles outside and inside the cell, (2.3.8), (2.3.7), includes two integration constants, $G$ and $Q$, as well as the unknown effective diffusion coefficient, $D^{eff}$. That is, we have system of three equations for three unknowns. This system has the following solution:

$$Q = \frac{C^{\infty} a^3}{2 + \gamma}, \hspace{1cm} (2.3.9)$$

$$G = \frac{2C^{\infty}}{2 + \gamma}, \hspace{1cm} (2.3.10)$$

$$D^{eff} = \left( 1 - \frac{3\gamma}{\gamma + 2} \right) D^{m}. \hspace{1cm} (2.3.11)$$

Eq. (2.3.11) has been obtained by (Maxwell, 1954) in a different approach.

2.4 Appendix 2

Calculation of the diffusion coefficient using the modified Bruggeman method

The volume fraction of particles is defined as
Viscosity of concentrated suspensions and properties of porous media

\[
\gamma = \frac{V^p}{V},
\]  

(2.4.1)

here \( V \) is the total volume of the porous medium, \( V^p \) is the total volume of particles.

The unknown dependency of the effective diffusion coefficient on the fraction of the particles is

\[
D^{\text{eff}} = D(D^m, \gamma),
\]  

(2.4.2)

which is calculated below.

In the case \( \gamma = 0 \) Eq. (2.4.2) is reduced to

\[
D^m = D(D^m, 0).
\]  

(2.4.3)

If the fraction of the particles is small, \( \delta \gamma < 1 \), the Eqs. (2.4.2) and (2.4.3) result in

\[
D^{\text{eff}} = D^m + A^{\text{diffusion}}(D^m) \delta \gamma,
\]  

(2.4.4)

where \( A^{\text{diffusion}} \) is the new function, which is determined earlier according to Eq. (2.4.3).

Let us mark randomly some small number of particles, and remaining particles are left non-marked. The volume fraction of marked particles \( \delta \theta \) is

\[
\delta \theta = \frac{\delta V}{V},
\]  

(2.4.5)

here \( \delta V \) is the volume of marked particles. The volume fraction of the non-marked particles, \( \gamma - \delta \gamma \) is

\[
\gamma - \delta \gamma = \frac{V^p - \delta V}{V - \delta V}.
\]  

(2.4.6)

Eqs. (2.4.1), (2.4.5), (2.4.6) result in the following relation between volume fractions

\[
\delta \gamma = (1 - \gamma) \frac{\delta \theta}{1 - \delta \theta},
\]  

or, keeping only first order small terms

\[
\delta \theta = \frac{\delta \gamma}{1 - \gamma}.
\]  

(2.4.7)

The porous structure can be considered now as a mixture of marked particles surrounded by the rest of the porous structure built up by non-marked particles. Thus, the effective diffusion coefficient can be expressed in two different ways: (i) using definition (2.4.2) and (ii) using
"marked particles" with volume fraction $\delta\theta$, surrounded by an effective medium of "non-marked particles" with volume fraction $\gamma - \delta\gamma$. Unknown diffusion coefficient in this medium according to definition (2.4.2) is $D(D^n,\gamma-\delta\gamma)$. As the effective diffusion coefficient does not depend on the way of its calculation, it yields the following equation:

$$D(D^n,\gamma) = D(D(D^n,\gamma-\delta\gamma),\delta\theta). \quad (2.4.8)$$

Decomposition of Eq. (2.4.8) using Taylor's series and saving terms of the first order proportional to $\delta\gamma$ and $\delta\theta$, gives

$$D(D(D^n,\gamma-\delta\gamma),\delta\theta) = D(D(D^n,\gamma),0) + \frac{\partial D(D(D^n,\gamma-\delta\gamma),\delta\theta)}{\partial \delta\gamma} \bigg|_{\delta\theta=0} \delta\gamma + \frac{\partial D(D(D^n,\gamma-\delta\gamma),\delta\theta)}{\partial \delta\theta} \bigg|_{\delta\gamma=0} \delta\theta. \quad (2.4.9)$$

Eq. (2.4.9) can be simplified using condition (2.4.3)

$$D(D(D^n,\gamma),0) = D(D^n,\gamma). \quad (2.4.10)$$

The combinations of Eqs. (2.4.3), (2.4.2) results in

$$\frac{\partial D(D(D^n,\gamma-\delta\gamma),\delta\theta)}{\partial \delta\theta} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = \frac{\partial D(D^n,\gamma,\delta\theta)}{\partial \delta\theta} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = \frac{\partial D(D^\text{eff},\gamma)}{\partial \delta\theta} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = A^\text{diffusion}(D^\text{eff}). \quad (2.4.11)$$

Condition (2.4.3) gives

$$\frac{\partial D(D(D^n,\gamma-\delta\gamma),\delta\theta)}{\partial \delta\gamma} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = \frac{\partial D(D(D^n,\gamma-\delta\gamma),0)}{\partial \delta\gamma} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = \frac{\partial D(D^n,\gamma-\delta\gamma)}{\partial \delta\gamma} \bigg|_{\delta\gamma=0}^{\delta\gamma=0} = \frac{\partial D(D^n,\gamma)}{\partial \gamma} = \frac{d D^\text{eff}}{d \gamma}. \quad (2.4.12)$$

Substitution of Eqs. (2.4.10)-(2.4.12) into Eq. (2.4.9) gives

$$0 = A^\text{diffusion}(D^\text{eff}) \delta\theta - \frac{d D^\text{eff}}{d \gamma} \delta\gamma. \quad (2.4.13)$$

Substitution of Eqs. (2.4.4), (2.4.8) into Eq. (2.4.13) result in the following differential equation

$$\frac{d D^\text{eff}}{d \gamma} = \frac{A^\text{diffusion}(D^\text{eff})}{1-\gamma}, \quad (2.4.14)$$
with boundary condition (2.4.3):

\[ D^{\text{eff}} \big|_{\gamma=0} = D^{\alpha}. \]  

(2.4.15)
Figure 2.1 Effective dielectric constant of emulsions on the droplet volume fraction (Dukhin, and Shilov, 1974). The symbols are available experimental data from (Dukhin, and Shilov, 1974); curves 1-5 according to:

1 Rayleigh;
2 Böttcher;
3 Bruggeman equation;
4 Kubo Nikamura;
5 Wiener
\[ \varepsilon^{\text{eff}}(\varepsilon^m, \varepsilon^p, \gamma) = \]
\[ = \varepsilon^{\text{eff}}(\varepsilon^{\text{eff}}(\varepsilon^m, \varepsilon^p, \gamma - \delta \gamma), \varepsilon^p, \delta \theta) \]

Figure 2.2 Schematic explanation of the modified Bruggeman’s method (see text for details).
Figure 2.3 Porous medium built up by impermeable particles. Liquid or the gas / vapor between particles contains an admixture, which diffuses in between particles.
Figure 2.4 The cell method for calculation of the effective diffusion coefficient. Spherical impermeable particle of radius $a$ is inside a spherical cell of radius $R$. The cell is surrounded by the medium with the effective diffusion coefficient $D^{\text{eff}}$. 
Figure 2.5 The dependence of the effective diffusion coefficient $D_{eff}$ on the particle volume fraction $\gamma$ (Whitaker, 1999). The solid lines correspond to the models of the different authors; experimental data from (Whitaker, 1999). The dashed line corresponds to our Eq. (2.2.8).
LIST OF SYMBOLS

$\varepsilon$  dielectric permeability
$\gamma$  volume fraction of the dispersed phase
$\phi = 1 - \gamma$  porosity
$D$  diffusion coefficient
$V$  volume
$\delta \theta$  volume fraction of marked particles
$a$  radius of particles
$R$  radius of cell
$A^{\text{diffusion}}$  function defined by Eq. (2.2.2)
$\Delta$  Laplacian
$C$  concentration
$V$  derivative
$r, \theta$  polar coordinates

Superscripts

$m$  matrix
$p$  particles
$\text{eff}$  effective
$\infty$  boundary conditions at the infinity
Chapter 3 VISCOSITY OF CONCENTRATED SUSPENSIONS: INFLUENCE OF CLUSTER FORMATION

3.1 Introduction

Dispersed particles can form clusters even at sufficiently low volume fractions. Colloidal and hydrodynamic forces are responsible for this phenomenon and these forces determine both structure and size of clusters. We assume that viscosity of concentrated suspension is completely determined by cluster size distribution, no matter if clusters form under the action of colloidal, hydrodynamic interactions or shear rates. Based on this assumption an equation, which describes dependency of viscosity on a volume fraction of dispersed particles taking into account cluster formation, is deduced. Under special restrictions the deduced dependency coincides with the well-known Dougherty-Krieger's equation except for a clear physical meaning of parameters entered. Our consideration shows that Dougherty-Krieger's equation has deeper physical background than it has been supposed earlier. Experimental verification of the suggested model shows a good agreement with the theory predictions and proves a presence of clusters even at low volume fractions of dispersed particles.

There is no need to emphasize an importance of concentrated suspensions for industrial applications as well as a number of theoretical approaches used for description of viscosity dependence on volume fraction of dispersed particles (Russel, Saville, and Schowalter, 1989). Colloidal and hydrodynamic interactions between particles result in formation of doublets, triplets and higher clusters (Russel, Saville, and Schowalter, 1989). Aggregation of particles is accompanied by destruction of aggregates caused by finite depth of potential well and/or shear stress applied. As a result a distribution of cluster sizes is formed in the suspension. Presence of clusters influences drastically viscosity of concentrated suspensions. Computer simulation is a useful tool for exploring the relationship between interparticle interactions and suspension rheological properties. Clustering and restructuring of colloidal systems under shear is observed in a number of computer simulations (Bosis, and Brady, 1984), (Heyes, and Melrose, 1993), (Lodge, and Heyes, 1999), (Heyes, and Branka, 1999).
However, computer simulations can not for substitute analytical modeling and interactions between these two types of modeling can provide a new insight. Here we present a new analytical method, which allows deducing a dependency of viscosity on particle volume fraction to be deduced taking into account cluster formation. Our new method taking into account cluster formation is used below.

### 3.2 Theory

Let us consider a suspension of volume $V$, which contains $N$ single spherical particles. Volume fraction of particles, $\gamma$, is

$$\gamma = \frac{v \cdot N}{V},$$  \hspace{1cm} (3.2.1)

where $v = \frac{4\pi}{3}a^3$, is the volume of a single particle and particle radius $a$, respectively. Let $n_i$, $i = 1, 2, 3, ...$ be a number of clusters of corresponding size in the volume $V$ and $\gamma_{i, \text{max}}$, $i = 1, 2, 3, ...$ be an averaged packing density of single particles inside clusters. $n_i$ is a number density of "clusters of size 1", that is, single particles, hence, $\gamma_{i, \text{max}} = 1$.

Volume fraction of clusters containing $i$ particles can be written as

$$\gamma_i = \frac{V_i}{V}, \quad V_i = \frac{i v n_i}{\gamma_{i, \text{max}}}, \quad i = 1, 2, 3, ...$$ \hspace{1cm} (3.2.2)

which satisfy the following mass conservation condition

$$\sum_{i=1}^{\infty} \gamma_i \gamma_{i, \text{max}} = \gamma.$$ \hspace{1cm} (3.2.3)

It is assumed below that the viscosity of the suspension is completely determined by cluster size distribution, that is, can be described by the following dependency

$$\eta(\eta_0, \gamma) = \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, ...],$$ \hspace{1cm} (3.2.4)

where $\eta_0$ is the viscosity of the pure liquid.

When all cluster volume fractions, $\gamma_i$, are zero, the suspension consists only of the pure liquid and Eq. (3.2.4) gives
\[ \eta_0 = \Psi(\eta_0, 0, 0, 0, \ldots), \quad (3.2.5) \]

which is used below.

When particle density, \( \gamma \), is small then all \( \gamma_i \) are also small and Eq. (3.2.4) can be written in accordance with Einstein's relation as

\[ \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] = \Psi[\eta_0, 0, 0, 0, \ldots] + 2.5 \sum_{i=1}^\infty \eta_0 A_i, \gamma_i, \quad (3.2.6) \]

where coefficients \( A_i, \quad i = 1, 2, 3, \ldots \) are deviations of friction coefficient of clusters with \( i \) particles from the corresponding value for solid particles. Obviously \( A_1 = 1 \). Coefficients \( A_i, \quad i = 1, 2, 3, \ldots \) are referred to below as friction coefficients for abbreviation. The meaning of friction coefficients can be understood using the following example. Let two spherical particles with the same diameter be considered: the first one is a solid particle, the second one is a particle composed of \( i \) smaller particles (a model of a cluster). The friction force exerted on each of two particles under consideration will be different if both particles are placed in a liquid flow. Let \( A_i \) be a ratio of the friction force in the case of the composed particle (cluster) to the corresponding force exerted to the solid particle. The friction force is changed in the case of the composed particle because of two reasons: (a) a solid surface exposed to the liquid flow is smaller than in the case of the solid particle, (b) the liquid flow partially penetrates inside the composed particle. Two mentioned trends, (a) and (b), change \( A_i, \quad i = 2, 3, \ldots \) values in different ways: because of the reason (a) these values decrease and increase because of the reason (b). That is, a complex interplay determines \( A_i, \quad i = 2, 3, \ldots \) values. Friction coefficients can be calculated based on theory developed in (Landau, Lifshits, 1959).

Deviation of cluster shapes from spherical is an additional cause of change of friction coefficient values (Happel, Brenner, 1965.).

It is obvious that parameters \( \gamma_{i,\text{max}}, A_i, \quad i = 2, 3, \ldots \) are functions of both colloidal, hydrodynamic interactions and applied shear stress.

Let a small amount of clusters, \( \Delta n, << n_i, \quad i = 1, 2, 3, \ldots \) be marked randomly in the whole volume of suspension. The suspension can be considered as a mixture of the marked clusters.
surrounded by a suspension of non-marked clusters. Volume fractions of the marked clusters, \( \Delta \theta_i, \quad i = 1,2,\ldots, \) are

\[
\Delta \theta_i = \frac{\Delta V_i}{V}, \quad \Delta V_i = \frac{i \Delta n_i}{\gamma_{i,\text{max}}}, \quad i = 1,2,\ldots
\]  

(3.2.7)

Volume fractions of non-marked clusters in the rest of the suspension are

\[
\gamma_i - \Delta \xi_i = \frac{V_i - \Delta V_i}{V - \sum_j \Delta V_j}, \quad i = 1,2,\ldots
\]

or keeping only first order terms:

\[
\Delta \xi_i = \frac{V_i - \Delta V_i}{V - \sum_j \Delta V_j} = \frac{\Delta \theta_i - \gamma_i \sum_{j=1}^{\infty} \Delta \theta_j}{1 - \sum_{j=1}^{\infty} \Delta \theta_j}, \quad i = 1,2,\ldots
\]  

(3.2.8)

Marked clusters are surrounded by the rest of the suspension, which is assumed to be a homogenous liquid with viscosity \( \Psi[\eta^0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \), where small volume fractions \( \Delta \xi_i, i = 1,2,\ldots \) in the latter expression are given by Eq. (2.8). Hence, viscosity of suspension can be expressed in two ways: according to Eq. (2.4) and considering the suspension as a mixture of marked and non-marked clusters:

\[
\eta = \Psi[\eta^0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots, \Delta \theta_1, \Delta \theta_2, \Delta \theta_3, \ldots] 
\]  

(3.2.9)

Right hand sides of Eqs. (2.4) and (2.9) should be equal, this gives

\[
\Psi[\eta^0, \gamma_1, \gamma_2, \gamma_3, \ldots] = \Psi[\eta^0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots, \Delta \theta_1, \Delta \theta_2, \Delta \theta_3, \ldots] 
\]  

(3.2.10)

A transformation of Eq. (3.2.10) is given in APPENDIX. The result is the following differential equation for dependence of viscosity of concentrated suspension, \( \eta \), on volume fraction of particles \( \gamma \)

\[
\frac{d\eta}{d\gamma} = 2.5 \eta \sum_{\gamma_i} A_i \frac{\gamma_i}{1 - \sum_{\gamma_i} A_i \gamma_i} \frac{d\gamma_i}{d\gamma}. 
\]  

(3.2.11)

Solution of Eq. (3.2.11) should satisfy boundary condition, which follows from Eq. (2.5)

\[
\eta(0) = \eta_0. 
\]  

(3.2.12)
Let us introduce the following averaged values

$$
\bar{A} = \frac{\sum r A_i \gamma_i}{\sum \gamma_i}, \quad \bar{\gamma}_{\text{max}} = \frac{\sum r_{\text{max}} \gamma_i}{\sum \gamma_i},
$$

(3.2.13)

which are an averaged resistance coefficient and averaged packing density of all clusters. Using Eq. (2.3) and definition of \( \gamma_{\text{max}} \) (according to Eq. (3.2.13)) we can conclude

$$
\bar{\gamma}_{\text{max}} = \frac{\gamma}{\sum r_i}, \quad \text{or} \quad \sum r_i = \frac{\gamma}{\bar{\gamma}_{\text{max}}},
$$

Substitution of the latter expression and (3.2.13) into Eq. (3.2.11) results in

$$
\frac{d\eta}{d\gamma} = 2.5\eta \left[ \frac{d\left( \frac{\gamma}{\bar{\gamma}_{\text{max}}} \right)}{d\gamma} + \frac{\bar{A} \gamma_{\text{max}} d\left( \frac{\gamma}{\bar{\gamma}_{\text{max}}} \right)}{1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}}} \right].
$$

(3.2.14)

Let us assume that \( \bar{A} \) is independent of volume fraction \( \gamma \). In this case the latter equation takes the following form

$$
\frac{d\eta}{d\gamma} = 2.5\eta \left[ \frac{d\left( \frac{\gamma}{\bar{\gamma}_{\text{max}}} \right)}{d\gamma} + \frac{\gamma_{\text{max}} d\left( \frac{\gamma}{\bar{\gamma}_{\text{max}}} \right)}{1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}}} \right]
$$

or

$$
\frac{d\eta}{d\gamma} = \frac{2.5\eta \bar{A} d\left( \frac{\gamma}{\bar{\gamma}_{\text{max}}} \right)}{1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}}} \quad \text{(3.2.15)}
$$

with boundary condition (3.2.12).

It is important to emphasise that \( \bar{\gamma}_{\text{max}} \) is not assumed to retain a constant value, independent of volume fraction \( \gamma \).

Solution of Eq. (3.2.15) with boundary condition (3.2.12) is
Viscosity of concentrated suspensions and properties of porous media

\[ \frac{\eta(\gamma)}{\eta_0} = \frac{1}{\left(1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}}\right)^{2.5A}}. \]  

Eq. (3.2.16) almost coincides with Dougherty-Krieger’s equation (Krieger, I.M., Dougherty, T.J., 1959), (Krieger, I.M., 1972), (Batchelor G.K, 1952)

\[ \frac{\eta(\gamma)}{\eta_0} = \frac{1}{\left(1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}}\right)^{[\eta]}/\bar{\gamma}_{\text{max}}}, \]  

where \([\eta]\) is an intrinsic viscosity. However, it is important to emphasize that \(\gamma_{\text{max}}\) in equation (3.2.16) is constant, whereas \(\bar{\gamma}_{\text{max}}\) can not be.

It is easy to conclude that Eqs. (3.2.16) and (3.2.17) coincide if we adopt

\[ \gamma_{\text{max}} = \bar{\gamma}_{\text{max}}, \quad [\eta] = \frac{2.5A}{\bar{\gamma}_{\text{max}}}. \]

It is necessary to stress here that in spite of a striking similarity of Eqs. (3.2.16) and (3.2.17) a physical meaning of parameters included in Eq. (3.2.16) is quite different from those used in Eq. (3.2.17). According to the theory developed above viscosity dependence on volume fraction is connected with cluster formation and this physical phenomenon is incorporated into Eq. (3.2.16).

If particles do not form clusters, that is, \(\gamma_i = \gamma; \quad \gamma_i = 0, i = 2,3,4,...\) and, hence, \(\bar{\gamma}_{\text{max}} = \bar{A} = 1\) should be adopted in Eq. (3.2.16), which gives

\[ \frac{\eta(\gamma)}{\eta_0} = \frac{1}{(1 - \gamma)^{2.5}}. \]  

The latter equation coincides with earlier obtained solution for the same case (3.2.8, 3.2.9): suspension of particles, which do not form clusters.
3.3 Comparison with known experimental data

A comprehensive review of experimental data on viscosity of concentrated suspensions is presented in (Thomas, 1965). In Figure 3.1 comparison of experimental data with predictions according to Eq. (3.2.18) (curve 1), and Eq. (3.2.16) (curves 2-4) is presented. Experimental points used in Figure 3.1 are specified in ref. (Thomas, 1965). Figure 3.1 shows that the whole array of experimental data can be described using Eq. (3.2.16) at different parameters $\varphi_{\text{max}}$ and $\overline{A}$: curve 4 ($\varphi_{\text{max}} = 0.56$, close to a simple cubic packing density; $\overline{A} = 0.72$); curve 3 ($\varphi_{\text{max}} = 0.65$, close to a cubic centered packing density; $\overline{A} = 0.67$), curve 2 ($\varphi_{\text{max}} = 0.73$, close to hexagonal packing density; $\overline{A} = 0.61$).

3.4 Results and discussion

Yeast suspensions at different low volume fraction were observed under microscope by Meireles and Molle (Starov, Zhdanov, Meireles, Molle, 2002). Results are presented in Figure 3.2 (a, b, c). All used volume fractions are low enough ($\gamma = 0.002$ in Figure 3.2a) and ($\gamma = 0.02$ and $\gamma = 0.04$ in Figures 3.2b and 3.2c, respectively). It is usually assumed at theoretical considerations that suspensions are monodisperse at such low volume fractions, which is in an obvious contradiction with Meireles, Molle observations.

Figure 3.3 presents comparison of the measured relative viscosity versus volume fraction of yeast suspension (points) and theoretical Eq. (3.2.16) (solid line, fitted parameters are $\varphi_{\text{max}} = 0.73$ and $\overline{A} = 1$).

According to our derivation parameters $\varphi_{\text{max}}$ and $\overline{A}$ are complex functions of (a) interparticle interaction potential, (b) hydrodynamic interactions between clusters. Both interactions are unknown in the case of yeast suspensions. In spite of this a reasonable agreement with experimental data is achieved using fitting procedure with these two parameters.

Here we investigate on an empirical level the influence of applied shear stress on the viscosity of concentrated suspensions. Our consideration is based on the experimental data presented in
(Krieger-Dougherty, 1959), which are summarised in Table 3.1. It is important to emphasise that below \( \bar{\gamma}_{\text{max}} \) is assumed to retain a constant value, independent of volume fraction \( \gamma \). However, both \( \bar{A} \) and \( \bar{\gamma}_{\text{max}} \) can be functions of applied shear stress, \( \tau \). Below both parameters \( \bar{A} \) and \( \bar{\gamma}_{\text{max}} \) are treated as functions of shear stress only, that is, they are assumed independent of particle volume fraction.

Two experimental values of the effective viscosity of suspension at particle volume fractions \( \gamma = 0.299 \) and \( \gamma = 0.6017 \) (the highest and the lowest available, respectively) at the fixed shear stress, \( \tau \), from Table 3.1 are used to find two unknown values, \( \bar{A} \) and \( \bar{\gamma}_{\text{max}} \). This procedure results in the system of two equations with two unknowns, \( \bar{\gamma}_{\text{max}}(\tau) \) and \( \bar{A}(\tau) \). In this way at each shear stress, \( \tau \), these two dependencies were determined. Determined in this way dependencies \( \bar{\gamma}_{\text{max}}(\tau) \) and \( \bar{A}(\tau) \) are presented in Figures 3.5 and 3.4, respectively. Figure 3.5 shows that averaged packing density inside clusters, \( \bar{\gamma}_{\text{max}}(\tau) \), increases with applied shear stress, that is, clusters become more dense. In this situation the averaged friction coefficient, \( \bar{A} \), should increase, which is in the agreement with Figure 3.4.

Now Eq. (3.2.16) can be rewritten as

\[
\eta(\gamma, \tau) = \eta_0 \left(1 - \frac{\gamma}{\bar{\gamma}_{\text{max}}(\tau)} \right)^{-2.5 \bar{A}(\tau)}.
\]  \hspace{1cm} (3.2.19)

Determined above \( \bar{\gamma}_{\text{max}}(\tau) \) and \( \bar{A}(\tau) \) dependences are used for calculation of \( \eta(\gamma, \tau) \) at all shear stresses, \( \tau \), and all volume fractions, \( \gamma \). Calculated viscosity according to Eq. (3.2.19) is compared with the experimental values of \( \gamma \) from the set of values \{0.397, 0.4398, 0.4876, 0.5390, 0.5603, 0.5866\} in Table 3.1. Comparison is presented in Figure 3.6, which shows that the assumed independency of \( \bar{\gamma}_{\text{max}}(\tau) \) and \( \bar{A}(\tau) \) from the volume fraction of particles is reasonably satisfied.
3.5 Conclusions

A new method is suggested for derivation of viscosity dependence on a volume fraction of dispersed particles taking into account cluster formation. We assume that viscosity of concentrated suspension is completely determined by cluster size distribution, no matter if clusters form under the action of colloidal, hydrodynamic interactions or shear stress. Based on this assumption an equation, which describes dependency of viscosity on a volume fraction of dispersed particles taking into account cluster formation, is deduced. Under special restrictions the deduced dependency coincides with the well-known Dougherty-Krieger's equation except for a clear physical meaning of entering parameters. Our consideration shows that Dougherty-Krieger's equation has deeper physical background than it has been supposed earlier. Comparison of the deduced equation with available experimental data on the dependency of the viscosity of concentrated suspensions on the volume fraction of particles shows the good agreement and reasonable fitted parameters. Meireles, Molle's observations of yeast suspensions prove a presence of clusters even at low volume fractions of dispersed particles. Viscosity dependency of yeast suspension on the volume fraction of yeast particles is in a good agreement with the deduced theoretical equation and gives reasonable value of parameters. The deduced equation is applied to the viscosity on shear stress dependency, which again shows a reasonable agreement with experimental data.

3.6 Appendix

Everywhere below only first order terms are kept in the consideration. Using Eq. (3.2.6) the right hand side of Eq. (3.2.10) can be transformed as
Viscosity of concentrated suspensions and properties of porous media

\[ \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] + 2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \Delta \phi_i = \]

\[ = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] + 2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] \Delta \phi_i = \]

Further transformation of right hand side of Eq. (3.6.1) keeping only first order terms gives

\[ \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] = \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \Delta \xi_i \] (3.6.2)

Using Eqs. (3.6.1) and (3.6.2) Eq. (3.6.10) transforms into

\[ 2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] \Delta \phi_i - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \Delta \xi_i = 0. \]

Substitution of expressions for \( \Delta \xi_\gamma \) from Eq. (3.2.8) into the latter equation and collecting all terms proportional to \( \Delta \phi \), gives

\[ \sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} i = 2.5 \sum_{i=1}^{\infty} A_i \Psi = 0, \quad i=1,2,3,\ldots \] (3.6.3)

Let Eq. (3.6.3) be multiplied by \( \gamma_j \) and summarised over \( j=1,2,3,\ldots \) this gives

\[ \sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j = \frac{2.5 \sum_{i=1}^{\infty} A_i \gamma_i}{1 - \sum_{j=1}^{\infty} \gamma_j}. \]

Substitution of the latter expression for \( \sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j \) into Eq. (3.6.3) gives
It is obvious that

\[ \frac{d\eta}{d\gamma} = \sum_{i=1}^{n} \frac{\partial \Psi}{\partial \gamma_i} \frac{d\gamma_i}{d\gamma}, \]

where \( \gamma \) is the volume fracture of particles. After multiplying of Eq. (3.6.4) by \( \frac{d\gamma_i}{d\gamma} \) and summation over \( i=1,2,3... \) Eq. (3.6.4) becomes

\[ \frac{d\eta}{d\gamma} = 2.5 \eta \sum_{i=1}^{n} \left[ 2.5A_i \gamma_i + \frac{\sum_{j=1}^{n} 2.5A_j \gamma_j}{1 - \sum_{j=1}^{n} \gamma_j} \right] \frac{d\gamma_i}{d\gamma}. \]
Figure 3.1  Relative viscosity as a function of volume fraction of dispersed particles. Experimental points from review (Thomas, 1965), solid lines according to Eq.(3.2.16) with different values of $\bar{\gamma}_{\text{max}}$ and $\bar{A}$

- curve 1  $\bar{\gamma}_{\text{max}}=1$, $\bar{A}=1$ (particles do not form clusters)
- curve 2  $\bar{\gamma}_{\text{max}}=0.73$ (close to hexagonal packing of particles inside clusters), $\bar{A}=0.61$
- curve 3  $\bar{\gamma}_{\text{max}}=0.65$ (close to cubic centered packing of particles inside clusters), $\bar{A}=0.67$
- curve 4  $\bar{\gamma}_{\text{max}}=0.56$ (close to simple cubic packing of particles inside clusters), $\bar{A}=0.72$
Figure 3.2a  Yeast suspension, volume fraction 0.002  
(M. Meireles, C. Molle)
Figure 3.2b  Yeast suspension, volume, fraction 0.02
(M. Meireles, C. Molle)
Figure 3.2c  Yeast suspension, volume fraction 0.04  
(M.Meireles, C.Molle)
Figure 3.3  Comparison of measured (M.Meireles, C.Molle) and predicted relative viscosity on the volume fraction of yeast suspension. Solid curve according to Eq.(3.2.16). Fitted parameters are $\bar{\rho}_{\text{max}}=0.73$ and $\bar{A}=1$. 
Table 3.1 Experimental dependence of the effective viscosity of butadiene-styrene latex suspensions. Average particle diameter was 1390 Å (Moron, and Fok, 1955) $\eta^\text{eff} / \eta_0$ on the shear stress ($\tau$ dynes/cm$^2$) at different values of volume fraction of the particles, $\gamma$. From (Krieger, and Dougherty, 1959)

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>$\gamma = 0.299$</th>
<th>$\gamma = 0.397$</th>
<th>$\gamma = 0.4398$</th>
<th>$\gamma = 0.4876$</th>
<th>$\gamma = 0.5390$</th>
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<tbody>
<tr>
<td>50</td>
<td>3.293</td>
<td>6.424</td>
<td>9.879</td>
<td>17.18</td>
<td>52.20</td>
</tr>
<tr>
<td>100</td>
<td>3.218</td>
<td>6.081</td>
<td>8.993</td>
<td>15.17</td>
<td>40.02</td>
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<tr>
<td>200</td>
<td>3.157</td>
<td>5.802</td>
<td>8.363</td>
<td>13.44</td>
<td>31.55</td>
</tr>
<tr>
<td>300</td>
<td>3.132</td>
<td>5.689</td>
<td>8.082</td>
<td>12.70</td>
<td>27.96</td>
</tr>
<tr>
<td>500</td>
<td>3.110</td>
<td>5.607</td>
<td>7.790</td>
<td>12.03</td>
<td>24.51</td>
</tr>
<tr>
<td>800</td>
<td>-</td>
<td>-</td>
<td>7.597</td>
<td>11.66</td>
<td>21.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\tau$</th>
<th>$\gamma = 0.5603$</th>
<th>$\gamma = 0.5866$</th>
<th>$\gamma = 0.6017$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>107.07</td>
<td>404.10</td>
<td>1089.3</td>
</tr>
<tr>
<td>100</td>
<td>71.18</td>
<td>208.78</td>
<td>464.0</td>
</tr>
<tr>
<td>200</td>
<td>52.20</td>
<td>122.21</td>
<td>241.8</td>
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<tr>
<td>300</td>
<td>45.39</td>
<td>96.58</td>
<td>176.9</td>
</tr>
<tr>
<td>500</td>
<td>39.15</td>
<td>79.28</td>
<td>131.2</td>
</tr>
<tr>
<td>800</td>
<td>34.80</td>
<td>68.01</td>
<td>105.3</td>
</tr>
</tbody>
</table>
Figure 3.4 Dependence of average parameter $\bar{A}$ on applied shear stress $\tau$. 
Figure 3.5 Dependence of average parameter $\bar{\gamma}_{\text{max}}$ on applied shear stress $\tau$. 
Figure 3.6 Dependency of the effective viscosity of suspensions on shear stress calculated according to Eq. (3.2.19) at different particle volume fractions. Experimental data from (Dougherty, Krieger, 1959). $A(\tau)$ and $\gamma_{\text{max}}(\tau)$ dependencies from Figure 3.4, 3.5, both assumed independent of the volume fraction of particles.
LIST OF SYMBOLS

\(a\) radius of particle
\(V\) volume of suspension
\(V_i\) volume of clusters containing \(i\) particles
\(n_i\) number of clusters containing \(i\) particles in the suspension
\(A_i\) friction coefficients

Greek letters
\(\eta\) viscosity
\(\nu\) volume of particle
\(\gamma\) volume fraction of particles
\(\gamma_{i,\text{max}}\) packing density of single particles inside the clusters containing \(i\) particles
\(\Psi\) function defined by Eq. (3.2.4)
\(\tau\) shear stress

Subscripts
\(i\) index with natural values
\(\text{max}\) packing density in clusters
Chapter 4 VISCOSITY OF EMULSIONS: INFLUENCE OF FLOCCULATION

4.1 Introduction

At the small volume fraction of droplets, $\gamma$, an effective viscosity of emulsion is given by the relation suggested by (Sir G. I. Taylor, 1932)

$$\eta = \eta_0 \left(1 + \frac{2\eta_0 + 5\eta_d}{2\eta_0 + 2\eta_d} \gamma \right)$$

(4.1.1)

where $\eta_0$ is the viscosity of the continuous liquid, $\eta_d$ is the viscosity of the liquid, which forms droplets, and $\eta$ is the effective viscosity of the emulsion. Eq. (4.1.1) is valid for very dilute emulsions, that is, $\gamma << 1$.

The hydrodynamic interaction between the neighboring droplets has been taken into account by (Choi, and Schowalter, 1975) and (Yaron, and Gal-Or, 1972) based on a cell model. Theoretical models presented in (Choi, and Schowalter 1975) and (Yaron, and Gal-Or, 1972) based on an assumption that dispersed droplets do not form clusters (flocks).

Starting from Tailor's Eq. (4.1.1) and using the concept of the mean field approximation, (Phan-Thien, and Pham, 1997) have deduced an equation, which gives dependence of the effective viscosity of concentrated emulsions on the volume fraction of droplets, $\gamma$:

$$\left(\frac{\eta}{\eta_0}\right)^{3/5} \left[\frac{2\eta + 5\eta_d}{2\eta_0 + 2\eta_d}\right]^{3/5} = (1 - \gamma)^{-1}.$$  

(4.1.2)

According to the theory developed in (Phan-Thien, and Pham, 1997) droplets do not form clusters either. Eq (4.1.2) agrees with experimental data only at a sufficiently low volume fraction of droplets.

A further step in the investigation of rheology of emulsions has been undertaken in (Pal, 2000) and an equation has been deduced, which describes reasonably well available experimental data. To deduce the final equation the author assumed that
droplets are covered with a layer of surfactant molecules (Pal, 2000). The latter means that the effective volume of a single emulsion droplet is increased by a factor $K > 1$.

Using $K$ as a fitting parameter, (Pal, 2000) have deduced an equation which agrees much better with available experimental data, than Eq. (4.1.2):

$$
\left( \frac{\eta}{\eta_0} \right)^{2/5} \left[ \frac{2\eta + 5\eta_0}{2\eta_0 + 2\eta_d} \right]^{3/5} = (1 - K \gamma)^{-1}.
$$

In Eq. (4.1.3) $K$ denotes a hypothetical increase in the effective volume of single droplets and has been used as a fitting parameter to fit experimental data. It has been found (1) that $K$ should vary between 1.166 and 2.070 for different emulsions to fit experimental data on viscosity of concentrated emulsions.

If a droplet of radius $a$ is covered by a layer of surfactant molecules of thickness $H$ then the new volume of the droplet is $\frac{4\pi}{3} a^3 + 4\pi a^2 H = \frac{4\pi}{3} a^3 \left( 1 + \frac{3H}{a} \right)$. The latter means: $K = 1 + \frac{3H}{a}$. The thickness of the layer on the droplet surface can be expressed now as $H = a \frac{K - 1}{3}$. If we use $K$ values from (Pal, 2000), then the latter expression shows that the thickness, $H$, should range from 0.055 $a$ to 0.357 $a$. If we adopt the drop radius $a \sim 1 \mu m$ for estimations then $H$ should range from 550 Å (which is ten times of the size of SDS micelles) to 3570 Å. If the droplet radius is bigger than $1 \mu m$, then the thickness of the adsorbed layer would be even bigger. If droplet surfaces were covered with such a thick layer then their surfaces would be completely immobilised and the dependency on the viscosity of the liquid inside droplets would disappear.

This estimation shows that in spite of a very good agreement with experimental data the derivation of Eq. (4.1.3) suggested in (Pal, 2000) should be reconsidered.

That is why we decided to look at the same problem from a different point of view. Our consideration below is based on our new method.
In emulsions dispersed droplets form doublets, triplets and higher clusters under the
action of colloidal, hydrodynamic and/or an applied shear (Selomulya, Amal, Bushell,
and Waute, 2001). These forces determine both a structure and a size distribution of
clusters. We assume that viscosity of concentrated emulsions is determined by cluster
size distribution, no matter if clusters are formed under the action of colloidal,
hydrodynamic interactions or an applied shear. Based on this assumption an equation,
which describes dependency of an effective viscosity of emulsions on a volume
fraction of dispersed droplets taking into account cluster formation, is deduced.

4.2 Influence of cluster formation on viscosity of flocculated emulsions

Let us consider an emulsion of volume $V$ and the volume fraction of droplets $\gamma$, where

$$\gamma = \frac{V_d}{V},$$

(4.2.1)

$V_d$ is the total volume of droplets in the volume $V$. Let $n_i, i = 1,2,3,...$ be a number of
clusters in the volume $V$ with corresponding number of single droplets and

$$\gamma_{i,\text{max}}, i = 1,2,3,...$$

be an averaged packing density of single droplets inside clusters of
the corresponding size. $n_I$ is a number of “clusters of size $I$”, that is, single droplets,
hence, $\gamma_{I,\text{max}} = 1$.

Volume fraction of clusters with $i$ single droplets can be written as

$$\gamma_i = \frac{V_i}{V} = \frac{in_i v_i}{V \gamma_{i,\text{max}}}, \quad i = 1,2,3,...,$$

(4.2.2)

where $V_i$ is the total volume of clusters containing $i$ droplets, $v_i$ is the volume of a
single droplet.

The following mass conservation condition is satisfied:

$$\sum_{i=1}^{\infty} \gamma_i \gamma_{I,\text{max}} = \gamma.$$

(4.2.3)

It is assumed below that the effective viscosity of emulsions is determined by the
cluster size distribution, that is, can be described by the following dependency:
\[ \eta(\eta_0, \gamma) = \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots]. \]  

4.2.4)

If all volume fraction of clusters, \( \gamma_i, \ i = 1, 2, 3, 4, \ldots \), are zero, the emulsion consists only of the initial liquid and Eq. (4.2.4) gives:

\[ \eta_0 = \Psi(\eta_0, 0, 0, 0, \ldots), \]  

(4.2.5)

which is used below as an initial condition.

Each cluster is considered below as a new effective droplet with the effective viscosity of “the inner liquid”, \( \eta_i, \ i = 1, 2, 3, \ldots \), which are determined below.

If the volume fraction of droplets, \( \gamma_i \), is small then all \( \gamma_i \) are also small and Eq. (4.2.4) can be rewritten as

\[ \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] = \Psi[\eta_0, 0, 0, 0, \ldots] + \sum_{i=1}^{\infty} \left. \frac{\partial \Psi}{\partial \gamma_i} \right|_{\gamma_i=0} \gamma_i = \]  

\[ = \eta_0 \left( 1 + \sum_{i=1}^{\infty} \frac{2\eta_0 + 5\eta_i \gamma_i}{2\eta_0 + 2\eta_i} \right) \]  

(4.2.6)

where \( \eta_i, \ i = 1, 2, 3, \ldots \) are effective viscosities inside cluster of the corresponding size.

Eq. (4.1.1) (derived by Tailor, 1932) is used for the last step in Eq. (4.2.6). In the case of single droplets \( \eta_i = \eta_d \).

Let a small amount of clusters, \( \Delta n_i << n_i, \ i = 1, 2, 3, \ldots \), be marked randomly in the whole volume of the emulsion, \( V \). Now the emulsion can be considered as a mixture of the marked clusters surrounded by the rest of the emulsion, which includes only non-marked clusters. Volume fractions of the marked clusters, \( \Delta \delta_i, \ i = 1, 2, 3, \ldots \), are

\[ \Delta \delta_i = \frac{\Delta V_i}{V}, \ i = 1, 2, 3, \ldots \]  

(4.2.7)

Volume fractions of non-marked clusters in the rest of the emulsion are

\[ \gamma_i - \Delta \xi_i = \frac{V_i - \Delta V_i}{V - \sum_{j=1}^{\infty} \Delta V_j}, \ i = 1, 2, 3, \ldots \]  

Keeping only first order terms in the latter equation we conclude:
\[ \Delta \xi_i = \frac{V_i}{V} - \frac{V_j - \Delta V_j}{V - \sum_{i=1}^{\infty} \Delta V_i} = \frac{\Delta \vartheta_i - \gamma_i \sum_{j=1}^{\infty} \Delta \vartheta_j}{1 - \sum_{j=1}^{\infty} \Delta \vartheta_j}, \quad i = 1, 2, 3, \ldots \]  \hspace{1cm} (4.2.8)

Marked clusters are surrounded by the rest of the emulsion (with non-marked clusters), which has the effective viscosity \( \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \), where small volume fractions \( \Delta \xi_i \), \( i = 1, 2, 3, \ldots \) are given by Eq. (4.2.8). Hence, the effective viscosity of the emulsion can be expressed in two different ways: according to Eq. (4.2.4) and considering the emulsion as a mixture of the marked clusters surrounded by the rest of the emulsion with non-marked clusters:

\[ \eta = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \]  \hspace{1cm} (4.2.9)

Right hand sides of Eqs. (4.2.4) and (4.2.9) should be equal, this gives an equation for the determination of the effective viscosity:

\[ \Psi[\eta_0, \phi_1, \phi_2, \phi_3, \ldots] = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \]  \hspace{1cm} (4.2.10)

Transformations of Eq. (4.2.10) are given in the APPENDIX A. It is necessary to notice that no further assumptions are made in the course of transformations of Eq. (4.2.10) in the APPENDIX A.

The result is the following differential equation for the determination of the effective viscosity of concentrated emulsions, \( \eta \), on the volume fraction of droplets, \( \gamma \):

\[ \frac{d \eta}{d \gamma} \eta = \sum_{i=1}^{\infty} \left[ \frac{\sum_{j=1}^{\infty} \gamma_j \eta_j + 2 \eta + 5 \eta_i}{2 \eta + 2 \eta_i} \right] \frac{d \eta_i}{d \gamma}. \]  \hspace{1cm} (4.2.11)

Solution of Eq. (4.2.11) should satisfy the following boundary condition, which follows from Eq. (4.2.5):

\[ \eta(0) = \eta_0. \]  \hspace{1cm} (4.2.12)

The only unknown values left are the effective viscosities inside clusters, \( \eta_i \), \( i = 2, 3, \ldots \), which are determined below.
Let us consider a cluster containing \(i\) droplets \((i=2,3,...)\) with the packing density \(\gamma_{i,\text{max}}\). The effective viscosity, \(\eta_i\), \(i=2,3,...\) inside this cluster can be calculated using the mean field approximation according to Eq. (1.7.4) (Phan-Thien and Pham, 1997):

\[
\left( \frac{\eta_i}{\eta_0} \right)^{2/5} \left[ \frac{2\eta_i + 5\eta_d}{2\eta_0 + 2\eta_d} \right]^{3/5} = (1 - \gamma_{i,\text{max}})^{-1}.
\]  

(4.2.13)

Dependency of the effective viscosity of emulsion on volume fraction of droplets is described by the system of two Eqs. (4.2.11) and (4.2.13). In order to solve these equations the following dependences should be determined

\[
\gamma_i(\gamma, \dot{s}), \quad \gamma_{i,\text{max}}(\gamma, \dot{s}), \quad i=1,2,3,...
\]

(4.2.14)

that is, the cluster size distribution and the packing density inside clusters as functions of the volume fraction of droplets, \(\gamma\), and the applied shear rate, \(\dot{s}\). It is worth noticing that Eqs. (4.2.11), (4.2.13) describe not only dependence of the effective viscosity of emulsions on the volume fraction of droplets, \(\gamma\), but also on the applied shear rate, \(\dot{s}\).

Fortunately, consideration can be substantially simplified in two limiting cases: (i) a developed flocculation, (ii) a low flocculated emulsion.

### 4.3 Developed flocculation

It is assumed that an emulsion consists mostly of flocks, that is, single droplets either completely disappeared or their volume fraction is negligibly small. Hence:

(i) \(\gamma_i = 0\) and probably volume fraction of "low sized clusters" doublets, triplets may be also neglected.

The following assumption looks like a reasonable approximation in the case when only big clusters are presented in the emulsion.
(ii) all clusters have the same packing density, \( \gamma_{r,\text{max}} = \gamma_m \), where \( \gamma_m \) now is an averaged packing density of single droplets inside any cluster.

Assumption (ii) allows a considerable simplification of the calculations below.

According to assumptions (i)-(ii) Eq. (4.5.3) can be rewritten as

\[
\gamma_m \sum_i \gamma_i = \gamma : \tag{4.3.1}
\]

According to assumption (ii) we conclude from Eq. (4.2.13) that effective viscosities inside all clusters are identical and determined according to the following equation:

\[
\left( \frac{\eta_c}{\eta_0} \right)^{2/5} \left[ \frac{2\eta_c + 5\eta_d}{2\eta_0 + 5\eta_d} \right]^{2/5} = (1 - \gamma_m)^{-1},
\]

where \( \eta_c \) is an averaged effective viscosity inside clusters.

The latter equation can be rewritten as

\[
\left( \frac{\eta_c}{\eta_0} \right)^{2/5} \left[ \frac{\frac{2\eta_c + 5\eta_d}{\eta_0}}{2 + 5 \frac{\eta_d}{\eta_0}} \right]^{2/5} = (1 - \gamma_m)^{-1}. \tag{4.3.2}
\]

Eq. (4.3.2) shows that the relative effective viscosity inside clusters, \( \frac{\eta_c}{\eta_0} \), is a function of the packing density inside clusters, \( \gamma_m \), and the viscosity ratio, \( F = \frac{\eta_d}{\eta_0} \).

Two limiting cases can be immediately found using Eq. (4.3.2): high viscosity ratio \( F = \frac{\eta_d}{\eta_0} \gg 1 \), which corresponds to the case, when the liquid inside the droplets is
either much more viscose than the outer liquid, or when the surface of the droplets is completely immobilized by the presence of adsorbed surfactants/polymers; and low viscosity ratio, \( F = \frac{\eta_d}{\eta_0} \ll 1 \), which corresponds to the case of a low viscosity liquid inside the droplets or bubbles. In the first case, \( F \gg 1 \) we conclude from Eq. (4.3.2):

\[
\frac{\eta_c}{\eta_0} = \frac{1}{(1 - \gamma_m)^{5/2}}.
\]

(4.3.3)

In the case \( F \ll 1 \), using Eq. (4.3.2):

\[
\frac{\eta_c}{\eta_0} = \frac{1}{(1 - \gamma_m)}.
\]

(4.3.4)

Dependence of the relative effective viscosity inside clusters, \( \frac{\eta_c}{\eta_0} \), according to Eq. (4.3.2) on the packing density inside clusters, \( \gamma_m \), at different values of the viscosity ratio, \( F = \frac{\eta_d}{\eta_0} \), is presented in Figure 4.1, which shows the influence of the viscosity ratio on the effective viscosity inside clusters.

Eqs. (4.3.1)-(4.3.2) show that Eq. (4.2.11) can be rewritten now as

\[
\frac{d\eta}{d(\gamma/\gamma_m)} \frac{1}{\eta} = \frac{5\eta_c + 2\eta}{2\eta_c + 2\eta} \frac{1}{1 - \gamma/\gamma_m}.
\]

(4.3.5)

It is worth noticing that the averaged packing density of droplets inside clusters, \( \gamma_m(\gamma, \dot{s}) \), can be still a function of both the total volume fraction of droplets, \( \phi \), and the applied shear rate, \( \dot{s} \). The latter dependence, \( \gamma_m(\gamma, \dot{s}) \), determines in its turn the effective viscosity inside clusters according to Eq. (4.3.2).
Eq. (4.3.5) can be integrated using boundary condition (4.3.12), which gives

\[
\left( \frac{\eta}{\eta_0} \right)^{2/5} \left[ \frac{2\eta + 5\eta_c}{2\eta_0 + 5\eta_c} \right]^{3/5} = \left( 1 - \frac{\gamma}{\gamma_m} \right)^{-1}.
\]

Eqs. (4.3.2), (4.3.6) give the system of two algebraic equation for the calculation of the dependence of the effective viscosity of emulsions, \( \eta \), on the volume fraction of droplets, \( \gamma \), with one fitting parameter, \( \gamma_m \), which is an averaged packing density of individual droplets inside clusters. The latter means, if the dependency of the averaged packing density inside clusters is specified then system of Eqs. (4.3.2), (4.3.6) gives the dependence of the effective viscosity of emulsions on both the volume fraction of the droplets, \( \gamma \), and the applied shear rate, \( \dot{\gamma} \).

Eq. (4.3.6) is similar to that deduced in ref. (Pal, 2000), however, has a completely different physical interpretation. Eq. (4.3.1) from ref. (Pal, 2000) is rewritten below in the following form

\[
\left( \frac{\eta}{\eta_0} \right)^{2/5} \left[ \frac{2\eta + 5\eta_d}{2\eta_0 + 2\eta_d} \right]^{3/5} = \frac{1}{1 - \frac{\gamma}{\gamma_m}},
\]

where \( \gamma_m = 1/K \). This transformation of the latter equation makes it easier the comparison with our calculations of the effective viscosity according to our Eqs. (4.3.2), (4.3.6). Figure 4.2 shows the comparison of the calculated effective viscosity of emulsions according to Eq. (4.3.1') and our Eqs. (4.3.2), (4.3.6) at different packing densities inside clusters, \( \gamma_m \), and viscosity ratio \( F = \frac{\eta_L}{\eta_0} \). This comparison shows that at low \( F \) (below \( F=10 \)) dependences calculated according to our theory is higher than the corresponding viscosity calculated according to Eq. (4.3.1') (Figure 4.2a). At \( F=10 \) our calculations almost coincide with calculations according to Eq. (4.3.1') (Figure 4.2b); at \( F>10 \) our calculations give the lower effective viscosity than Eq. (4.3.1') (Figure 4.2c).
4.4 Low flocculated emulsion, transition to develop flocculation

In this case the emulsion includes both single droplets as well as doublets, triplets and other “low sized clusters”.

Bellow the following simplifying assumption is adopted:

- All clusters starting from doublets have the identical packing density, \( \phi_m \), which is independent of the volume fraction of droplets. This means:
  \[ \gamma_{1,\text{max}} = 1, \gamma_{2,\text{max}} = \gamma_{3,\text{max}} = \gamma_{4,\text{max}} = \ldots = \gamma_m. \]

Under this assumption we conclude: \( \eta_1 = \eta_d, \eta_2 = \eta_3 = \eta_4 = \ldots = \eta_c \), where \( \eta_c \) is calculated according to Eq. (4.3.2).

Eq. (4.3.3) can be rewritten now as

\[
\sum_{l=2}^{m} \gamma_{l} = \gamma / \gamma_m - \gamma_1 / \gamma_m. \tag{4.4.1}
\]

The latter equation shows that

\[
\sum_{l=2}^{m} \frac{d\gamma_l}{d\gamma} = \frac{1}{\gamma_m} \left( 1 - \frac{d\gamma_1}{d\gamma} \right) \tag{4.4.2}
\]

Eq. (4.3.1) can be written now using Eqs. (4.3.7), (4.3.8) as

\[
\frac{1}{\eta} \frac{d\eta}{d\gamma} = \frac{2\eta + 5\eta_d}{2\eta + 5\eta_d} \gamma \left( 1 - \frac{d\gamma_1}{d\gamma} \right) + \frac{2\eta + 5\eta_d}{2\eta + 5\eta_d} \frac{\gamma - \gamma_1}{1 - \gamma - \gamma_1 / \gamma_m} \left( \frac{1}{\gamma_m} + \frac{d\gamma_1}{d\gamma} \left( 1 - \frac{1}{\gamma_m} \right) \right) \tag{4.4.3}
\]

Effective viscosity, \( \eta \), of a low flocculated emulsion can be calculated using Eqs. (4.4.3), (4.3.2) with the initial condition (4.3.12).
In order to solve Eqs. (4.4.2) and (4.4.3) the following dependencies should be known: the averaged packing density inside clusters, \( \gamma_n(s) \), and the dependency of the volume fraction of single droplets, \( \gamma_i(\gamma, s) \).

In the case of developed flocculation the volume fraction of single droplets can be neglected, that is, \( \gamma_i = \frac{d\gamma_i}{d\gamma} = 0 \). In this case Eq. (4.4.2) transforms into Eq. (4.3.5), which has been deduced for the case of the developed flocculation. If droplets do not form clusters, that is \( \gamma_i = \gamma, \frac{d\gamma_i}{d\gamma} = 1, \gamma_n = 1 \), then Eq. (4.4.3) after some transformation gives solution (1.7.4). The latter consideration shows that Eq. (4.4.3) gives the effective viscosity of concentrated emulsions in both limiting cases, of the developed flocculation and when droplets do not form clusters at all, as well as in all intermediate cases.

That is the problem now is to calculate \( \gamma_i(\gamma) \) dependency, which should be used in Eq. (4.4.3).

\( \gamma_i(\gamma) \) dependency is calculated below under the following simplifying assumptions:

- cluster formation goes via exchange by single droplets and this exchange goes by one droplet at the time;
- only an equilibrium cluster distribution is considered with no imposed shear.

Details of calculations are presented in the APPENDIX B, where dependency \( \gamma_i(\gamma) \) is given by Eqs. (4.7.11)-(4.7.12).

4.5 Discussion and comparison with available experimental data

In Figures 4.5a and 4.5b the dependence of the relative viscosity, \( \eta/\eta_0 \), on the relative volume fraction of droplets, \( \gamma/\gamma_m \), is presented. Curves 2-7 are calculated according to
Eqs. (4.2.2), (4.4.3), (4.7.11), (4.7.12) at two different viscosity ratio, \( F = \frac{\eta_d}{\eta_0} \), and characteristic volume fractions of doublet formation, \( \gamma^* \), ranging from 0.01 to 1. Two additional curves are presented on Figures 4.5a and 4.5b for comparison: curve 1 according to Eq. (4.3.6) (highly flocculated emulsion), and curve 8 according to Eq. (1.7.4) (no flocculation at all).

The following conclusions can be drawn using Figure 4.5 are as follows:

- All viscosity dependences, \( \eta/\eta_0 \), on the volume fraction, \( \gamma_{ym} \), are situated in between two limiting cases: the developed flocculation case (curve 1) and non-flocculated emulsion (curve 8). In the case of developed flocculation the effective viscosity is the highest possible viscosity of emulsions. The region between two limiting cases decreases with the viscosity ratio increase: compare Figure 4.5a (the viscosity ratio \( F = \eta_d/\eta_0 = 0.01 \)) and Figure 4.5b (the viscosity ratio \( F = \eta_d/\eta_0 = 100 \)).
- At fixed volume fraction of droplets, \( \gamma \), the effective viscosity increases with degree of flocculation. Non-flocculated emulsion show the lowest viscosity at the same volume fraction of droplets.
- If the characteristic volume fraction, \( \gamma^* \), (the characteristic volume fraction of doublet formation) becomes very small, the effective viscosity of emulsions tends to the dependence in the case of the developed flocculation in the whole range of the droplet volume fraction, \( \chi \). This result has a clear physical meaning, because a degree of flocculation is obviously increases at any fixed volume fraction, \( \chi \); if the characteristic volume fraction of doublet formation, \( \gamma^* \), decreases (more clusters are present in the emulsion).

In general Eqs. (4.3.2), (4.4.3) describe the whole range of possible situations: from non-flocculated emulsions (\( \gamma_i = \gamma \)) to the case of the developed flocculation (\( \gamma_i = 0 \)).

In Figure 4.6 the comparison of calculations according to Eqs. (4.3.2), (4.4.3) with experimental data from (Pal, 2000) is presented. All the relevant characteristics of emulsions under investigation are taken from (Selomulya, G., Amal, R., Bushell, G., and Waite, 2001), and give in the Table. 4.1. Comparison shows very good agreement.
between our theory predictions and presented experimental data on viscosity of concentrated emulsions.

According to the microscopy observations clusters (doublets, triplets and so on) start to form in milk at the volume fraction of fat above 0.2 (Kosvintsev, Holdich, private communication). That is, the characteristic volume fraction of doublet formation in milk, \( \gamma^* \), is in the range 0.2-0.3, hence, is sufficiently high. The latter means that cluster formation in milk is not highly developed in the volume fraction range from 0 to 0.4. For this reason milk has been selected for comparison with our calculations according to Eqs. (4.4.3), (4.3.2) using Eqs. (4.7.11)-(4.7.12) (low flocculated case) with experimental data from (Leviton, A, and Leighton, A., 1936). In Figure 4.7 two theoretical curves are presented: curve 2 is calculated according to Eq. (1.7.4) (no cluster formation) and curve 1 is fitted to experimental data (Leviton, A, and Leighton, A., 1936) using Eqs. (4.4.3), (4.3.2) and Eqs. (4.7.11)-(4.7.12), that is, taking into account cluster formation. Two fitting values are the packing density inside clusters and the characteristic volume fraction of the doublet formation, \( \gamma_m \) and \( \gamma^* \), respectively. The comparison shows that the curve 2 underestimates the measured viscosity (Leviton, and Leighton, 1936). According to our theory the discrepancy is attributed to the cluster formation. The fitted values of the packing density inside clusters and the characteristic volume fraction of the doublet formation are as follows: \( \gamma_m=0.663 \) (close to the cubic centered) and \( \gamma^*=0.395 \). The latter value shows that the maximum clusters formation occurs at \( 0.75 \times 0.395 = 0.296 \), which is in a reasonable agreement with the microscopy observations.

4.6 Appendix A
Transformations of Eq. (4.2.10)

Everywhere below only first order terms are kept in the calculations. The right hand side of Eq. (4.2.10) can be transformed as:
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\[
\Psi[\Psi[n_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \Delta \theta_1, \Delta \theta_2, \Delta \theta_3, \ldots] = \\
= \Psi[\Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots]0,0,0,\ldots] + \\
+ \sum_{i=1}^{\infty} \frac{\partial \Psi[\Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots] \Delta \theta_1, \Delta \theta_2, \Delta \theta_3, \ldots]}{\partial \Delta \theta_i} \Delta \theta_i + \\
+ \sum_{i=1}^{\infty} \frac{\partial \Psi[\Psi[n_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots]0,0,0,\ldots]}{\partial \Delta \xi_i} \Delta \xi_i.
\]

Transformation of the derivatives in the right hand side of Eq. (4.6.1) taking into account Eq. (4.2.6) gives

\[
\frac{\partial \Psi[\Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots] \Delta \theta_1, \Delta \theta_2, \Delta \theta_3, \ldots]}{\partial \Delta \theta_i} \bigg|_{\Delta \theta_i=0} = \\
= \frac{2\Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots] + 5\eta_i \Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots]}{2\Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots] + 2\eta_i} = \frac{2\eta + 5\eta_i}{2\eta + 2\eta_i}, \quad i = 1, 2, 3, \ldots
\]

Using Eq. (4.2.5) we conclude that

\[
\sum_{i=1}^{\infty} \frac{\partial \Psi[\Psi[n_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots]0,0,0,\ldots]}{\partial \Delta \xi_i} \bigg|_{\Delta \xi_i=0} = -\frac{\partial \Psi[n_0, \gamma_1, \gamma_2, \gamma_3, \ldots]}{\partial \gamma_i}.
\]

Using Eqs. (4.6.1), (4.6.2) and (4.6.3) Eq. (4.2.10) transforms into

\[
\sum_{i=1}^{\infty} \frac{2\eta + 5\eta_i}{2\eta + 2\eta_i} \Delta \theta_i - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \Delta \xi_i = 0.
\]

Substitution of expressions for \(\Delta \xi_i\) from Eq. (4.2.11) into the latter equation and collecting all terms proportional to \(\Delta \theta_j\) gives

\[
\sum_{j=1}^{\infty} \frac{\partial \Psi_{\gamma_j}}{\partial \gamma_j} \gamma_j - \frac{\partial \Psi}{\partial \gamma_i} + \frac{2\eta + 5\eta_i}{2\eta + 2\eta_i} \eta = 0, \quad i = 1, 2, 3, \ldots
\]

After Eq. (4.6.4) is multiplied by \(\gamma_i\) and summarised over \(i=1,2,3,\ldots\), we arrive to:

\[
\sum_{j=1}^{\infty} \frac{2\eta + 5\eta_j}{2\eta + 2\eta_j} \eta \gamma_j - \sum_{j=1}^{\infty} \frac{\partial \Psi_{\gamma_j}}{\partial \gamma_j} \gamma_j = \frac{\sum_{j=1}^{\infty} \frac{2\eta + 5\eta_j}{2\eta + 2\eta_j} \eta \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j}.
\]
Substitution of the latter expression for \( \sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \) into Eq. (4.6.4) gives

\[
\frac{\partial \Psi}{\partial \gamma_i} = \frac{2\eta + 5\eta_i}{2\eta + 2\eta_i} \eta + \frac{\sum_{j=1}^{\infty} \frac{2\eta + 5\eta_j}{2\eta + 2\eta_j} \eta \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j}.
\]

(4.6.5)

It is obvious that

\[
\frac{d\eta}{d\gamma} = \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \frac{d\gamma_i}{d\gamma}.
\]

After Eq. (4.6.5) is multiplied by \( \frac{d\gamma_i}{d\gamma} \) and summarised over \( i=1,2,3 \ldots \) Eq. (4.6.5) becomes

\[
\frac{d\eta}{d\gamma} \frac{1}{\eta} = \sum_{i=1}^{\infty} \left[ \frac{2\eta + 5\eta_i}{2\eta + 2\eta_i} \eta + \frac{\sum_{j=1}^{\infty} \frac{2\eta + 5\eta_j}{2\eta + 2\eta_j} \eta \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j} \right] \frac{d\gamma_i}{d\gamma},
\]

(4.6.6)

which is the first order differential equation for the determination of the dependency of the effective viscosity of emulsions on the volume fraction of droplets.

### 4.7 Appendix B

**Equilibrium cluster size distribution**

It is assumed below that the emulsion includes single droplets as well as doublets, triplets and other "low sized clusters". We assume that the formation of doublets as well other cluster is determined by exchange by single droplets and this exchange goes by one droplet at the time.

Only an equilibrium cluster distribution is considered below, that is no imposed shear is considered.
Let \( n_i \) be a number of initial droplets, \( n_i, i=2, \ldots \) be a number of doublets, triplets and higher clusters in the volume \( V \), where \( i \) is a number of single droplets in a cluster. All possible events with a cluster of size \( i=2,3,4,\ldots \) are as follows:

- connection of a single droplet to a cluster of \( i-1 \) size, which results in an increase of \( n_i \);
- disconnection of a single droplet from a cluster of size \( i+1 \), which results in an increase of \( n_i \);
- disconnection of a single droplet from a cluster of size \( i \), which results in a decrease of \( n_i \);
- connection of a single droplet to a cluster of size \( i \), which results in a decrease of \( n_i \).

Taking all these events into consideration the following system of equations can be deduced

\[
0 = B n_{i-1} n_i + A n_{i+1} - A n_i - B n_i n_i, \quad i=2,3,\ldots, \quad (4.7.1)
\]

where \( B \) and \( A \) are connection and disconnection rates of a single droplet to and from the cluster, respectively. Both rates are determined by the colloidal and hydrodynamic interaction of a single droplet with one of the droplet in the cluster and are assumed independent of the cluster size \( i \).

The condition of the conservation of the total number of droplets reads:

\[
\sum_{i=1}^{\infty} i n_i = N_0, \quad (4.7.2)
\]

where \( N_0 \) is a fixed initial number of the single droplets in the volume \( V \).

The interaction between two droplets goes in the region of the closest contact, where flattening of the drop profiles may occur. In the case of equal size droplets the existence of a critical drop radius, \( a_{cr} \), is established (4.2.12)-(4.2.14): if the drop radius, \( a \), is smaller than \( a_{cr} \), then both "small" drops do not deform in the region of
their contact, that is they behave in the similar way to solid particles; if, however, the drop radius, $a$, is bigger than the critical value, $a_{cr}$, then both “big” drops flatten in the region of their contact. The critical radius, $a_{cr}$, is determined by the interplay between capillary force (which tends to make the drop shape spherical in the contact region) and disjoining pressure (which tends to flatten the interfaces) (Starov, and Churaev, 1982, 1983), (Churaev, and Starov, 1985) and the critical radius, $a_{cr}$, is in the range of 0.1-1 μm. This means that in the case of “small” drops (considered below) aggregation/disaggregation rates can be determined in the similar way to the case of rigid particles according to (4.7.3)-(4.7.4).

Aggregation and disaggregation rates of small droplets, $A$ and $B$, can be determined via shape of the interaction potential, $\Phi(h)$ (Figure 4.3), and the hydrodynamic retardation (4.2.2). Aggregation/disaggregation process is determined by the potential of colloidal interactions between droplets, which has either the shallow primary minimum (Figure 4.3a) or the sufficiently deep secondary minimum and the high potential barrier between the secondary and the primary minima (Figure 4.3b). The latter is assumed in order to neglect the aging of emulsions.

Following the Smoluchowski type consideration (Russel, Saville, and Schowalter, 1999), the aggregation rate, $B$, can be determined as

$$B = \frac{4kT}{3\eta_0 a} \int_{2a + h_0}^{\infty} \frac{\exp(\Phi(r - 2a))dr}{r^2m(r/a)}$$

(4.7.3)

where $m(r/a)$ is calculated in (Russel, Saville, and Schowalter, 1999) and describes the hydrodynamic retardation; $h_0$ is a distance between droplet surfaces there interaction potential tends to infinity, that is, $h_0 = 0$ in the case 3a (Figure 4.3a) or $h_0 = H_{max}$ in the case 3b (Figure 4.3b); where $k$, $T$ are the Boltzman constant and the absolute temperature, respectively. In the case 3b $\Phi_{max} \gg I$ and it is possible to neglect the transfer of droplet over the potential barrier.
Disaggregation rate can be estimated using consideration presented in (Russel, Saville, and Schowalter, 1999), which gives

\[ A = \frac{kT}{6\pi \eta_0 a^3} \exp(\Phi_{\text{int}}). \] (4.7.4)

In the case of “big” droplets deformation in the contact region should be taken into account and expressions for the aggregation/disaggregation rates become more sophisticated.

Let a fraction of clusters of size \( i \) be introduced as \( f_i = n_i / N_0 (i = 1, 2, 3, \ldots) \), and a dimensionless volume fraction be determined as \( \alpha = \frac{BN_0}{A} = \frac{\gamma}{\gamma^*} \), where \( \gamma^* = \frac{A}{B} \). If \( \gamma^* \leq \gamma_m \) then \( \gamma^* \) is a characteristic volume fraction of doublets formation (see below). However, if \( \gamma^* > \gamma_m \) then \( \gamma^* \) is a parameter equal to the ratio of the association/dissociation rates.

Using these notations system of Eqs. (4.7.1, 4.7.2) takes the following form

\[ 0 = \alpha f_i f_i + f_i f_i - f_i - \alpha f_i f_i, \quad i = 2, 3, \ldots, \] (4.7.5)

\[ \sum_{i=1}^{\infty} i f_i = 1. \] (4.7.6)

Solution to system of Eqs. (4.7.5), (4.7.6) is

\[ f_i = \frac{1}{\alpha + 0.5 + \sqrt{\alpha + 0.25}} \] (4.7.7)

\[ f_i = \frac{\alpha^{i-1}}{[\alpha + 0.5 + \sqrt{\alpha + 0.25}]^i}, \quad i = 2, 3, \ldots. \] (4.7.8)

We can conclude from Eq. (4.7.8) that \( f_i \), \( i = 2, 3, \ldots \) dependencies on \( \alpha \) go from zero at \( \alpha = 0 \) to zero at \( \alpha \to \infty \) via maximum value at
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\[ \alpha_i^{\text{max}} = \frac{i^2 - 1}{4}, \quad (4.7.9) \]

and this maximum value is equal to

\[ f_i^{\text{max}} = 4 \frac{(i-1)^{i-1}}{(i+1)^{i+1}}, \quad (4.7.10) \]

In the case \( i=2 \) (doublets) Eq. (4.7.9) gives: \( \alpha_2^{\text{max}} = 0.75 \), or \( \gamma_2^{\text{max}} = 0.75 \gamma^* \). The latter presents the physical meaning of \( \gamma^* \): \( \gamma^* \) is close to the volume fraction when the fraction of doublets reaches its maximum value.

\( f, i=I, 2, 3, \ldots \) dependencies according to Eqs. (4.7.7)-(4.7.8) are shown in Figure 44.

It is worth reminding that \( \alpha = \gamma / \gamma^* \) is the dimensionless droplet volume fraction; that is, all dependencies on \( \alpha \) present actually the dependencies on the volume fraction of the droplets.

Volume fraction of clusters, \( \gamma_i \), \( i=1,2,3,\ldots \), are related to the fractions of clusters, \( f_i \), \( i=1,2,3\ldots \), in the following way: \( \gamma_i = f_i \frac{i \gamma}{\gamma_{i,\text{max}}} \), \( i=1,2,3,\ldots \). Using the latter relation and expressions (4.7.7)-(4.7.8) we conclude:

\[ \gamma_i = \frac{\gamma}{0.5 + \gamma / \gamma^* + \sqrt{0.25 + \gamma / \gamma^*}}, \quad (4.7.11) \]

\[ \frac{d \gamma_i}{d \gamma} = \frac{2}{\sqrt{1 + 4 \gamma / \gamma^*}} \frac{1}{1 + 2 \gamma / \gamma^* + \sqrt{1 + 4 \gamma / \gamma^*}}. \quad (4.7.12) \]
Figure 4.1 Dependence of the relative effective viscosity inside clusters, $\frac{\eta_c}{\eta_0}$, on the packing density inside clusters, $\gamma_m$, at different values of the viscosity ratio, $F = \frac{\eta_d}{\eta_0}$, according to Eq. (4.3.2)

1. according to Eq. (4.3.3), immobilised surface of droplets or high viscosity ratio $F \gg 1$.
2. $F = 100$
3. $F = 10$
4. $F = 1$
5. $F = 0.1$
6. according to Eq. (4.3.4), low viscosity ratio, $F \ll 1$. 
Figure 4.2a Comparison of the relative effective viscosity of emulsions, $\eta/\eta_0$, calculated according to Eq. (4.3.1') and our Eqs. (4.3.2), (4.32.6) at different packing density inside clusters, $\gamma_m$, and viscosity ratio $F = \eta_r/\eta_0 = 0.01$.

Curve 1,3,5 (solid lines) according to Eqs. (4.3.2), (4.3.6).
Curve 2,4,6 (broken lines) according to Eq. (4.3.1') (Pal, 2000).
Curves 1,2, $\gamma_m = 0.739$ (hexagonal packing)
Curves 3,4, $\gamma_m = 0.679$ (cubic centered)
Curves 5,6, $\gamma_m = 0.524$ (simple cubic)
Figure 4.2b Comparison of the relative effective viscosity of emulsions, $\eta/\eta_0$, calculated according to Eq. (4.3.1') and our Eqs. (4.3.2), (4.3.6) at different packing density inside clusters, $\gamma_m$, and viscosity ratio $F = \frac{\eta_s}{\eta_0} = 10$

Curves 1,2, $\gamma_m = 0.739$ (hexagonal packing)
Curves 3,4, $\gamma_m = 0.679$ (cubic centered)
Curves 5,6, $\gamma_m = 0.524$ (simple cubic)
Figure 4.2c Comparison of the relative effective viscosity of emulsions, \( \frac{\eta}{\eta_0} \), calculated according to Eq. (4.3.1') and our Eqs. (4.3.2), (4.3.6) at different packing density inside clusters, \( \gamma_m \), and viscosity ratio \( F = \frac{\eta_d}{\eta_0} = 1000 \).

Curves 1,2, \( \gamma_m = 0.739 \) (hexagonal packing)

Curves 3,4, \( \gamma_m = 0.679 \) (cubic centered)

Curves 5,6, \( \gamma_m = 0.524 \) (simple cubic)
Figure 4.3a potential of interaction with a sufficiently shallow primary minimum. Potential of colloidal interaction between droplets, $\Phi$, against the closest separation between the droplet surfaces, $h$. 
Figure 4.3b Potential of interaction with sufficiently deep secondary minimum and high potential barrier between secondary and primary minima.

Potential of colloidal interaction between droplets, $\Phi$, against the closest separation between the droplet surfaces, $h$. 
Figure 4.4 Dependencies of cluster fractions, $f_i$, $i=1, 2, 3, \ldots$, according to Eqs. (4.7.7)-(4.7.8) on the dimensionless volume fraction of droplets, $\alpha = \gamma / \gamma^*$. Fractions of
1 single droplets,
2 doublets,
3 triplets,
4 quadruplets.
Figure. 4.5a $F=0.01$

Dependency of the relative viscosity $\eta/\eta_0$, on the relative volume fraction of droplets, $\gamma/\gamma_m$, $\gamma_m = 0.679$ (cubic centered packing density inside clusters). Curves 2-7 according to Eqs. (4.3.2), (4.4.3), (4.7.11), (4.7.12) at viscosity ratio, $F = \eta_d/\eta_0 = 0.01$, and six different characteristic volume fractions of doublet formation, $\gamma^*$

1 according to Eqs. (4.3.2), (4.3.6) (developed flocculation)
2 $\gamma^* = 0.01$
3 $\gamma^* = 0.1$
4 $\gamma^* = 0.2$
5 $\gamma^* = 0.3$
6 $\gamma^* = 0.4$
7 $\gamma^* = 1$
8 according to Eq (1.7.4) (no flocculation).
Figure 4.5b  F=100

Dependency of the relative viscosity, $\eta/\eta_0$, on the relative volume fraction of droplets, $\gamma/\gamma_m$, $\gamma_m = 0.679$ (cubic centered packing density inside clusters). Curves 2-7 according to Eqs. (4.3.2), (4.3.6), (4.7.11), (4.7.12) at viscosity ratio, $F = \eta_d/\eta_0 = 100$, and six different characteristic volume fractions of doublet formation, $\gamma^*$.

1. according to Eqs. (4.3.2), (4.3.6) (developed flocculation)
2. $\gamma^* = 0.01$;
3. $\gamma^* = 0.1$;
4. $\gamma^* = 0.2$;
5. $\gamma^* = 0.3$;
6. $\gamma^* = 0.4$;
7. $\gamma^* = 1$;
8. according to Eq. (1.7.4) (no flocculation).
Figure 4.6

Solid line effective viscosity of emulsions on volume fraction of droplets according to Eqs. (4.3.2), (4.3.6) (developed flocculation).


Sets A: experimental data from (Pal, 2000)
Fitted values of the packing density inside clusters, $\phi_m$:
A1: $\gamma_m = 0.826$;
A2: $\gamma_m = 0.85$;
A3: $\gamma_m = 0.825$;
A4: $\gamma_m = 0.869$.

Fitted values of the packing density inside clusters, $\gamma_m$:
B1: $\gamma_m = 0.695$;
B2: $\gamma_m = 0.73$. 
1 Experimental data from (Leviton, A, and Leighton, A., 1936) (milk at different volume fractions of fat) are fitted according to Eqs. (4.3.2), (4.4.3). Fitted values: $\gamma_m = 0.663$, $\gamma^* = 0.395$. $\eta_c = 11.674$ calculated according to Eq. (4.3.2) using the fitted value $\gamma_m = 0.663$.

2 According to Eq. (1.7.6) (in the absence of cluster formation).
# LIST OF SYMBOLS

## Latin

- **a**: radius of droplets  
- **A**: aggregation rate  
- **B**: disaggregation rate  
- **γₗ**: volume fraction of clusters size i  
- **H, h**: thickness  
- **k**: the Boltzmann constant  
- **K**: constant in equation (4.1.3)  
- **m**: retardation function (Eq (4.7.3))  
- **n**: number of clusters in the volume of emulsion, **V**  
- **N**: initial number of single droplets in the volume of emulsion, **V**  
- **r**: radial distance  
- **T**: the absolute temperature  
- **V**: volume

## Greek

- **α=ϕ/ϕ***: dimensionless volume fraction of droplets  
- **γ**: shear rate  
- **ϕ**: volume fraction of droplets  
- **Φ**: potential of colloidal interactions  
- **η**: viscosity  
- **Δξ**: introduced in Eq (4.2.8)  
- **Δθ**: volume fraction of marked clusters  
- **Ψ**: introduced in Eq. (4.2.4)

## Subscripts

- **0**: dispersion liquid (continuous phase)  
- **d**: droplets  
- **i**: number of single droplets in the cluster
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max variable packing density inside clusters
m averaged packing density inside clusters

Superscripts

* characteristic volume fraction of doublet formation
max maximum value
Chapter 5 EFFECTIVE VISCOSITY AND PERMEABILITY OF POROUS MEDIUM BUILT UP BY SPHERICAL PARTICLES

5.1 Introduction

The effective properties of porous media built up by equal sized spherical particles are investigated in this Chapter. Flow inside porous medium is modelled using Brinkman’s equations, which include two semi-empirical coefficients: an effective viscosity and a resistance coefficient (1/permability). Our new method is used to deduce the dependencies of these coefficients on both porosity and particle size. The deduced dependency of permeability on porosity is found to agree reasonably well with known dependencies, which have been deduced using computer simulations of flow in randomly packed porous media.

Viscous flow of a liquid in a porous medium is frequently modelled using Darcy’s equations:

\[ \text{grad} \, p = -K_D(\gamma)\bar{u}, \]

(5.1.1)

where \( K_D \) is the porous medium resistance coefficient (1/\( K_D \) is the porous medium permeability); \( \gamma \) is the particle volume fraction (\( \varphi = 1 - \gamma \) is the porosity); \( p \) and \( \bar{u} \) are the pressure and average velocity, respectively. Eq (5.1.1) should also be coupled with the incompressibility equation

\[ \text{div} \, \bar{u} = 0. \]

(5.1.2)

The dependency of the effective permeability \( 1/K_D \) on the volume fraction of particles is considered in a number of publications (Adrover, and Giona, 1996), (Bird, et al., 1960), (Foster, and Butt, 1966), (Katz, and Thompson, 1986), (Happel, and Brenner, 1965.).
Darcy's model suffers from a well-known disadvantage: it is impossible to match flows inside and outside the porous medium. To overcome this difficulty two different approaches have been suggested: a slippage at the boundary between flows inside and outside the porous medium (Beaverse, and Johns, 1967) and Brinkman's equations (Brinkman, 1952; 1947). In the first approach, an empirical slippage coefficient is defined, whereas in Brinkman's approach two, physically meaningful, coefficients are introduced: an effective viscosity, $\eta_B$ (which is obviously different from the liquid viscosity $\eta_0$) and the porous medium resistance coefficient, $K_B$. Brinkman's equations have the following form

$$\text{grad} p = \eta_B(\gamma) \Delta \bar{u} - K_B(\gamma) \bar{u}.$$  \hspace{1cm} (5.1.3)

Eq.(5.1.2) should also be considered.

Let $L_B$ be a characteristic length scale for Eqs.(5.1.3). This length scale can be determined in the following manner: both terms in the right hand side of Eqs.(5.1.3) have to be of the same order of magnitude. This requirement gives:

$$\frac{\eta_B}{L_B^2} = K_B,$$

or

$$L_B = \sqrt[2]{\frac{\eta_B}{K_B}}.$$

where $L_B$ is referred to as the 'Brinkman's length'. If the distance $L$ in the depth of the porous medium and remote from the porous medium-liquid interface satisfies the following inequality $L >> L_B$, then the viscosity term in the right hand side of Eq.(5.1.3) can be neglected and Brinkman's equations coincide with Darcy's Eqs. (5.1.1). This consideration shows that hydrodynamic resistance in both equations are equal; that is, $K_D = K_B$. Kozeny-Carman and Happel-Brenner equations (Happel, and Brenner, 1965.) are frequently used to describe the dependency of hydrodynamic resistance on porosity and particle radius.

The porous medium resistance, $K_B$, vanishes in two cases: either when volume fraction of the particles is zero (i.e. for a pure liquid, when $\eta_B = \eta_0$, where $\eta_0$ is the pure liquid viscosity) or
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when the particles move with the same average velocity as the liquid (concentrated suspension). In the latter case \( \eta_B = \eta_s \), where \( \eta_s \) is the viscosity of the concentrated suspension. The last observation gives a very important hint, namely, the dependency of \( \eta_B \) on particle volume fraction should be close to the viscosity of concentrated suspension with the same particle volume fraction in the case when \( K_B \) is small enough. It is well known that the dependency of \( \eta_s \) on particle volume fraction is an increasing function of particle volume fraction, \( \gamma \). Consequently, it is reasonable to assume that \( \eta_B \) dependency should also be an increasing function of particle volume fraction. In contrast to this assumption, a decrease of effective viscosity with particle volume fraction \( \gamma \) has been predicted (Koplik, and Levine, 1983). Hence, at the moment there is no agreement in the literature even on the value of the effective viscosity in Brinkman equations. Using our new method we show below that the effective viscosity and permeability are solutions of system of two differential equations, which is deduced and solved below in this Chapter.

5.2 Derivation of the system differential equations for calculation of viscosity and permeability

The idea of our method is illustrated in Figure 5.1.

It is assumed below that a porous medium is built up by equal size spherical particles, which are randomly distributed in space and form the porous medium under consideration. The total volume fraction of solid particles, \( \gamma = \frac{V_p}{V} \), \( V_p = \nu N \), \( \nu = \frac{4\pi a^3}{3} \), where \( N \) is the total number of particles in the volume \( V \); \( a \) is the particle radius. The porous medium is assumed completely saturated with a liquid with viscosity \( \eta_0 \). It is convenient to introduce a resistance coefficient of pure liquid medium, \( K_0 \), which is obviously equal to zero.
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It is assumed both effective resistance coefficient of the porous medium, $K^{\text{eff}}$, and effective viscosity, $\eta^{\text{eff}}$, can be presented as the following functions

$$K^{\text{eff}}(\gamma) = \Psi[K_0, \eta_0, \gamma], \quad (5.2.1)$$

$$\eta^{\text{eff}}(\gamma) = \Lambda[K_0, \eta_0, \gamma], \quad (5.2.2)$$

that is, completely determined by the volume fraction of particles, viscosity and resistance coefficient of the surrounding medium, which is at the moment the liquid inside the porous medium and, hence, $K_0=0$. The System of two differential equations for determination of functions in the right hand side of Eqs. (5.2.1) and (5.2.2) is deduced below.

If all the volume fraction, $\gamma = 0$, vanishes when the volume $V$ includes only pure liquid and Eqs. (5.2.1), (5.2.2) give

$$K_0 = \Psi[K_0, \eta_0, 0], \quad (5.2.3)$$

$$\eta_0 = \Lambda[K_0, \eta_0, 0], \quad (5.2.4)$$

which are used below as initial conditions. It should be remembered that $K_0=0$.

Let us randomly mark a small number of particles inside the porous medium, $\delta N << N$. Now the whole porous medium can be considered as a mixture of the marked particles surrounded by the porous medium with non-marked particles. Let the volume fraction of the marked particles be $\delta \theta$

$$\delta \theta = \frac{\delta V}{V}, \quad (5.2.5)$$

where $\delta V = v \delta N$ is the volume of the marked particles.

Volume fraction of non-marked particles in the rest of the porous medium is different from the initial volume fraction $\gamma$ by a small amount $\delta \zeta$, which can be either positive or negative and is determined as $\gamma + \delta \zeta = \frac{V_p - \delta V}{V - \delta V}$, or keeping only first order terms

$$\delta \zeta = \frac{V_p - \delta V}{V - \delta V} - \frac{V_p}{V} = -\frac{\delta \theta + \gamma \delta \theta}{1 - \delta \theta} = -\delta \theta + \gamma \delta \theta. \quad (5.2.6)$$
Now (see Figure 5.1) effective viscosity and the resistance coefficient of the porous media can be expressed in two different ways: according to Eqs. (5.2.1)-(5.2.2) and considering the marked particles with small concentrations $\delta \theta$, surrounded by the rest of the porous media built up by non-marked clusters with resistance coefficient and effective viscosity $\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi]$. In the latter case resistance coefficient and viscosity of the porous medium can be written as

$$K^{\text{eff}}(\gamma) = \Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], \Delta \theta]. \tag{5.2.7}$$

$$\eta^{\text{eff}}(\gamma) = \Lambda[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], \Delta \theta]. \tag{5.2.8}$$

Obviously, two different expressions for the calculation of the resistance coefficient (Eqs (5.2.1) and (5.2.7)) and the viscosity (Eqs. (5.2.2) and (5.2.8)) should be equal. Equating the right hand sides of Eqs.(5.2.1) and (5.2.7) gives an equation for resistance coefficient determination:

$$\Psi[K_0, \eta_0, \gamma] = \Psi[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], \Delta \theta]. \tag{5.2.9}$$

The same procedure using Eqs.(5.2.2) and (5.2.8) gives an equation for viscosity determination:

$$\Lambda[K_0, \eta_0, \gamma] = \Lambda[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], \Delta \theta]. \tag{5.2.10}$$

Transformation of the right handside of Eq. (5.2.9) gives

$$\Psi[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], \Delta \theta] =$$

$$= \Psi[\Psi[K_0, \eta_0, \gamma], \Lambda[K_0, \eta_0, \gamma], 0] +$$

$$+ \frac{\partial \Psi[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma], 0]}{\partial \Delta \xi} \Delta \xi + \frac{\partial \Psi[\Psi[K_0, \eta_0, \gamma + \Delta \xi], \Lambda[K_0, \eta_0, \gamma + \Delta \xi], 0]}{\partial \Delta \theta} \Delta \theta. \tag{5.2.11}$$

If the volume fraction of marked particles vanishes ($\Delta \theta = 0$), the volume $V$ includes only the rest of porous medium, consequently
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\[ \Psi[K_0, \eta_0, \gamma, \Lambda[K_0, \eta_0, \gamma], 0] = \Psi[K_0, \eta_0, \gamma] \]  \hspace{1cm} (5.2.12)

\[ \Psi[K_0, \eta_0, \gamma + \Delta \xi, \Lambda[K_0, \eta_0, \gamma], 0] = \Psi[K_0, \eta_0, \gamma + \Delta \xi] \]  \hspace{1cm} (5.2.13)

and

\[ \Psi[K_0, \eta_0, \gamma, \Lambda[K_0, \eta_0, \gamma + \Delta \xi], 0] = \Psi[K_0, \eta_0, \gamma] \]  \hspace{1cm} (5.2.14)

Eqs. (5.2.9) (5.2.11)-(5.2.14), yield the following equation

\[ 0 = \frac{\partial \Psi[K_0, \eta_0, \gamma + \Delta \xi]}{\partial \Delta \xi} \Delta \xi + \frac{\partial \Psi[K_0, \eta_0, \gamma, \Lambda[K_0, \eta_0, \gamma], \Delta \delta]}{\partial \Delta \delta} \Delta \delta \]  \hspace{1cm} (5.2.15)

Eq. (5.2.15) can be rewritten as

\[ \frac{d\Psi[K_0, \eta_0, \gamma]}{d\gamma} \Delta \xi = -A_k(\Psi, \Lambda) \Delta \delta, \]  \hspace{1cm} (5.2.16)

where function \( A_k \) is defined by

\[ A_k[\Psi[K_0, \eta_0, \gamma], \Lambda[K_0, \eta_0, \gamma], \Delta \xi, \Delta \delta] = \frac{\partial \Psi[K_0, \eta_0, \gamma, \Lambda[K_0, \eta_0, \gamma], \Delta \delta]}{\partial \Delta \delta} \bigg|_{\Delta \delta = 0}. \]  \hspace{1cm} (5.2.17)

Relations (5.2.16) and (5.2.6) give

\[ \frac{d\Psi}{d\gamma} = \frac{A_k(\Psi, \Lambda)}{1-\gamma}. \]  \hspace{1cm} (5.2.18)

Using definition

\[ A_k[\Psi[K_0, \eta_0, \gamma], \Lambda[K_0, \eta_0, \gamma], \Delta \xi, \Delta \delta] = \frac{\partial \Lambda[\Psi[K_0, \eta_0, \gamma], \Lambda[K_0, \eta_0, \gamma], \Delta \delta]}{\partial \Delta \delta} \bigg|_{\Delta \delta = 0}. \]  \hspace{1cm} (5.2.19)

the similar approach gives the equation

\[ \frac{d\Lambda}{d\gamma} = \frac{A_\eta(\Psi, \Lambda)}{1-\gamma}. \]  \hspace{1cm} (5.2.20)

Eqs. (5.2.18), (5.2.20) gives the following system of coupled differential equations

\[ \begin{align*}
\frac{dK_B}{d\gamma} &= \frac{A_K[\eta_B, K_B]}{1-\gamma}, \\
\frac{d\eta_B}{d\gamma} &= \frac{A_\eta[\eta_B, K_B]}{1-\gamma},
\end{align*} \]  \hspace{1cm} (5.2.21)

with boundary conditions
Values of functions $A_K(\eta_B, K_B)$ and $A_\eta(\eta_B, K_B)$ are calculated in Appendix 1 and Appendix 2 in this chapter. Eqs. (5.5.23), (5.4.16) give the required functions $A_K(\eta_B, K_B)$ and $A_\eta(\eta_B, K_B)$. After substitution of these expressions into system (5.2.22) we have the final system of differential equations for determination of $K_B$ and $\eta_B$ dependences on the volume fraction of particles in the porous medium:

$$\frac{dK_B}{d\gamma} = \frac{9\eta_B}{2a^2} \left( 1 + a \sqrt{\frac{K_B}{\eta_B}} + a^2 \frac{K_B}{9\eta_B} \right),$$  \hspace{1cm} (5.2.23)$$

$$\frac{d\eta_B}{d\gamma} = \frac{K_B a^2}{6} \left( 1 - \gamma \right) \left( 1 + a \sqrt{\frac{K_B}{\eta_B}} \right),$$ \hspace{1cm} (5.2.24)

with boundary conditions (5.2.22).

Let us introduce two dimensionless functions $Z(\gamma) = \frac{K_B a^2}{\eta_0}$, $\eta(\gamma) = \frac{\eta_B}{\eta_0}$. Using these functions the system (5.2.23-5.2.24) with boundary conditions (5.2.22) can be rewritten as

$$\frac{dZ}{d\gamma} = \frac{9\eta}{2} \left( 1 + \sqrt{\frac{Z}{\eta} + \frac{1}{9} \frac{Z}{\eta}} \right),$$  \hspace{1cm} (5.2.25)
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\[
\sqrt{\frac{Z}{\eta}} + \frac{15}{Z} + \frac{15}{Z} \eta \\
\frac{d\eta}{dy} = \frac{Z}{6} \frac{\eta}{(1-\gamma) \left( 1 + \frac{Z}{\sqrt{\eta}} \right)}
\]

with boundary conditions

\[
Z(0) = 0, \\
\eta(0) = 1.
\]

5.3 Discussion

At low particle fraction, \(\gamma\), the dimensionless resistance coefficient \(Z(\gamma)\) becomes small and Eqs. (5.2.6-5.2.7) can be rewritten as

\[
\frac{dZ}{d\gamma} = \frac{9\eta}{2} \frac{1}{1-\gamma},
\]

\[
\frac{d\eta}{d\gamma} = \frac{5\eta}{2(1-\gamma)}.
\]

The latter system of equations with boundary conditions (5.2.3) has the following solutions (using dimensional variables)

\[
\eta_B(\gamma) = \eta_0 (1-\gamma)^{-5/2},
\]

\[
K_B(\gamma) = \frac{9}{5} \frac{\eta_0}{a^2} \left( (1-\gamma)^{-5/2} - 1 \right).
\]

Eqs. (5.3.3-5.3.4) determine the dependence of the effective viscosity and the resistance coefficient of Brinkman's medium on the volume fraction of particles, \(\gamma\), in the case of a low
particle volume fraction. Both dependencies are increasing functions of particle volume fraction, \( \gamma \).

Eq. (5.3.4) can be rewritten as

\[
K_B(\gamma) = \frac{9}{5a^2} \left[ \eta_B(\gamma) - \eta_0 \right].
\]  

(5.3.5)

The latter equation gives the dependency of the hydrodynamic resistance on the particle volume fraction, \( \gamma \), if \( \gamma \) is small. According to Eq. (5.3.5) the hydrodynamic resistance becomes negative if the effective viscosity is lower than the liquid viscosity, which is obviously impossible.

Let us introduce the dimensionless permeability \( k = \frac{1}{Z} = \frac{\eta_0}{K_B a^2} \) and investigate its dependence on porosity \( \varphi \).

According to Eq (5.3.5) at high porosity, \( \varphi \to 1 \):

\[
k(\varphi) = \frac{5}{9} \frac{\varphi^{5/2}}{1 - \varphi^{5/2}}, \quad \varphi \to 1.
\]  

(5.3.6)

This dependency is shown by curve 4 in Figure 5.2. At low porosity, \( \varphi \to 0 \), according to Appendix 3, \( k = \frac{1}{t^2_\infty \eta} \) and \( \eta = C_\infty \varphi^{-4.130} \), hence:

\[
k = \frac{\varphi^{4.130}}{t^2_\infty C_\infty}.
\]  

(5.3.7)

This dependency is shown by curve 5 in Figure 5.2. Curve 3 in the same figure represents the permeability dependency on porosity calculated according to Eqs.(5.2.6)-(5.2.7). Curves 1
and 2 in Figure 5.2 give the permeability calculated according to Happel-Brenner and Kozeny-Carman equations (Happel, and Brenner, 1965.), respectively. Points and squares show permeability obtained by direct computer simulations of liquid flow in a random three-dimensional (Koponen, Kataja, and Timonen, 1997) and a two-dimensional porous medium (Cancelliere, Chang, Foti, Rothman, and Succi, 1990), correspondingly. In two papers (Koponen, Kataja, and Timonen, 1997) and (Cancelliere, Chang, Foti, Rothman, and Succi, 1990) simulated porous medium consist of penetrating particles, which form clusters at high volume fractions. It is necessary to mention that according to the model adopted here, particles do not penetrate into each other and do not form clusters. It appears that mutual particle penetration and clustering are more important in the case of a three-dimensional porous medium (Koponen, Kataja, and Timonen, 1997). This results in a close agreement between our prediction (curve 3, Figure 5.3) and permeability dependency in the case of a two-dimensional porous medium (squares, according to (Cancelliere, Chang, Foti, Rothman, and Succi, 1990)).

The relative viscosity at high porosity (that is, at \( \phi \to 1 \)) according to Eq.(5.3.3) can be rewritten as

\[
\log_{10} \eta = -2.5 \log_{10} \phi, \quad \phi \to 1.
\]  

(5.3.9)

The latter dependency is shown as asymptote 2 in Figure 5.3. At low porosity, \( \phi \to 0 \), according to Appendix 3 the relative viscosity is

\[
\log_{10} \eta = -4.130 \log_{10} \phi - 0.2249, \quad \phi \to 0.
\]  

(5.3.10)

The latter dependency is shown by asymptote 3 in Figure 5.3. Curve 1 represents the relative viscosity dependence on porosity calculated according to Eqs.(5.2.6)-(5.2.7).
5.4 Appendix 1 Uniform flow

Calculation of function $A_K(\eta_B, K_B)$

Let us consider a single spherical particle with radius $a$ placed in a uniform flow inside homogeneous Brinkman's homogeneous medium. Far from the particles the following boundary conditions should be satisfied

$$\vec{u}\bigg|_{r \to \infty} = \vec{U} = (0, 0, U), \quad (5.4.1)$$

that is, $U_1 = U_2 = 0$, $U_3 = U$.

In the case under consideration our aim is to calculate the force exerted on the particle.

The flow obeys Brinkman's Eqs. (5.1.3) and the incompressibility condition (5.1.2).

If we apply $\nabla \times$ operation to Eq. (5.1.3), then we obtain

$$\eta_B \nabla \times \nabla \times \vec{u} - K_B \nabla \times \vec{u} = 0. \quad (5.4.2)$$

In the same way as in ref. (Landau, and Lifshitz, 1959) the velocity vector can be presented in the following form

$$\vec{u} = \vec{U} + \nabla \times \nabla \times f(r) \vec{U}, \quad (5.4.3)$$

where $f(r)$ is a new unknown function, $r = |\vec{r}|$ is the radial distance from the origin (the origin is selected in the particle centre). Hence,

$$\nabla \times \vec{u} = \nabla \times \nabla \times (f \vec{U}) = \nabla \cdot \nabla \times \nabla (f \vec{U}) - \Delta \nabla \times (f \vec{U}) =$$

$$= \Delta \nabla \times (f \vec{U})$$

or
$$\text{rot}_{\mathbf{i}} \mathbf{u} = \sum_{j,k=1}^{3} \varepsilon_{ijk} \nabla_j u_k = - \sum_{j,k=1}^{3} \varepsilon_{ijk} U_k \Delta \nabla_j f =$$

$$= - (\Delta f)^{\prime} \sum_{j,k=1}^{3} \varepsilon_{ijk} U_k \frac{x_j}{r},$$

where \( \varepsilon_{ijk} \) is the anti-symmetric unit tensor \( (\varepsilon_{123} = 1, \varepsilon_{ijk} = - \varepsilon_{jik} = - \varepsilon_{ikj}) \).

Substitution of the latter expression in Eq. (4.4.2) gives the following equation for determination of unknown function \( f(r) \):

$$0 = \left( \Delta^2 f(r) - \frac{K_B}{\eta_B} \Delta f(r) \right)^{\prime} \sum_{j,k=1}^{3} \varepsilon_{ijk} U_k \frac{x_j}{r}. \quad (5.4.4)$$

It is obvious, that \( \sum_{j,k=1}^{3} \varepsilon_{ijk} U_k \frac{x_j}{r} \neq 0 \) everywhere, hence Eq. (5.4.4) yields

$$0 = \left( \Delta^2 f - \frac{K_B}{\eta_B} \Delta f \right)^{\prime}. \quad (5.4.5)$$

After substitution \( f = \psi/r \), where \( \psi(r) \) is a new unknown function, and integration Eq.(5.4.5) can be written in the following form

$$\frac{\psi^{''''}(r)}{r} - \frac{K_B}{\eta_B} \frac{\psi^{''}(r)}{r} = \text{const.} \quad (5.4.6)$$

An integration constant should be set to zero because the fluid velocity remains finite far from the particle. Eq. (5.4.6) has the following solution:

$$\psi = G + Qr + Me^r + He^{-r}, \quad (5.4.7)$$
where $G$, $Q$, $M$ and $H$ are integration constants. Taking into account substitution $f = \psi/r$
the latter equation gives:

$$f = \frac{G}{r} + Q + \frac{\eta_B}{K_B} \left( e - \sqrt{\frac{K_B}{\eta_B}} \frac{1}{r} - 1 + \sqrt{\frac{K_B}{\eta_B}} \right)$$  \hspace{1cm} (5.4.8)$$

Eq. (5.4.3) can be rewritten as

$$u_i = U_i + \text{grad div } fU_i - \Delta fU_i, i=1,2,3.$$  \hspace{1cm} (5.4.9)$$

From Eqs. (5.4.8) and (5.4.9) we can conclude

$$u_i = U_i + \frac{3}{r^3} \sum_{j=1}^{3} n_i n_j U_j - \frac{1}{r^3} U_i G +$$

$$+ \frac{H}{K_B} \eta_i \left[ \frac{K_B e}{\eta_B} \frac{1}{r} - \frac{3}{r} n_i \sum_{j=1}^{3} n_j U_j - \frac{K_B e}{\eta_B r} U_i - \right.$$  \hspace{1cm} (5.4.10)$$

$$- \frac{K_B e}{\eta_B r^2} U_i + \frac{3}{r^2} n_i \sum_{j=1}^{3} n_j U_j -$$

$$- \frac{K_B e}{\eta_B r^2} U_i - \frac{3}{r^3} n_i \sum_{j=1}^{3} n_j U_j .$$

The latter equations and non-slip conditions at the particle surface $r = a$ determine the value of constants $G$ and $N$: 

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All functions under consideration below (components of velocity vector, viscous stress tensor and pressure) are presented as $F = F^{(0)} + F^{(1)}$, where $F^{(0)}$ is caused by the flow far from the particle and $F^{(1)}$ is caused by the presence of the particle. Below we are interested only in values caused by the particle and, hence, in first order terms. Superscript (1) is omitted.

The pressure can be calculated after substitution in Eq. (5.1.3) as the velocity expression via function $f(r)$ (Eq. (5.4.3)): 

$$\nabla p = \nabla \left[ \eta_B \Delta \nabla f \vec{U} - K_B \nabla f \vec{U} \right] = \left( \eta_B \vec{U} \Delta^2 f - K_B \vec{U} \Delta f \right) = \nabla \left[ \eta_B \Delta \nabla f \vec{U} - K_B \nabla f \vec{U} \right].$$

And after integration:

$$p = \eta_B \Delta \nabla f \vec{U} - K_B \nabla f \vec{U}.$$ 

Using Eq.(5.4.8) the latter equation gives:

$$p = \left( K_B \frac{G}{r^3} - \eta_B \frac{N}{r^3} \right) \sum_{j=1}^{3} x_j U_j,$$

where constants $G$ and $N$ are given by Eq. (5.4.11).
Let us rewrite the velocity vector (5.4.10) and pressure (5.4.12) using spherical co-ordinate system with polar axe along the direction of the velocity vector, $\vec{U}$. This gives:

$$u_r = U \cos \theta \left( \frac{\eta_B}{K_B} \left[ -\sqrt{\frac{K_B}{r^2}} \frac{1}{\eta_B} - \sqrt{\frac{K_B}{r^3}} \frac{2}{r^3} + 2G \right] \right),$$

$$u_\theta = -U \sin \theta \left( \frac{\eta_B}{K_B} \left[ -\sqrt{\frac{K_B}{r^2}} \frac{1}{\eta_B} - \sqrt{\frac{K_B}{r^3}} \frac{2}{r^3} + 2G \right] \right),$$

$$p = \left( \frac{K_B G}{r^2} - \frac{\eta_B H}{r^2} \right) U \cos \theta.$$

Components of the stress tensor at the particle surface, $r = a$ can be deduced using the latter expressions as

$$\sigma_{rr} = \left( \frac{K_B a}{2} + \frac{3}{2} \sqrt{\frac{\eta_B K_B}{a}} + \frac{3 \eta_B}{2 a} \right) U \cos \theta,$$

$$\sigma_{r\theta} = \left( \frac{3}{2} \sqrt{\frac{\eta_B K_B}{a}} + \frac{3 \eta_B}{2 a} \right) U \sin \theta,$$

(5.4.13)

where $\sigma_{rr}$, $\sigma_{r\theta}$ are components of the stress tensor in polar co-ordinate system. The force, $F_B$, exerted to the spherical particle according to (Happel, and Brenner, 1965) can be calculated as:

$$F_B = \sum_a \int \left( \sigma_{rr} \cos \theta - \sigma_{r\theta} \sin \theta \right) \frac{1}{\Sigma a},$$

(5.4.14)
where \( \Sigma_a \) is the particle surface, \( d\Sigma \) is the surface element.

Eqs. (5.4.2) and (5.4.3) yield

\[
F_B = 6\pi \eta_B aU \left( 1 + a \frac{K_B}{\eta_B} + \frac{1}{9} a^2 \frac{K_B}{\eta_B} \right).
\]  
(5.4.15)

Additional resistance cause by the presence of marked particles inside the porous structure is

\[
\delta K_B = \frac{F_B \delta n}{V} = \frac{3F_B \delta \mu}{4\pi a^3} = \frac{3F_B \delta \gamma}{4\pi a^3 (1-\gamma)}.
\]

After substitution of Eq.(5.4.15) into the latter equation the result is

\[
\delta K_B = \frac{3F_B \delta \gamma}{4\pi a^3 (1-\gamma)} = \frac{6\pi \eta_B aU \left( 1 + a \frac{K_B}{\eta_B} + \frac{1}{9} a^2 \frac{K_B}{\eta_B} \right)}{4\pi a^3 (1-\gamma)} \frac{3\delta \gamma}{4\pi a^3 (1-\gamma)} = \\
= \frac{9}{2a^2 (1-\gamma)} \eta_B U \left( 1 + a \frac{K_B}{\eta_B} + \frac{1}{9} a^2 \frac{K_B}{\eta_B} \right) \delta \gamma.
\]

The latter equation shows that

\[
A_K = \frac{9\eta_B}{2a^2} \left( 1 + a \frac{K_B}{\eta_B} + \frac{1}{9} a^2 \frac{K_B}{\eta_B} \right)
\]  
(5.4.16)

5.5 Appendix 2 Extensional flow

**Calculation of function** \( A_\eta(\eta_B, K_B) \)

An extensional flow in the Brinkman’s medium 2 around a single sphere of radius \( a \) is considered below. The origin coincides with the particle centre. Far from the particle the flow is given by

\[
u_i \bigg|_{r \to \infty} = \sum_{j=1}^{3} a_{ij} x_j.
\]  
(5.5.1)
where \( a_{ij} \) is a symmetric tensor, \( \sum_{k=1}^{3} a_{kk} = 0 \). Brinkman’s Eq. (5.1.3) and the equation of incompressibility (5.1.2) describe the flow around the sphere.

On the particle surface non-slip conditions are

\[ \bar{u}_r = a = 0. \quad (5.5.2) \]

In the same way as in Appendix 1 the velocity vector can be presented in the following form

\[ \bar{u} = a \times \bar{x} + \text{rot} \left[ \text{rot} (a \times \nabla f) \right], \quad (5.5.3) \]

where an unknown function \( f(r) \) depends on radial distance \( r \) only, \( a \times \bar{x}_i = \sum_{j=1}^{3} a_{ij} x_j \).

Applying \( \text{rot} \) to the both sides of Eq. (5.1.3) yields

\[ \eta_B \Delta \text{rot} \bar{u} - K_B \text{rot} \bar{u} = 0. \quad (5.5.4) \]

From Eq. (5.5.3) we find

\[ \text{rot} \bar{u} = \text{rot} \left[ \text{rot} \left[ \text{rot} (a \times \nabla f) \right] \right] = \]

\[ = \text{grad} \left[ \text{div} (a \times \nabla f) \right] - \Delta \text{rot} (a \times \nabla f) = - \Delta \text{rot} (a \times \nabla f). \]

Substitution of the latter equation into Eq.(5.5.4) gives

\[ -\eta_B \Delta^2 \text{rot} (a \times \nabla f) + K_B \Delta \text{rot} (a \times \nabla f) = 0. \quad (5.5.5) \]

Using the antisymmetric unit tensor \( \varepsilon_{ijk} \) \((\varepsilon_{123} = 1, \varepsilon_{ijk} = - \varepsilon_{jik} = - \varepsilon_{ikj})\) in Eq. (5.5.5) we arrive (in the same way as in Appendix 1) to the following equation for \( f(r) \) determination:

\[ \eta_B \Delta^2 f - K_B \Delta f = 0, \quad (5.5.6) \]
where ' means a derivative in respect to \( r = |r| \). After substitution \( f = \psi/r \) (where \( \psi(r) \) is a new unknown function) we obtain from the Eq. (5.5.6):

\[
\left( \eta_B \frac{\psi'''}{r} - K_B \frac{\psi''}{r} \right) = 0. \tag{5.5.7}
\]

Equation (5.5.7) has the following solution

\[
f = \frac{\psi(r)}{r} = \frac{Q}{r} + G + \frac{Me}{r} + \frac{He}{r^2} + Ar^4 + Br^2,
\]

where \( Q, G, M \) and \( H \) are integration constants. In order to satisfy boundary conditions far from the particle (5.5.1) constants \( M, A \) and \( B \) must be set to zero and constant \( G \) can be easily determined, this gives:

\[
f = \frac{Q}{r} + H \left( \frac{1}{r} + \frac{K_B \eta_B}{r^4} \right). \tag{5.5.8}
\]

Eq. (5.5.3) can be rewritten as

\[
\tilde{u} = \alpha \ast \tilde{x} + \text{grad} \{\text{div}(\alpha \ast \nabla f)\} - \alpha \ast \nabla \Delta f. \tag{5.5.9}
\]

Using latter two equations we obtain

\[
u_k = -15 \frac{Q}{r^4} + H \left( \frac{K_B e}{r} - \frac{K_B e}{\eta_B} \right) - 6 \frac{e}{r^2} - 15 \frac{\eta_B e}{K_B r^3} - 15 \frac{e}{K_B r^4} + 15 \frac{\eta_B 1}{K_B r^4} \sum_{i,j=1}^{3} a_{ij} n_i n_j k + \\
+ r^4 \left( \frac{K_B e}{r} - \frac{K_B e}{\eta_B} + 3 \frac{e}{r^2} + 6 \frac{\eta_B e}{K_B r^3} + 6 \frac{e}{K_B r^4} + 6 \frac{\eta_B 1}{K_B r^4} \sum_{i=1}^{3} a_{ik} n_i \right) \tag{5.5.10}
\]
Non-slip conditions at the particle surface result in the following values of integration constants $N$ and $Q$:

$$H = \frac{5}{3} \sqrt[3]{\frac{K_B a}{\eta_B}} \left( 1 + \frac{K_B a}{\eta_B} \right),$$

$$Q = \frac{a^5}{9} \left( 1 + \frac{K_B a}{\eta_B} \right) \left( \frac{K_B}{\eta_B} + 6 + 15 \frac{\eta_B}{K_B a} + \frac{1}{K_B a} \right).$$

Now function $f(r)$ is completely determined.

According to Eqs. (5.1.3) and (5.5.3) the pressure gradient can be expressed as

$$\nabla p = \text{grad div} \left[ \eta_B a \ast \nabla f - K_B a \ast \nabla f \right] - K_B a \ast \vec{x}.$$

After integration of the latter equation

$$p = -\frac{1}{2} K_B \sum_{i,j=1}^{3} \sigma_{ij} x_i x_j + 3 \left( H \eta_B - Q K_B \right) \sum_{i,j=1}^{3} \sigma_{ij} x_i x_j + \frac{3}{5} \sum_{i,j=1}^{3} \sigma_{ij} n_i n_j.$$  

Using the definition of the stress tensor $\sigma_{ij} = -p \delta_{ij} + \eta_B \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$ and Eqs (3.5.10), (3.5.11) and (3.5.12) gives the following expression for the viscose stress tensor:

$$\sigma_{km} = \left[ \frac{1}{2} K_B r^2 - \frac{3(H \eta_B - Q K_B)}{r^3} \right] \delta_{km} \sum_{i,j=1}^{3} \sigma_{ij} n_i n_j + \cdots.$$
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Let us calculate a correction to the viscous stress tensor at a low volume fraction of particles. For any function \( \Xi \) we introduce an average value as

\[
\langle \Xi \rangle = \frac{1}{V_R V_R} \int \Xi dV,
\]

where \( V \) is the volume of the large sphere with a centre which coincides with the particle centre. Volume \( V_R \) does not include any other particles (low particles volume fraction). Integration of the viscous stress tensor over volume \( V_R \) results in

\[
\left\langle \sigma_{ij} \right\rangle = -(p) \delta_{ij} + \eta_B \left( \frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_j} \right) + \frac{1}{V_R V_R} \int \left\{ \sigma_{ij} + p \delta_{ij} - \eta_B \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right\} dV. \quad (5.5.14)
\]

The expression under the integral in the right hand side of the latter equation is zero outside the particle and differs from zero inside the particles. A direct calculation of the integral
inside the particle requires investigations of the stress tensor inside the particle. However, it is possible to avoid this problem by transformation of the integral over volume to the integral over comprising surfaces: inner surface of the volume $V_R$, $\Sigma_R$, which does not go through any other particle.

The stress tensor we can rewrite the stress tensor as

$$\sigma_{ij} = \frac{1}{2} \sum_{k=1}^{3} \left( \frac{\partial (\sigma_{ik} x_j)}{\partial x_k} + \frac{\partial (\sigma_{jk} x_i)}{\partial x_k} - K_B \frac{\partial (u_k x_i x_j)}{\partial x_k} \right).$$  \hfill (5.5.15)

Substitution of Eq. (5.5.15) into (5.5.14) gives

$$\langle \sigma_{ij} \rangle = \frac{1}{\Sigma} \sum_{i=1}^{3} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \frac{1}{2V} \sum_{k=1}^{3} \left( \sigma_{ik} x_j df_k + \sigma_{jk} x_i df_k - K_B^{ik} x_i x_j df_k \right) - 2n^{ik} df_i - 2n^{jk} df_i.$$  \hfill (5.5.16)

The value $\langle p \rangle$ disappears because the average pressure is equal to zero: $\langle p \rangle$ is a scalar, which must be determined by a linear combination of components of the tensor $\sigma_{ik}$, the latter scalar is equal to $\sum_{i=1}^{3} \sigma_{ii} = 0$.

In order to calculate the integral in (5.5.14) the following relations which are valid at integration over spherical surface, are used:

$$\frac{1}{\Sigma} \sum_{i=1}^{3} \sum_{j=1}^{3} n_i n_j d\Sigma = \frac{1}{3} \delta_{ij},$$

$$\frac{1}{\Sigma} \sum_{i=1}^{3} \sum_{j=1}^{3} n_i n_k n_l d\Sigma = \frac{1}{15} \left( \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right).$$  \hfill (5.5.17)
where \( n_i = x_i / r \), \( d\Sigma \) is the differential on the spherical surface.

Eq. (5.5.16) may be rewritten in the following way

\[
\langle \sigma_{ij} \rangle = \eta_B \left( \left( \frac{\partial u_i}{\partial x_j} \right) + \left( \frac{\partial u_j}{\partial x_i} \right) \right) + \frac{1}{2V} \int \sum_{k=1}^{3} \left( \sigma_{ik} n_j n_k + \sigma_{jk} n_i n_k - K_B n_i n_j n_k r^2 \right) - 2\eta_B u_i n_j - 2\eta_B u_j n_i \right) d\Sigma. \tag{5.5.18}
\]

For calculation of the integral (5.5.18) we will use stress tensor given by Eq. (5.5.15) and the velocity vector given by Eq. (5.5.10). In the final equation we keep terms proportional to \( 1/r^2 \) and omit those tends faster to zero:

\[
\langle \sigma_{ij} \rangle = \eta_B \left( \left( \frac{\partial u_i}{\partial x_j} \right) + \left( \frac{\partial u_j}{\partial x_i} \right) \right) + \frac{1}{2V} \sum \frac{15(\eta_B - QK_B)}{r^2} \left( \sum_{p,q=1}^{3} \left( \frac{\alpha_{pq} n_p n_q}{\eta_B} \right) \right) n_i n_j d\Sigma, \tag{5.5.19}
\]

where

\[
\left( \frac{\partial u_i}{\partial x_j} \right) + \left( \frac{\partial u_j}{\partial x_i} \right) = 2\alpha_{ij}. \tag{5.5.20}
\]

After substitution of integration constants \( N \) and \( Q \) from Eq. (5.5.11) find using Eqs. (5.5.13), (5.5.18), (5.5.19) we obtain

\[
\frac{1}{2V} \sum \frac{15(\eta_B - QK_B)}{r^2} \sum_{p,q=1}^{3} \left( \frac{\alpha_{pq} n_p n_q}{\eta_B} \right) n_i n_j d\Sigma =
K_B \left( a^3 + \frac{K_B}{\eta_B} + 15 \left( \frac{\eta_B}{K_B} a^3 + 15 \left( \frac{\eta_B}{K_B} + \frac{\eta_B}{K_B} \right) \right) \right) \frac{4}{3} \pi a^3
= \frac{1}{3} \left( 1 + \frac{K_B a}{\eta_B} \right) \alpha_{ij}, \tag{5.5.21}
\]
In the case under consideration, $\delta \mu = \frac{3}{V}$, hence, from Eqs. (5.5.18)-(5.5.21) we conclude

$$\langle \sigma_{ij} \rangle = \eta_B 2a_{ij} + \frac{K_B \left( a^3 \sqrt{\frac{K_B}{\eta_B}} + 6a^2 + 15 \sqrt{\frac{\eta_B}{K_B}} a + 15 a \right)}{3 \left( 1 + \sqrt{\frac{K_B}{\eta_B}} a \right)} \delta \mu.$$  

The latter equation can be rewritten as

$$\langle \sigma_{ij} \rangle / 2a_{ij} = \eta_B + \frac{K_B \left( a^3 \sqrt{\frac{K_B}{\eta_B}} + 6a^2 + 15 \sqrt{\frac{\eta_B}{K_B}} a + 15 a \right)}{6 \left( 1 + \sqrt{\frac{K_B}{\eta_B}} a \right)} \delta \mu. \quad (5.5.22)$$

Comparison of Eqs. (5.5.22) and (5.2.1) gives

$$A_\eta = \frac{K_B \left( a^3 \sqrt{\frac{K_B}{\eta_B}} + 6a^2 + 15 \sqrt{\frac{\eta_B}{K_B}} a + 15 a \right)}{6 \left( 1 + \sqrt{\frac{K_B}{\eta_B}} a \right)}.$$

If $\sqrt{\frac{K_B}{\eta_B}} a \to 0$ then the latter equation gives $A_\eta = \frac{5}{2}$, which coincides with Einstein’s equation.
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5.6 Appendix 3

Solution of the system differential equations for calculation of viscosity and permeability

The resulting system of the differential equations is (S.2.4), (S.2.5) with boundary conditions (S.2.6), which is under consideration below. Dividing Eq. (S.2.4) by Eq. (S.2.5) gives

\[
\frac{dZ}{d\eta} = \frac{27\eta}{Z} \left( 1 + \frac{Z}{\eta} + \frac{1}{9\eta} \right) \left( 1 + \frac{Z}{\eta} \right)
\]

After substitution \( Z = t^2(\eta) \times \eta \), where \( t(\eta) \) is a new unknown function, the differential Eq. (S.6.1) becomes

\[
\frac{1}{n} \frac{dn}{dt} = \frac{2t\left(t^3 + 6t^2 + 15t + 15\right)}{-t^5 - 6t^4 - 12t^3 + 15t^2 + 54t + 27}
\]

Eq. (S.6.2) can be directly integrated

\[
\ln \eta + C = \int \frac{2t\left(t^3 + 6t^2 + 15t + 15\right)}{-t^5 - 6t^4 - 12t^3 + 15t^2 + 54t + 27} dt,
\]

where \( C \) is an integration constant.

Polynomial function in the denominator can be presented as

\[-t^5 - 6t^4 - 12t^3 + 15t^2 + 54t + 27 = -(t + 1.63209) \times \]
\[\times (t + 0.67371)(t - 1.89389)(t^2 - 5.58797t - 12.96558)\].

Using the latter representation the integral in the right hand side of Eq. (S.6.3) can be directly calculated. The result is:
The integration constant $C$ can be calculated using the condition

$$t|_{\eta=1} = 0,$$

(5.6.5)

which can be directly deduced from the boundary conditions (5.2.3). Eq. (5.6.4) and boundary condition (5.6.5), which gives: $C=-1.368995$.

Below the case when the volume fraction of the particles, $\gamma$, tends to 1 is investigated.

It is clearly seen from Eq. (5.6.2) that $t$ ranges between 0 and value 1.89389. It occurs because $t$ starts from 0 at $\eta=1$ and can not pass value $t_\infty=1.89389$ (this value arises in the third term $-1.10585 \ln|1.89389-t|$, Eq. (5.6.2)). Consequently, at $\eta$ tends to infinity

$$\sqrt{Z/\eta} \to t_\infty.$$  

Eq. (3.10) after substitution $Z=t_\infty^2 \eta$ yields

$$\frac{d\eta}{d\gamma} = \frac{\eta}{(1-\gamma)},$$

(5.6.6)
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where \( \lambda = \left( \tilde{t}_\infty^3 + 6\tilde{t}_\infty^2 + 15\tilde{t}_\infty + 15 \right) / 6(1 + \tilde{t}_\infty) = 4.130 \). Eq. (5.6.6) corresponds to the limiting case \( \gamma \to 1 \). The solution of this equation is

\[ \eta = C_\infty (1 - \gamma)^{-4.130} , \quad (5.6.7) \]

where \( C_\infty \) is an integration constant. According to Eq.(5.6.7) the exact solution should satisfy the following requirement

\[ \eta \varphi^{4.130} \to C_\infty \text{, at } \varphi \to 0. \quad (5.6.8) \]

Constant \( C_\infty \) is calculated using direct integration of system (5.2.6)-(5.2.8) (see Figure 5.4 for details). The result is \( C_\infty = 0.5957 \) and \( \log_{10} 0.5957 = -0.2249 \). The asymptotic dependence \( \log_{10} \eta = -4.130 \log_{10} \varphi - 0.2249 \) of the viscosity on porosity is presented in Figure 5.4 (asymptote 3).
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\[
K_{\text{eff}}(K, \eta, \gamma) = \\
= K_{\text{eff}}(K_{\text{eff}}(K, \eta, \gamma + \delta\gamma), \eta_{\text{eff}}(K, \eta, \gamma + \delta\gamma), \delta\theta)
\]

**Figure 5.1** Schematic explanation of our method (see text for details).
Figure 5.2 Dependence of relative permeability, $k = \frac{\eta_0}{K_B a^2}$ on the porosity of porous media, $\varphi = 1 - \gamma$.

1. ---------------- according to Happel-Brener equation (Happel, and Brenner, 1965),

2. ------------------ according to Kozeny-Carman equation (Happel, and Brenner 1965),

3. -------------------- calculated according to Eqs. (5.2.25)-(5.2.26),

4. ------ high porosity asymptote, $\varphi \to 1$, according to Eq.(5.3.5),

5. ------ low porosity asymptote, $\varphi \to 0$, according to Eq.(5.3.6),

- from (Cancelliere et al., 1990),

- from (Koponen et al., 1977).
Figure 5.3 Dependence of relative viscosity \( \eta = \frac{\eta_B}{\eta_0} \) of porous medium on the porosity, \( \phi = 1 - \gamma (\log - \log \text{co-ordinates}) \).

1 - solution of Eqs. (5.2.25)-(5.2.26)
2 - high porosity asymptote, \( \phi \to 1 \), according to Eq.(5.3.9)
3 - low porosity asymptote, \( \phi \to 0 \), according to Eq (5.3.10).
Figure 5.4 Dependence of $\eta \varphi^{4.130}$ on porosity $\varphi$ (calculated according to Eqs. (5.2.25)-(5.2.26)).

Broken horizontal line corresponds to 0.5957.
LIST OF SYMBOLS

\( p \) pressure
\( \bar{u} \) velocity
\( \cdot \bar{U} \) constant velocity far from particle
\( K \) hydrodynamic resistance
\( N \) number of particles
\( L \) character length scale
\( V \) volume
\( a \) radius of particles
\( A_\eta \) function defined by Eq.(5.2.19)
\( A_\kappa \) function defined by Eq.(5.2.17)
\( R \) distance from fixed particle center
\( \bar{x} \) Cartesian coordinates
\( n_i = \frac{x_i}{r}, n_j = \frac{x_j}{r}, n_k = \frac{x_k}{r} \)
\( F \) force
\( K = \frac{l}{Z} \) relative permeability
\( U \) absolute value of velocity
\( G, Q, N, M, C \) integration constants

**Greek letters**

\( \gamma \) volume fraction of particles
\( \phi = 1 - \gamma \) porosity
\( \delta_\eta \) symmetric unit tensor
\( \Delta \) Laplacian
\( \eta \) viscosity
\( \varepsilon_{\eta k} \) anti-symmetric unit tensor
\( \alpha_\eta \) constant tensor
\( \sigma \) stress tensor
\( \Sigma \) spherical tensor
Viscosity of concentrated suspensions and properties of porous media

Subscripts

D  Darcy
B  Brinkman
p  particles
0  liquid phase
i, j, k, m, n  indexes with value 1, 2, 3
Chapter 6 EFFECTIVE ELASTIC PROPERTIES OF RUBBER OR POLYMER SHEETS WITH CRACKS

6.1 Calculation of the effective elastic properties

In this chapter effective elastic properties of a flat sheet of rubber or polymer with cracks is considered (see Figure 6.1). Let \( M \gg 1 \) is the number of cracks per area \( S \). All cracks are randomly oriented and \( l_i \) is the length of the crack \( i=1,2,\ldots M \). Cracks are assumed do not intersect with each other.

Density of cracks, \( \lambda \), is determined in the following way:

\[
\lambda = \frac{M \sum l_i^2}{S} \tag{6.1.1}
\]

According to the above definition \( \lambda \) is always positive and ranges between zero and infinity.

Let \( E_0 \) and \( v_0 \) be Young's modulus and Poisson's ratio of the rubber sheet without cracks. It is assumed below that dependencies Poisson's ratio of the Young's modulus, \( E^{\text{eff}} \), and Poisson's ratio, \( v^{\text{eff}} \), of the rubber sheet with cracks are given by the following dependencies on the density of cracks, \( \lambda \), to be determined:

\[
E^{\text{eff}} = E(E_0, v_0, \lambda) \tag{6.1.2}
\]

and

\[
v^{\text{eff}} = v(E_0, v_0, \lambda) \tag{6.1.3}
\]

In the case \( \lambda=0 \) (no cracks) Eqs. (6.1.2) and (6.1.3) reduce to

\[
E_0 = E(E_0, v_0, 0) \tag{6.1.4}
\]
and
\[ \nu_0 = \sqrt{E_0, \nu_0, 0} \]  \hspace{1cm} (6.1.5)

If the density of cracks is small, \( \delta \alpha \ll 1 \), then Eqs. (6.1.2) and (6.1.3) result in
\[ E_{\text{eff}} = E_0 + A^E(E_0, \nu_0) \delta \alpha \] \hspace{1cm} (6.1.6)

and
\[ \nu_{\text{eff}} = \nu_0 + A^\nu(E_0, \nu_0) \delta \alpha . \] \hspace{1cm} (6.1.7)

where \( A^E \), \( A^\nu \) are two new unknown functions, which are determined below.

Let \( \delta M \) cracks in this sheet of rubber be marked and the rest of the cracks be unmarked; \( \delta M \ll M \). The density of marked cracks, \( \delta \theta \), is
\[ \delta \theta = \frac{\delta M}{\sum_{i=1}^{M} \frac{l_i^2}{S}}. \] \hspace{1cm} (6.1.8)

The density of unmarked cracks is
\[ \lambda - \delta \lambda = \frac{M - \delta M}{\sum_{i=1}^{M} \frac{l_i^2}{S}}. \] \hspace{1cm} (6.1.9)

Eqs. (6.1.1), (6.1.8)-(7.1.9) result in
\[ \delta \theta = \delta \lambda. \] \hspace{1cm} (6.1.10)

A sheet of rubber with cracks can be considered as a mixture of the marked cracks surrounded by a sheet of rubber with unmarked cracks. That is, effective coefficients \( E_{\text{eff}} \) and \( \nu_{\text{eff}} \) can be expressed in two different ways: (i) according to Eqs. (6.1.2)-(6.1.3) and (ii) using "marked cracks" (with density \( \delta \theta \)) surrounded by "non-marked" cracks (with the density \( \lambda - \delta \lambda \)), which are treated as a medium with unknown Young’s module and Poisson’s ratio.
This gives the following system of equations:

\[
E\left(E_0, v_0, \lambda - \delta \lambda \right) = E\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta \tag{6.1.11}
\]

and

\[
v\left(E_0, v_0, \lambda \right) = v\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta \tag{6.1.12}
\]

Eqs. (6.1.11) and (6.1.12) are developed below into Taylor's series using the small parameters \( \delta \lambda \) and \( \delta \theta \)

\[
v\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta = v\left(E_0, v_0, \lambda \right) v \left(E_0, v_0, \lambda \right) 0 + \\
+ \frac{\partial v\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta}{\partial \delta \theta} \bigg|_{\delta \theta = 0} \delta \theta + \\
+ \frac{\partial v\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta}{\partial \delta \lambda} \bigg|_{\delta \lambda = 0} \delta \lambda \tag{6.1.13}
\]

Eq. (6.1.13) can be simplified using Eqs. (6.1.3), (6.1.5)

\[
v\left(E_0, v_0, \lambda \right) v \left(E_0, v_0, \lambda \right) 0 = v\left(E_0, v_0, \lambda \right) = v^{\text{eff}} \tag{6.1.14}
\]

Combination of Eqs. (6.1.3), (6.1.7) results in

\[
\frac{\partial v\left(E_0, v_0, \lambda - \delta \lambda \right) v \left(E_0, v_0, \lambda - \delta \lambda \right) \delta \theta}{\partial \delta \theta} \bigg|_{\delta \theta = 0} = \\
= \frac{\partial v\left(E_0, v_0, \lambda \right) v \left(E_0, v_0, \lambda \right) \delta \theta}{\partial \delta \theta} \bigg|_{\delta \theta = 0} = \\
= A^v\left(E_0, v_0, \lambda \right) v \left(E_0, v_0, \lambda \right) = A^v\left(E^{\text{eff}}, v^{\text{eff}} \right) \tag{6.1.15}
\]
Eq. (6.5.3) results in
\[
\frac{\partial \nu(E(E_0, \nu_0, \lambda - \delta \lambda), v(E_0, \nu_0, \lambda - \delta \lambda), \delta \theta)}{\partial \delta \lambda} \bigg|_{\delta \lambda = 0} = 0
\]
(6.1.16)
\[
= \frac{\partial v(E(E_0, \nu_0, \lambda - \delta \lambda), v(E_0, \nu_0, \lambda - \delta \lambda), 0)}{\partial \delta \lambda} \bigg|_{\delta \lambda = 0} = 0
\]
\[
= \frac{\partial v(E_0, \nu_0, \lambda - \delta \lambda)}{\partial \delta \lambda} \bigg|_{\delta \lambda = 0} = \frac{\partial E_0, \nu_0, \lambda}{\partial \lambda} \frac{dv^{eff}}{d\lambda}.
\]

Eq. (6.1.13) can be simplified using Eqs. (6.1.12), (6.1.14)-(6.1.16) as
\[
0 = A \nu \left( E^{eff}, v^{eff} \right) \delta \theta - \frac{dv^{eff}}{d\lambda} \delta \lambda.
\]
(6.1.17)

Eqs. (6.1.17), (6.1.10) yield
\[
\frac{dv^{eff}}{d\lambda} = A \nu \left( E^{eff}, v^{eff} \right).
\]
(6.1.18)

The same method of consideration results in the equation
\[
\frac{dE^{eff}}{d\lambda} = A E \left( E^{eff}, v^{eff} \right).
\]
(6.1.19)

Eqs. (6.1.4), (6.1.5) give the boundary conditions
\[
\nu^{eff} \bigg|_{\lambda = 0} = \nu_0
\]
(6.1.20)
and
\[
E^{eff} \bigg|_{\lambda = 0} = E_0.
\]
(6.1.21)

In ref. (Vavakin, and Salganik, 1975, 1978) the following expressions for both Young's and Poisson's ratio have been deduced at the low crack density, \( \delta \lambda \)
\[ \varepsilon_{\text{eff}} = \varepsilon_0 \left( 1 - \frac{1}{4} \pi \delta \lambda \right), \]
\[ \nu_{\text{eff}} = \nu_0 \left( 1 - \frac{1}{4} \pi \delta \lambda \right). \]

Comparison of the latter two equations with Eqs (6.1.6) and (6.1.7) results in
\[ A^E(E_0, \nu_0) = -\frac{\pi}{4} \varepsilon_0 \]
and
\[ A^\nu(E_0, \nu_0) = -\frac{\pi}{4} \nu_0. \]

Using the latter two equations system of differential Eqs. (6.1.18), (6.1.19) can be rewritten as
\[
\frac{d \varepsilon_{\text{eff}}}{d \lambda} = -\frac{\varepsilon_{\text{eff}} \pi}{4}, \tag{6.1.22}
\]
\[
\frac{d \nu_{\text{eff}}}{d \lambda} = -\frac{\nu_{\text{eff}} \pi}{4}. \tag{6.1.23}
\]

System (6.1.22) with boundary conditions (6.1.20), (6.1.21) has the following solution:
\[ \varepsilon_{\text{eff}} = \varepsilon_0 e^{-\frac{1}{4} \pi \lambda}, \tag{6.1.23} \]
\[ \nu_{\text{eff}} = \nu_0 e^{-\frac{1}{4} \pi \lambda}. \tag{6.1.24} \]
6.2 Comparison with available experimental data

In Figure 6.1 an example of a rubber sheet with cracks is shown, which has been used for experimental investigations in (Vavakin, and Salganik, 1975). Modules $E^{\text{eff}}$ and $\nu^{\text{eff}}$ are calculated according to Eqs. (6.1.23), (6.1.24) and compared with experimental data of (Vavakin, and Salganik, 1975). Figures 6.2 and 6.3 show the results of comparison, which is surprisingly good.
Figure 6.1 Sample of a rubber sheet with the cracks used in experiments (Vavakin, and Salganik, 1975).
Figure 6.2 Young's module on density of cracks, $\lambda$. Solid line corresponds to Eq. (6.1.23). Experimental data are from (Vavakin, Salganik, 1975).
Figure 6.3 Poisson's ratio on density of cracks, \( \lambda \). Solid line according to Eq. (6.1.24). Experimental data are from (Vavakin, Salganik, 1975).
LIST OF SYMBOLS

\( v \) Poisson’s ratio
\( E \) Young’s module
\( M \) number of cracks per area \( S \)
\( A^E \) function introduced by equations (7.1.6)
\( A^r \) function introduced by equations (7.1.7)
\( \lambda \) density of cracks

**Superscripts**

\( \text{eff} \) effective

**Subscripts**

\( 0 \) denotes properties of the rubber sheet without cracks
Chapter 7 EFFECTIVE ELASTIC PROPERTIES OF POROUS AND COMPOSITE MATERIALS

7.1 Introduction

Based on our new method the dependency of effective diffusion coefficient in porous media on porosity is predicted (Chapter 2) as well as other problems have been solved in Chapters 3-7. Comparison with available experimental data shows the good agreement between the theory predictions and experimental data in all cases. This shows the applicability of our method to a variety of problems. In this chapter we apply our method to the calculation of effective elastic properties of composite materials and show that the resulting equations agree better with available experimental data than the well known Mori-Tanaka equations.

7.2 Effective elastic properties of the laminated composite materials

In this section the elastic properties of the laminated composite materials (Figure 7.1) are calculated using our new method, which results in a system of differential equations describing dependency of the elastic properties of the laminated composites on volume fractions of inclusions of different types. Earlier the same problem has been solved with the help of the average method (Khorshun, Maslov, Shikulda, and Nazarenko, 1993) where analytical expressions for the elastic properties have been obtained. The main result in this section is as follows: the analytical solution in (Khorshun, Maslov, Shikulda, and Nazarenko, 1993) is the solution of our system of differential equations, which are deduced using our method. That is, both methods in the case of laminated composites give identical results.

Let the axes of symmetry be directed perpendicular to the layers of the laminated composite material (Figure 7.1). The equations of equilibrium are considerably simplified in this case. Derivatives of both the stress tensor and the fluctuation of displacements $u_i - \sum_{j=1}^{3} \langle \epsilon_{ij} \rangle x_j$ vanish in any direction tangential to the layers. Here $\bar{u}$ is the displacement, $\langle \epsilon_{ij} \rangle$ are averaged deformations ($i, j = 1, 2, 3$). This gives the possibility to solve the equations of equilibrium and to calculate the stress tensors, deformations and effective elastic modulus (Khorshun, Maslov, Shikulda, and Nazarenko, 1993).
Expression \( h^{\text{eff}} = h\left(h^m, h^1, h^2, ..., h^M, \gamma^1, \gamma^2, ..., \gamma^M \right) \) for the case of laminated composite with the orthotropic layers and common axes of isotropy one of which is perpendicular to the layers have been obtained in (Khorshun, Maslov, Shikulda, and Nazarenko, 1993) and they are presented below

\[
\begin{align*}
h_{3333}^{\text{eff}} &= \left\langle h_{3333} \right\rangle + \left\langle h_{1133} / h_{1111} \right\rangle \left\langle 1 / h_{1111} \right\rangle - \left\langle h_{1133}^2 / h_{1111} \right\rangle \\
h_{2222}^{\text{eff}} &= \left\langle h_{2222} \right\rangle + \left\langle h_{1122} / h_{1111} \right\rangle \left\langle 1 / h_{1111} \right\rangle - \left\langle h_{1122}^2 / h_{1111} \right\rangle \\
h_{1111}^{\text{eff}} &= \left\langle 1 / h_{1111} \right\rangle \\
h_{2233}^{\text{eff}} &= \left\langle h_{2233} \right\rangle + \left\langle h_{1133} / h_{1111} \right\rangle \left\langle h_{1122} / h_{1111} \right\rangle \left\langle 1 / h_{1111} \right\rangle - \left\langle h_{1133} h_{1122} / h_{1111} \right\rangle \\
h_{1133}^{\text{eff}} &= \left\langle h_{1133} / h_{1111} \right\rangle \left\langle 1 / h_{1111} \right\rangle \\
h_{2323}^{\text{eff}} &= \left\langle h_{2323} \right\rangle \\
h_{1212}^{\text{eff}} &= \left\langle 1 / h_{1212} \right\rangle \\
h_{1313}^{\text{eff}} &= \left\langle 1 / h_{1313} \right\rangle.
\end{align*}
\]

(7.2.1)

Here \( h \) are elastic modules and \(<...>\) means the volume averaging (Khorshun, Maslov, Shikulda, and Nazarenko, 1993).

Derivatives \( A^{\text{angle},k} \) are defined below as follows:

\[
A^{\text{angle},k}(h^m, h^k) = \frac{\partial \left[ \left[ h^m, h^1, h^2, ..., h^M, \delta \gamma^1, \delta \gamma^2, ..., \delta \gamma^M \right] \right]}{\partial \delta \gamma^k} \bigg|_{\delta \gamma^1=\delta \gamma^2=...=\delta \gamma^M=0}, \quad (k=1,2,...,M). \quad (7.2.2)
\]

The system of the differential equations for calculation of the elastic modules of the composite materials with different types of inclusions (7.4.19) is deduced in Appendix. The same system can be used in the case of multicomponent laminated composite materials. Earlier, in (Mc. Laughlin, 1977) the similar calculation have been performed for the case of two-component laminated material

Let now functions \( A^{\text{angle},k}(h^0, h^k) \), which are calculated according to Eqs. (7.2.2), be substituted into the system of equation (7.4.19). After a lot of calculations (not presented in this thesis) it is possible to show, that solutions according to Eqs. (7.2.1) being substituted into the system of equations (7.4.19) gives their exact solution in the case of multi-component composite material. Thus we have excellent agreement between mean field approximation
method and method developed in paper (Khorshun, Maslov, Shikulda, and Nazarenko, 1993) for laminated composite materials.

7.3 Effective elastic modules of isotropic composite material containing spherical isotropic particles and isotropic matrix

The system of the differential equations obtained in Appendix can be applied for calculation of the effective elastic modules of the elastic isotropic composite materials with spherical isotropic particles (inclusions) and isotropic matrix. Earlier in (Christensen, 1990) these modules have been obtained with the help of the cell method and Bruggerman’s method in the case of inclusion of only one type. However, the equations are given in (Christensen, 1990) practically without any derivation. It does not allow either to judge the correctness of the results obtained not to develop further generalization in more complex cases (inclusions of different types). Below our method is applied to the calculation of the elastic properties of the composite materials with several different types of inclusions.

Hooke’s law for the particles and for the matrix reads

\[ \sigma_y = k^p \left( \sum_{n=1}^{3} \mathcal{E}_{mn} \right) \delta_y + 2\mu^p \varepsilon_y, \quad \sigma_y = k^m \left( \sum_{n=1}^{3} \mathcal{E}_{mn} \right) \delta_y + 2\mu^m \varepsilon_y, \]

where \( k^p, \mu^p, k^m, \mu^m \) are elastic coefficients of the particles and matrix, respectively.

The same law gives the relation between stresses \( \sigma \) and deformations \( \varepsilon \) averaged over a volume:

\[ \langle \sigma_y \rangle = k^{\text{eff}} \left( \sum_{n=1}^{3} \langle \mathcal{E}_{mn} \rangle \right) \delta_y + 2\mu^{\text{eff}} \langle \varepsilon_y \rangle. \] (7.3.3)

The Young’s module, \( E \), and the Poisson’s ratio, \( \nu \), are usually used instead of the coefficients \( k \) and \( \mu \):

\[ E = \frac{9k\mu}{3k + \mu}, \quad \nu = \frac{3k - 2\mu}{2(3k + \mu)}. \] (7.3.4)

If the volume fraction of inclusions is small, \( \delta\gamma << 1 \), then the Taylor series expansion of the coefficients \( k^{\text{eff}} \) and \( \mu^{\text{eff}} \) is obtained using the cell method in (Christensen, 1990):

\[ \mu^{\text{eff}} = \mu^m + A^\mu (\mu^m, k^m, \mu^p, k^p) \delta\gamma, \]
\[ k^{\text{eff}} = k^n + A^n(m,n,\mu,\mu^p,\mu^p) \delta \gamma, \quad (7.3.5) \]

where

\[ A^n(m,n,\mu,\mu^p,\mu^p) = \frac{15(1 - \nu^m)\left(\frac{\mu^p}{\mu^m} - 1\right)\mu^m}{7 - 5\nu^m + 2(4 - 5\nu^m)\frac{\mu^p}{\mu^m}}, \quad (7.3.6) \]

and

\[ A^k(m,n,\mu,\mu^p,\mu^p) = \frac{\left(\frac{k^p}{k^m} - 1\right)k^m}{k^p - k^m + 1}, \quad \frac{k^m + 4\mu^m}{3}, \quad (7.3.7) \]

where

\[ \nu^m = \frac{3k^m - 2\mu^m}{2(3k^m + \mu^m)}. \]

The system of differential equations (7.4.19) in the case under consideration using Eqs. (7.3.5) - (7.3.7) results in the following system of differential equations:

\[ \frac{d\mu^{\text{eff}}}{d\gamma} = \frac{15(1 - \nu^{\text{eff}})\left(\frac{\mu^b}{\mu^{\text{eff}}} - 1\right)\mu^{\text{eff}}}{\left(7 - 5\nu^{\text{eff}} + 2(4 - 5\nu^{\text{eff}})\frac{\mu^b}{\mu^{\text{eff}}}\right)(1 - \gamma)}, \quad (7.3.8) \]

and

\[ \frac{dk^{\text{eff}}}{d\gamma} = \frac{\left(\frac{k^b}{k^{\text{eff}}} - 1\right)k^{\text{eff}}}{\left(\frac{k^b - k^{\text{eff}}}{k^{\text{eff}} + 4\mu^{\text{eff}}} + 1\right)(1 - \gamma)}, \quad (7.3.9) \]

where

\[ \nu^{\text{eff}} = \frac{3k^{\text{eff}} - 2\mu^{\text{eff}}}{2(3k^{\text{eff}} + \mu^{\text{eff}})}. \]

The system of differential equations (7.3.8), (7.3.9) should be subjected the following obvious boundary conditions:

\[ \mu^{\text{eff}} \big|_{\gamma = 0} = \mu^n, \quad k^{\text{eff}} \big|_{\gamma = 0} = k^n. \quad (7.3.10) \]

The numerical solution of the system of differential equations (7.3.8)-(7.3.9) with the boundary conditions (7.3.10) allows determination of the dependency of the effective elastic coefficients of the composite material on the volume fraction of inclusions. The system of
differential equations (7.3.8)-(7.3.10) coincides with that presented in (Christensen, 1990), where it has been given without proper derivation.

The derivation given above allows generalization for the case of the composite material with inclusions of several different types (according to Eq. (7.4.19)).

\[
\frac{\partial \mu^{\text{eff}}}{\partial \gamma^p} = A^p \left[ \sum_{\gamma'=1}^{M} \frac{A^{\gamma'}(\mu^{\text{eff}}, k^{\text{eff}}, \mu^p, k^p) \gamma'}{1 - \sum_{\gamma'=1}^{M} \gamma'} \right] , \quad p = 1, 2, ..., M
\]

(7.3.11)

and

\[
\frac{\partial k^{\text{eff}}}{\partial \gamma^p} = A^p \left[ \sum_{\gamma'=1}^{M} \frac{A^{\gamma'}(\mu^{\text{eff}}, k^{\text{eff}}, \mu^p, k^p) \gamma'}{1 - \sum_{\gamma'=1}^{M} \gamma'} \right] , \quad p = 1, 2, ..., M
\]

(7.3.12)

where relations \( A^p(\mu^m, k^m, \mu^p, k^p) \) and \( A^m(\mu^m, k^m, \mu^p, k^p) \) are given by Eqs.(7.3.6), (7.3.7). Eqs. (7.3.11), (7.3.12) require the boundary conditions, which are as follows (compare with Eqs. (7.4.21))

\[ k^{\text{eff}} \bigg|_{\gamma^p=0} = k^m, \quad p = 1, 2, ..., M \]

(7.3.13)

and

\[ \mu^{\text{eff}} \bigg|_{\gamma^p=0} = \mu^m, \quad p = 1, 2, ..., M. \]

(7.3.14)

In Figures 7.2 and 7.3 the comparison is presented of the available experimental measurements of elastic properties of concrete (Simeonov, and Ahmad, 1995) with two theories predictions. Calculations according to Eqs. (7.3.8)-(7.3.10) (curves 1) and according to the Mori- Tanaka theory (Mura, 1987) (curves 2) are given for the dependency of the Young's modulus of the composite materials on the volume fraction of inclusions.

The square deviation is taken for an estimation of the deviation from experimental data:

\[
\chi = \sum_{i=1}^{N} \left[ E_{i,\text{exp}}^{\text{eff}} - E_{i,\gamma}^{\text{eff}}(\gamma) \right]^2 ,
\]

(7.3.15)

where \( N \) is the number of data points (\( N = 5 \) in Figure 7.2 and \( N = 3 \) in Figure 7.3); \( E_{i,\text{exp}}^{\text{eff}} \) are the experimental values of Young's module (Simeonov, and Ahmad, 1995). Figures 7.2 and 7.3 show, that the calculations according to Eq. (7.3.8)-(7.3.10) results in the better
agreement with the experimental data, than the calculations based on the Mori-Tanaka theory.

In Table 7.1 comparison of the experimental data on the elastic properties of the concrete with two types of inclusions from (Simeonov, and Ahmad, 1995) are compared with our predictions calculated according to (7.3.11)-(7.3.14). Comparison shows that the predictions according to our theory in all cases over-estimate the experimental value. Calculations according to Mori-Tanaka theory in all cases under-estimate the same experimental data. Both theories give similar deviation from the experimental data.

7.4 Appendix

System of partial differential equations for the calculation of elastic properties of composite materials containing different types of inclusions

The differential equation for dependency of the effective elastic properties of the composite materials on volume fractions of several different type inclusions is obtained below with the help of our method. The volume fraction of inclusions of type \( k \), \( \gamma^k \), is defined as follows:

\[
\gamma^k = \frac{V^k}{V},
\]

(7.4.1)

here \( V \) is the volume of the composite, \( V^k \) is the volume of inclusions of type \( k \) (\( k=1,2,\ldots,M \)).

Let \( h^{\text{eff}} \) is an effective elastic coefficient of the composite material; \( h^m \) is the elastic coefficient of the matrix; \( h^k \) is the elastic coefficient of the inclusions of type \( k \) (\( k=1,2,\ldots,M \)). The coefficients \( h^{\text{eff}} \), \( h^m \) and \( h^k \) can be tensors, vector or scalars (for example, both Young’s module and Poisson’s ratio) depending on the problem under consideration. It is assumed below, that the following relation describes the effective elastic coefficients:

\[
h^{\text{eff}}_j = h_j[h^m,h^1,h^2,\ldots,h^M,\gamma^1,\gamma^2,\ldots,\gamma^M], \quad j=1,2,\ldots,N.
\]

(7.4.2)

Below index \( j \) is dropped for simplicity.

In the case \( \gamma^1 = \gamma^2 = \ldots = \gamma^M = 0 \) (no inclusions) Eq. (7.4.2) results in

\[
h^m = h[h^m,h^1,h^2,\ldots,h^M,0,0,\ldots,0].
\]

(7.4.3)
which is used below as the boundary condition. In the case \( \gamma = 0 \) (\( i=1,2,...,k-1,k+1,...,M \)) (only inclusions of type \( k \)) Eq. (7.4.2) results in

\[
h^\text{angle},k [h^m, h^k, \gamma^k] = h[h^m, h^1, h^2, ..., h^M, 0,0,...,0, \gamma^k, 0,...,0]
\]  

(7.4.4)

Dependences \( A^\text{angle},k \) (\( k=1,2,...,M \)) are defined as

\[
A^\text{angle},k (h^m, h^k) = \frac{\partial h^\text{angle} [h^m, h^k, \delta \gamma^k]}{\partial \delta \gamma^k} \bigg|_{\delta \gamma^k = 0}, \quad (k=1,2,...,M).
\]  

(7.4.5)

Let us mark randomly a small number of inclusions of each type. The small volume fractions of the marked inclusions, \( \delta \theta^k \) (\( k=1,2,...,M \)), are equal to

\[
\delta \theta^k = \frac{\delta V^k}{V},
\]  

(7.4.6)

where \( \delta V^k \) is the volume of marked inclusions. The volume fraction of the non-marked inclusions are

\[
\gamma^k - \delta \gamma^k = \frac{V^k - \delta V^k}{V - \sum_{i=1}^{M} \delta V^i}.
\]  

(7.4.7)

Eqs. (7.4.1), (7.4.6), (7.4.7) result in

\[
\delta \gamma^k = \frac{\left( \delta \theta^k - \gamma^k \sum_{i=1}^{M} \delta \theta^i \right)}{1 - \sum_{i=1}^{M} \delta \theta^i}.
\]  

(7.4.8)

or neglecting the small volume fractions of higher order:

\[
\delta \gamma^k = \delta \theta^k - \gamma^k \sum_{i=1}^{M} \delta \theta^i.
\]  

(7.4.9)

The composite material can be treated now as a mixture of marked inclusions surrounded by an effective medium with non-marked inclusions. Thus, the effective elastic coefficients of the composite material, \( h^\text{ef} \), can be expressed in two different ways: (i) according to definition (7.4.2) and (ii) using "marked" inclusions (with the volume fractions \( \delta \theta^k, \ k=1,2,...,M \)) surrounded by the effective medium with "non-marked" inclusions (with the volume fractions given by (7.4.9)). The latter effective medium has the elastic property \( h[h^m, h^l, h^2, ..., h^M, \gamma - \delta \gamma^k, \gamma^2 - \delta \gamma^2, ..., \gamma^M - \delta \gamma^M] \) according to definition (7.4.2).
The coefficients calculated in these two ways should be equal, this results in the following system of equations:

\[
\begin{align*}
&h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}] = \\
&= h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}, \delta \gamma^1, \delta \gamma^2, \ldots, \delta \gamma^M].
\end{align*}
\]  

(7.4.10)

The system of Eqs. (7.4.10) is decomposed below using the Taylor series using small parameters \( \delta \gamma \) and \( \delta \theta \):

\[
\begin{align*}
&h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}, \delta \gamma^1, \delta \gamma^2, \ldots, \delta \gamma^M] = \\
&= h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}, \delta \gamma^1, \delta \gamma^2, \ldots, \delta \gamma^M] + \\
&+ \sum_{k=1}^{M} \frac{\partial h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}, \delta \gamma^1, \delta \gamma^2, \ldots, \delta \gamma^M]}{\partial \delta \gamma^k} \delta \gamma^k + \\
&+ \sum_{k=1}^{M} \frac{\partial h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}, \delta \gamma^1, \delta \gamma^2, \ldots, \delta \gamma^M]}{\partial \delta \gamma^k} \delta \gamma^k.
\end{align*}
\]

(7.4.11)

In the latter equation and below the following abbreviation is used: \( \delta \theta = 0 \) stands for

\[
\delta \theta^1 = \ldots = \delta \theta^M = 0,
\]

\[
\delta \gamma^1 = \ldots = \delta \gamma^M = 0.
\]

Eq (7.4.11) can be simplified using relations (7.4.3), (7.4.2):

\[
\begin{align*}
&h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}] = h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}] = h^{ef}.
\end{align*}
\]

(7.4.12)

Combination of Eqs. (7.4.3) - (7.4.5) results in

\[
\begin{align*}
&\frac{\partial h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}]}{\partial \delta \gamma^k} \bigg|_{\delta \gamma = 0} = \\
&= \frac{\partial h[h^{\prime\prime}, h^{'}, h^{2}, \ldots, h^{M}, \gamma^{\prime}, \gamma^{2}, \ldots, \gamma^{M}]}{\partial \delta \gamma^k} \bigg|_{\delta \gamma = 0} = \Lambda^{anh, k}(h^{ef}, h^{k}).
\end{align*}
\]

(7.4.13)

Eqs. (7.4.4), (7.4.2) give
\[
\frac{\partial h}{\partial \delta y_k} = \frac{\partial h}{\partial \delta y_k} \bigg|_{\delta y_0 = 0} = 0
\]
\[
\frac{\partial h}{\partial \delta y_k} = \frac{\partial h}{\partial \delta y_k} \bigg|_{\delta y_0 = 0}
\]
\[
\frac{\partial h}{\partial \delta y_k} = \frac{\partial h}{\partial \delta y_k} \bigg|_{\delta y_0 = 0}
\]
\[
\frac{\partial h}{\partial \delta y_k} = \frac{\partial h}{\partial \delta y_k} \bigg|_{\delta y_0 = 0}
\]
\[
\frac{\partial h}{\partial \delta y_k} = \frac{\partial h}{\partial \delta y_k} \bigg|_{\delta y_0 = 0}
\]

Now Eq. (7.4.11) can be simplified using Eqs. (7.4.12) - (7.4.14) as follows:

\[
0 = \sum_{k=1}^{M} A^{\text{angle},k}(h^{\text{eff}}, h^k) \delta y_k - \sum_{k=1}^{M} \frac{\partial h^{\text{eff}}}{\partial \gamma^k} \delta y_k.
\]

The “marked” inclusions are selected randomly, therefore the small volume fractions \( \delta y_k \) (\( i=1,2,\ldots,M \)) are independent of each other. Therefore, Eq. (7.4.9) after substitution in Eq (7.4.15) and collecting of terms proportional to \( \delta y^k \) results in

\[
0 = A^{\text{angle},k}(h^{\text{eff}}, h^k) - \frac{\partial h^{\text{eff}}}{\partial \gamma^k} + \sum_{i=1}^{M} \frac{\partial h^{\text{eff}}}{\partial \gamma^k} \gamma^k, \quad k=1,2,\ldots,M.
\]

Multiplying Eqs (7.4.17) by \( \gamma^k \) and summation over \( k \) yields

\[
\sum_{i=1}^{M} \frac{\partial h^{\text{eff}}}{\partial \gamma^i} = \frac{\sum_{i=1}^{M} A^{\text{angle},i}(h^{\text{eff}}, h^i) \gamma^i}{1 - \sum_{i=1}^{M} \gamma^i}.
\]

Substitution of Eq. (7.4.18) into Eq. (7.4.17) results in the required system of differential equations:

\[
\frac{\partial h^{\text{eff}}}{\partial \gamma^k} = A^{\text{angle},k}(h^{\text{eff}}, h^k) + \frac{\sum_{i=1}^{M} A^{\text{angle},i}(h^{\text{eff}}, h^i) \gamma^i}{1 - \sum_{i=1}^{M} \gamma^i}, \quad k=1,2,\ldots,M.
\]

The effective elastic coefficients of the composite material, \( h^{\text{eff}} \), can be calculated as solutions of the system of non-linear partial differential equations (7.4.19) with the boundary conditions obtained from condition (7.4.3)

\[
h^{\text{eff}} \bigg|_{\gamma^i=\gamma^j=\cdots=\gamma^M=0} = h^m.
\]
Figure 7.1 Laminated composite material.
Figure 7.2 The Young module, $E_{\text{eff}}$, of concrete

Experimental data from (Simeonov, and Ahmad, 1995)

1. according to Eqs (7.3.8) - (7.3.11); $\chi=23.948$

2. according to the Mori- Tanaka theory (Yang , and Huang, 1996);
   $\chi=27.724$.

Matrix: cement paste $E^m = 12 \text{ GPa}$, $\nu^m = 0.22$.

Particles: sand $E^p = 80 \text{ GPa}$, $\nu^p = 0.21$. 
Figure 7.3 The Young module, $E_{\text{eff}}$, of concrete

Experimental data from (Simeonov, and Ahmad, 1995)

1 according to Eqs (7.3.8)-(7.3.11); $\chi=32.577$

2 according to Mori- Tanaka theory (Yang, and Huang, 1996); $\chi=131.782$

Matrix: cement paste $E^m = 12$ GPa, $\nu^m = 0.22$

Particles: steel $E^p = 207$ GPa, $\nu^p = 0.3$
Tab. 7.1 Elastic properties of three component concrete

<table>
<thead>
<tr>
<th>Cement phase (matrix)</th>
<th>Sand (phase 1)</th>
<th>Gravel (phase 2)</th>
<th>Concrete E(GPa)</th>
<th>Concrete E(GPa)</th>
<th>Concrete E(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E^m = 12 \text{ GPa}$ &amp; $\nu^m = 0.22 \text{ GPa}$</td>
<td>$E^m = 800 \text{ GPa}$ &amp; $\nu^m = 0.21 \text{ GPa}$</td>
<td>$E^m = 69 \text{ GPa}$ &amp; $\nu^m = 0.23 \text{ GPa}$</td>
<td>Calculated Mori-Tanaka method (Yang, and Huang, 1996)</td>
<td>According to our equations (7.3.11-8.3.13)</td>
</tr>
<tr>
<td>volume fraction, $\gamma_1$</td>
<td>volume fraction, $\gamma_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.374</td>
<td>0.446</td>
<td>0.18</td>
<td>32.14</td>
<td>34.96</td>
<td>34.90</td>
</tr>
<tr>
<td>0.342</td>
<td>0.408</td>
<td>0.25</td>
<td>33.92</td>
<td>37.00</td>
<td>34.20</td>
</tr>
<tr>
<td>0.328</td>
<td>0.392</td>
<td>0.28</td>
<td>34.73</td>
<td>37.93</td>
<td>35.40</td>
</tr>
<tr>
<td>0.319</td>
<td>0.381</td>
<td>0.30</td>
<td>35.29</td>
<td>38.55</td>
<td>36.20</td>
</tr>
<tr>
<td>0.297</td>
<td>0.353</td>
<td>0.35</td>
<td>36.74</td>
<td>40.09</td>
<td>38.60</td>
</tr>
<tr>
<td>0.274</td>
<td>0.326</td>
<td>0.40</td>
<td>38.28</td>
<td>41.78</td>
<td>39.60</td>
</tr>
</tbody>
</table>

Loughborough University
Conclusions and suggestions for future work

In this thesis new generalized method for the utilization of mean field approximation technique for calculation of effective properties of porous and dispersed materials is suggested. The generalization is with respect to the description of properties of multi-component materials. Effective elastic characteristics of multi-component composites and also viscosity of suspensions and emulsions containing clusters with different number of particles are calculated and compared with experimental data as well theoretical relationships. Comparisons show good agreement.

This work has vaulted in very promising model to describe of a modeling of emulsions behavior. Theoretical dependencies of the effective viscosity on the volume fraction of droplets are deduced in two cases: developed flocculation and low flocculated emulsions. The new theory takes into account flocculation of droplets. All clusters in the model of low flocculated emulsions, except singlets, have equal packing density $\gamma_m$. This model includes one fitting parameter ($\gamma_m$) which yields very accurate fits for experimental data. The comparison of the theory predictions with experimental data shows good agreement in both of the deduced cases.

The effective diffusion coefficient in porous media is also calculated by the mean field approximation method. Comparison shows good agreement with the experimental data.

Fluid flow in porous media is frequently described by the Brinkman equation. These equations include two semi-empirical parameters: effective viscosity and permeability. The system of two differential equations for the calculation of the effective viscosity and permeability is developed. The solution of this system is compared with the result of computer simulations and analytical dependencies published by other authors.
Our new method is applied for the calculation of elastic properties of different composite materials: rubber/polymer sheets with cracks, laminated composite materials, composite materials with more than one type of inclusions. In each case deduced theoretical dependences are compared with available experimental data. In the case of rubber/polymer sheets with cracks this comparison shows a very good agreement with experimental data. In the case of concretes the comparison shows better agreement with the experimental data than the frequently used Mori-Tanaka method.

Successful application of the mean field approximation method for description of the elastic properties of rubber/polymer sheet with cracks is the first step for description of the transport properties of similar membranes with crack-like pores. Crack-like pores are more effective than fiber-like pores membranes because area of membranes is used more effectively.

The influence of cluster formation on effective properties of dispersed, composite and porous materials has shown in this thesis. However, the cluster size distribution in suspensions and emulsions, its dependency on the colloidal and hydrodynamic conditions (applied shear rate) is the subject for future investigations. At the moment we can only propose a new model of cluster formation. This model must be evaluated in the future. Depending on the cluster size distribution the rheological behaviour of emulsions and suspensions differs significantly. Therefor the rheological behavior of emulsions must be further investigated.

In this connection a theory of aggregation/disaggregation, that is, reversible coagulation will be investigated in the future. The process of flocculation/deflocculation in emulsions/suspensions is of vital importance, however, a reliable device for the
experimental determination of cluster distribution in suspension or emulsion does not exist. This problem deserves special research.

Surfactants (surface active agents) are organic chemical wetting, cleaning and disinfecting agents. They find a wide utility in such diverse products as detergents and washing compounds, water softeners, textile softeners, antistatic agents, lubricants, plastics manufacture, shampoos, cosmetics, and medicinal agents. The process of micelle formation results in existing of long-lived aggregates at some special concentration of surfactant molecules (CMC). Properties of emulsions with surfactant molecules can be investigated using our method in future.
Viscosity of concentrated suspensions and properties of porous media

Proceedings of the 13th International Congress on Rheology

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Viscosity of concentrated suspensions and properties of porous media

XIIIth International Congress on Rheology, Cambridge, UK, 2000

INFLUENCE OF CLUSTERS FORMATION ON VISCOSITY OF CONCENTRATED SUSPENSIONS

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ABSTRACT

Dispersed particles can form clusters even at low concentrations. Colloidal and hydrodynamic forces are responsible for this phenomenon and these forces determine the structure and size of clusters. It is assumed that clusters can be characterized by two averaged parameters. (i) mean concentration of particles inside clusters \( n_{\text{ave}} \) and (ii) mean deviation of friction coefficients of clusters, \( P_c \), from the same value for solid particles. A differential method is used for the derivation of viscosity dependence on concentration of dispersed particles, taking into account cluster formation. The derived dependency of viscosity on concentration is the same as is the well-known Krieger's equation except for a different physical meaning of parameters. A mechanism of cluster formation is briefly discussed. Comparison with available experimental data shows a good agreement with the theoretical predictions.

KEYWORDS VISCOSITY, SUSPENSION, CLUSTERS

INTRODUCTION

The differential method has been used for determination of effective properties of non-homogeneous media Bruggeman [1] first suggested the differential method and then it was used for the determination of viscosity of concentrated suspensions without cluster formation [2,3]. Elastic properties of solid non-homogeneous materials were investigated with the help of the same method [4,5].

\[ 1 \begin{array}{ccc} \text{1} & \text{2} & \text{3} \\ \text{4} \end{array} \]

\[ \gamma + \Delta \gamma \]

Figure 1. Schematic explanation of differential method

1 suspension with volume concentration \( \gamma \) of dispersed particles (suspension 1), 2 effective homogeneous liquid with the same viscosity as suspension 1, 3 suspension with volume concentration \( \gamma + \Delta \gamma \), where \( \Delta \gamma \ll 2 \) liquid 2 with a small volume concentration \( \Delta \gamma \) of dispersed particles.

The essence of the differential method is explained here using, as an example, a concentrated suspension of particles, which do not form clusters. In Figure 1 a schematic of the differential method is presented. Consider suspension 1 with a volume concentration \( \gamma \) of dispersed particles. Dependency of viscosity of this suspension on concentration, \( \eta(\gamma) \), is to be determined. Let a new homogeneous liquid 2 be introduced. It is assumed that liquid 2 has the same viscosity as suspension 1. Now let a small number of particles with concentration \( \Delta \gamma \), where \( \Delta \gamma \ll \gamma \), be added to both suspension 1 and liquid 2. In this way two new suspensions are obtained — suspension 3 with particle concentration \( \gamma + \Delta \gamma \) and suspension 4 with low concentration of particles. It must be accounted that added particles change the total volume of corresponding suspensions. It is important to note that accounting for this volume change means an introduction of a simplest hard core model of particle-particle interaction. Viscosity of suspension 4 with the low concentration of particles, \( \Delta \gamma \), can easily be calculated using Einstein's model. The main assumption of the differential method is viscosity of suspensions 3 and 4 are equal.

Using this hypothesis a differential equation for viscosity dependency on concentration, \( \eta(\gamma) \), can be deduced [2,3]. The solution to this equation is

\[ \frac{\eta }{ \eta_0 } = \frac{1}{ (1 - \gamma)^{2+\alpha} } \]

where \( \eta_0 \) is the viscosity of the pure liquid, the exponent 2.5 stems from Einstein's equation.

Colloidal and hydrodynamic interactions between particles result in a formation of doublets, triplets and higher clusters [6]. Aggregation of particles is accompanied by destruction of aggregates caused by finite depth of the colloidal potential well and/or shear stress applied. As a result a distribution of cluster sizes is formed in the suspension. Obviously, the presence of clusters drastically influences viscosity of concentrated suspensions.

The differential method is applied below for the case when dispersed particles form clusters. It is supposed that

(i) an average packing density of single particles inside any cluster, \( n_{\text{ave}} \), does not change with concentration and cluster size;

(ii) a liquid-cluster friction can be described by a single parameter, \( P_c \), which is independent of concentration and cluster size.

The latter parameter may be explained using the following example. Let two spherical particles with the same diameter, \( d \), be considered. The first one is a solid particle, the second one is a particle composed of smaller particles (a model of a cluster) A friction force exerted on each of the particles under consideration will be different if both particles are placed in a liquid flow. Let \( P \) be a ratio of the friction force in the case of the composed particle (clusters) to the corresponding force exerted on the solid particle. The friction force is changed in the case of the composed particle because of two reasons: (a) the solid surface exposed to the liquid flow is smaller than in the case of the solid particle, (b) the liquid flow partially penetrates inside the composed particle. The two trends mentioned, (a) and (b), change the value of \( P \) in different ways. The value of \( P \) decreases due to reason (a) and increases due to reason (b). That is, a complex interplay determines \( P \) value. Deviation of cluster shapes from sphericity is an additional cause of change in the value of \( P \) [7].

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According to Einstein's relation the viscosity of suspension at low concentrations of dispersed particles is a linear function of volume concentration \( \gamma \)

\[ \eta(\gamma) = \eta_0 + 2.5 \eta_0 P \gamma \]  

(2)

If particles form clusters the latter equation must be modified. First, cluster concentration, \( \gamma_c \), is different from the single particle concentration \( \gamma \) and is given by the following relation

\[ \gamma = \gamma \gamma_{\text{max}} \]  

(3)

where \( \gamma_{\text{max}} \) is an averaged particle concentration inside clusters. Secondy, according to the previous consideration, friction coefficient of clusters, \( P \) is different from the corresponding value for solid particles. Hence, Einstein's relation (2) must be modified in the case under consideration.

\[ \eta = \eta_0 + 2.5 \eta_0 P \gamma_c \]  

(4)

A differential equation, which describes dependence of suspension viscosity on particle concentration, is derived in the Appendix. The solution to that equation is

\[ \frac{\eta(\gamma)}{\eta_0} = \frac{1}{1 - \frac{\gamma}{\gamma_{\text{max}}}} \]  

(5)

Eq (5) almost coincides with Krieger’s equation \( [8,9] \)

\[ \frac{\eta(\gamma)}{\eta_0} = \frac{1}{1 - \frac{\gamma}{\gamma_{\text{max}}}} \]  

(6)

where \( [\eta] \) is an intrinsic viscosity. It is easy to conclude that Eqs. (5) and (6) coincide if we adopt

\[ P = \frac{\eta(\gamma)}{\eta_0} \]  

(6a)

It is necessary to stress here that, in spite of a striking similarity of Eqs. (5) and (6), a physical meaning of parameters included in Eq (5) is quite different from those used in Eq (6). According to the theory developed above, viscosity dependence on concentration is related to cluster formation and this physical phenomenon is incorporated in Eq (5).

A comprehensive review of experimental data of viscosity dependence on concentration of different suspensions is presented in \( [10] \). A comparison of the dependency according to Eq (5), with experimental data taken from \( [10] \), is presented in Figure 2. This shows that the whole array of experimental data can be described using Eq (5)

1. \( \gamma_{\text{max}}=1, P=1 \) (particles do not form clusters)
2. \( \gamma_{\text{max}}=0.73, P=0.61, 3, \gamma_{\text{max}}=0.65, P=0.67, \)
4. \( \gamma_{\text{max}}=0.56, P=0.72 \)

WHY DO CLUSTERS FORM? WHY ARE THEY POLYDISPERSED?

A brief explanation of a cluster formation mechanism is shown below and it is argued that clusters are always polydispersed. Only equilibrium cluster distribution is considered below. Let \( n_1 \) be a number density of initial particles, \( n_2 = 2 \), be a number density of doublets, triplets and higher clusters, here \( r \) is a number of single particles in a cluster. It is supposed that exchange between clusters goes by one particle at a time. Taking into account all possible events with a cluster of size \( r \) the following system of algebraic equations can be deduced, which describes a steady state condition of the dispersed system

\[ 0 = bn_{r+1}n_r - an_{r+1} - bn_r n_1, \quad r=2,3, \quad  \]  

(7)

with the condition that the total number of particles is conserved

\[ \sum_{r=1}^{\infty} n_r = N_0 \]  

(8)

where \( N_0 \) is a fixed number concentration of single particles, \( a/b \) are reaction rates of the process of the disconnection/connection of a single particle to/from the clusters. Reaction constants \( a, b \) can be determined via the shape of interaction potential between particles.

The solution to the system of equations (7)-(8) is as follows

\[ f_r = \frac{1}{\alpha + 0.5 + \sqrt{\alpha + 0.25}} \]  

(9)

\[ f_{r+1} = \frac{\alpha^{r+1}}{\alpha + 0.5 + \sqrt{\alpha + 0.25}} \]  

(10)

where \( f_r \) is the fraction of clusters containing \( r \) particles, \( \alpha = bN_0/a \) is a dimensionless concentration.

APPENDIX DERIVATION OF EQ (5)

It is supposed below that dispersed particles form cluster of different sizes but with the same packing density \( \gamma_{\text{max}} \) inside each cluster, which is an average value. Figure 3 is used below for the derivation with a slightly modified legend (see below).

Let \( V_p \) be the particle's volume in suspension 1, \( V_p + \Delta V_p \) is the particle's volume in suspension 3. Liquid 2 did not have particles initially, so the particle's volume in suspension 4 is \( \Delta V_p \). Let \( V^+ \) be the volume of suspension 1 and liquid 2, then \( V + \Delta V_p \) is the volume of suspensions 3 and 4. Let \( \gamma_c \) be the cluster concentration in suspension 1, it follows that

Figure 2 Relative viscosity as a function of volume concentration of dispersed particles. Experimental points from review \([10]\), solid lines according to Eq (5) with different values of \( \gamma_{\text{max}} \) and \( P \)
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\[ \gamma_c = \frac{\gamma_p}{\gamma_{\text{min}}} = \frac{\gamma}{\gamma_{\text{max}}} \]  \hspace{1cm} (11)

where \( \gamma \) is the volume concentration of single particles in suspension 1, \( \gamma_p/\gamma_{\text{min}} \) is the volume of all clusters in suspension 1.

\[ \gamma_c + \Delta \xi_c = \frac{\frac{\gamma_p}{\gamma_{\text{max}}} - \Delta V_p/\gamma_{\text{max}}}{\gamma + \Delta V_p} \]  \hspace{1cm} (14)

According to the differential method viscosity of suspensions 3 and 4 must be equal giving

\[ \tau(\eta_{\text{pp}}, \gamma_c + \Delta \xi_c) = \tau(\eta_{\text{pp}}, \gamma_c + \Delta \xi_c, \Delta A \nu). \]  \hspace{1cm} (15)

Eq (15) is the main hypotheses of the differential method and it gives a differential equation for viscosity of the suspension based on the concentration of dispersed particles, in the case when particles form clusters. Now using a Taylor expansion and equation (4) and keeping only first order terms \( \Delta \gamma_c, \Delta \xi_c, \Delta A \nu \) one can obtain a differential equation solution, given by Eq (5).

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Determination of the Effective Viscosity of Concentrated Suspensions

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Abstract—The problem of determining the effective viscosity of concentrated suspensions was solved. It was assumed that clusters change the flow hydrodynamics of a suspension of a fairly high concentration of disperse particles. The obtained theoretical dependence of the viscosity of the suspension on the concentration of the dispersed phase is compared to the known experimental data on the measurement of the viscosity of concentrated suspensions. The packing density of particles \( \gamma_{\text{max}} \) is assumed to be the same in all clusters and plays a crucial role in the solution of the problem. It is possible to describe the whole set of the known experimental data by varying \( \gamma_{\text{max}} \) from the value corresponding to the least dense cubic packing to that corresponding to the densest hexagonal packing.

INTRODUCTION

In this work, we apply a differential method to calculate the dependence of the viscosity of concentrated suspensions on the concentration of a dispersed phase. The differential method for the determination of the effective properties of inhomogeneous materials was proposed for the first time in [1]. Subsequently [2, 3], the differential method was applied to determine the effective viscosity of a suspension containing single disperse particles. The same method was applied [4, 5] to determine the effective elastic properties of materials. In [6], the differential method was used to calculate the coefficients of viscosity and permeability of a porous medium (Brinkman’s medium).

In this work, the differential method was generalized for the case where particles in a suspension are able to form clusters. The developed theory was applied to calculate the viscosity of a concentrated suspension.

1. DIFFERENTIAL METHOD

Let us call a suspension containing porous particles suspension 1, and a homogeneous liquid of the same volume as that of suspension 1, liquid 2 (Fig. 1). In addition, let us introduce the same porous particles of volume \( \Delta V^p \) to both suspension 1 and liquid 2. Thus, we obtain suspensions 3 and 4, respectively. The main assumption of the differential method is the coincidence between the effective viscosities of suspensions 3 and 4.

Below, it is supposed that the disperse particles in a concentrated suspension form clusters of various sizes, but having the same packing density \( \gamma_{\text{max}} \).

Assume \( V^p \) to be the volume of particles in suspension 1, and \( V^p + \Delta V^p \) the volume of particles in suspension 3. Since the same particles are added to suspension 1 as to liquid 2, then \( \Delta V^p \) is the volume of particles in suspension 4. Let \( V \) be the volume of suspension 1 and liquid 2, and \( V + \Delta V^p \) the volume of suspensions 3 and 4. We determined the concentration of clusters \( \gamma^* \) in suspension 1 as

\[
\gamma^* = \frac{V^p/\gamma_{\text{max}}}{V} = \frac{\gamma}{\gamma_{\text{max}}} \tag{1}
\]

where \( \gamma \) is the volume concentration of single particles in suspension 1 and \( V^p/\gamma_{\text{max}} \) is the volume of all clusters.
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in suspension 1. Define

\[ \mu = \frac{\Delta V^*/\gamma_{\text{max}}}{V + \Delta V^*}, \tag{2} \]

where \( \mu \) is the volume concentration of clusters in suspension 4. On adding the volume \( \Delta V^* \) of particles to the suspension, the volume of the whole suspension increases by the same value \( \Delta V^* \). Consequently,

\[ \gamma^* + \Delta \gamma^* = \frac{(V + \Delta V^*)/\gamma_{\text{max}} - V^*/\gamma_{\text{max}}}{V + \Delta V^* - \Delta V^*/\gamma_{\text{max}}}, \tag{3} \]

where \( \gamma^* + \Delta \gamma^* \) is the concentration of the clusters in suspension 3.

Let us determine the concentration of the clusters \( \gamma^* + \xi \) in the suspension, which should remain if all the clusters formed by the additional particles together with the liquid imbibed by these clusters were removed from suspension 3:

\[ \gamma^* + \xi = \frac{V^*/\gamma_{\text{max}}}{V + \Delta V^* - \Delta V^*/\gamma_{\text{max}}} \tag{4} \]

Assume that the desired viscosity of the suspension is preassigned by the dependence to be determined,

\[ \eta = \eta(\eta_0, \gamma^*), \tag{5} \]

where \( \eta_0 \) is the viscosity of the dispersion medium.

From relationships (1)–(3), we find an increment of the cluster concentration \( \Delta \gamma^* \):

\[ \Delta \gamma^* = \frac{(V^* + \Delta V^*)/\gamma_{\text{max}} - V^*/\gamma_{\text{max}}}{V + \Delta V^* - \Delta V^*/\gamma_{\text{max}}} = \mu - \gamma^* \mu_{\gamma_{\text{max}}}. \]

Hence, we determine the value of \( \mu \),

\[ \mu = \frac{\Delta \gamma^*}{1 - \gamma^*/\gamma_{\text{max}}}. \tag{6} \]

Now, using relationships (1), (2), and (4), we find the value of \( \xi \),

\[ \xi = \frac{V^*/\gamma_{\text{max}}}{V + \Delta V^* - \Delta V^*/\gamma_{\text{max}}} - \frac{V^*/\gamma_{\text{max}}}{V} = \gamma^* \frac{\mu - \mu_{\gamma_{\text{max}}}}{1 - \mu}. \tag{7} \]

Since \( \mu \) is a small parameter, we ignore it in the denominator of relationship (7). Using relationships (7) and (6), we obtain the following expression for the value of \( \xi \):

\[ \xi = \gamma^* \mu (1 - \gamma_{\text{max}}) = \gamma^* (1 - \gamma_{\text{max}}) \frac{\Delta \gamma^*}{1 - \gamma^*/\gamma_{\text{max}}}. \tag{8} \]

On adding additional clusters to suspension 1, we obtain suspension 3. As assumed, the added clusters have the same size distribution as the clusters in the initial liquid, the same packing density \( \gamma_{\text{max}} \) of single particles, and are “dry.” After the clusters have imbibed the liquid, we replace the remaining quantity of the suspension by a medium with effective properties, the viscosity of this medium being equal to \( \eta(\eta_0, \gamma^* + \xi) \). The concentration of the clusters composed of additional particles in suspension 4 will be equal to \( \mu \). The viscosity of suspension 3 by definition (5), is, obviously, equal to \( \eta(\eta_0, \gamma^* + \Delta \gamma^*) \), where \( \gamma^* + \Delta \gamma^* \) is the concentration of all clusters in suspension 3. Hence, equating the viscosities of suspensions 3 and 4, we obtain

\[ \eta(\eta_0, \gamma^* + \Delta \gamma^*) = \eta(\eta_0, \gamma^* + \xi), \mu, z. \tag{9} \]

Equation (9) is just the main assumption of the differential method.

Let us introduce the function

\[ A(\eta_0) = \frac{d\eta(\eta_0, \gamma^*)}{d\gamma^*} \bigg|_{\gamma^* = 0}. \tag{10} \]

Expand the left-hand side of relationship (9) by the Taylor’s formula, which gives

\[ \eta(\eta_0, \gamma^* + \Delta \gamma^*) = \eta(\eta_0, \gamma^*) + \frac{d\eta(\eta_0, \gamma^*)}{d\gamma^*} \Delta \gamma^* + o(\Delta \gamma^*). \tag{11} \]

Using definition (10), we expanded the right-hand side of relationship in the same way (9):

\[ \eta(\eta_0, \gamma^* + \xi), \mu, z = \eta(\eta_0, \gamma^*), 0 + \eta'_1(\eta_0, \gamma^* + \xi), \mu, \xi \bigg|_{\xi = 0, \mu = 0} + \eta'_2(\eta_0, \gamma^* + \xi), \mu, \xi \bigg|_{\xi = 0, \mu = 0} + \eta'_3(\eta_0, \gamma^* + \xi), \mu, \xi \bigg|_{\xi = 0, \mu = 0} + o(\mu, \xi). \tag{12} \]

In deriving relationship (12), we used equalities

\[ \eta(\eta_0, \gamma^*), 0 = \eta(\eta_0, \gamma^*) \]

and

\[ \eta(\eta_0, \gamma^* + \xi), 0 = \eta(\eta_0, \gamma^* + \xi), \]

which follow from the fact that, if the concentration of a dispersed phase is equal to zero, then the suspension as a whole consists of the dispersion medium.

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From relationships (9), (11), and (12), we obtain the following expression:

$$\frac{d\eta}{d\gamma^*} \Delta \gamma^* = A(\eta) \mu + \frac{d\eta}{d\gamma^*} \xi.$$  \hspace{1cm} (13)

On substituting the expression for $\mu$ from relationship (6) and that for $\xi$ from [8] into (13), we obtain

$$\frac{d\eta}{d\gamma^*} = \frac{A(\eta)}{1 - \gamma^*} + \frac{d\eta}{d\gamma^*} \frac{1 - \gamma^*}{1 - \gamma^* \gamma_{\text{max}}}.$$  \hspace{1cm} (14)

After making some transformations in this relation, we derive a differential equation

$$A(\eta) \frac{d\eta}{d\gamma^*} = \frac{\eta}{1 - \gamma^*}$$  \hspace{1cm} (15)

Differentiation equation (14) with the boundary condition (15) defines the desired dependence of the effective viscosity of the suspension on concentration. For the complete definition of equation (14), it is necessary to know the dependence $A(\eta)$, which will be derived below.

The viscosity $\eta$ of the suspension with a low particle concentration $\gamma$ is (Einstein's formula [7]) equal to

$$\eta = \eta_0 + 2.5 \eta_0 \gamma^*.$$  \hspace{1cm} (16)

In deriving Einstein's formula (16), the friction of the particles against the surrounding liquid during their motion was taken into consideration. In our case, the formation of clusters resulted in the friction of clusters both with liquid and with each other. That is why formula (16) must be replaced by the following expression

$$\eta = \eta_0 + 2.5 \eta_0 F \gamma^*,$$  \hspace{1cm} (17)

where $F$ is the empirical parameter accounting for the aforementioned effects, which cannot be determined within the framework of the theory under consideration.

Using relationships (17), (1) and definition (10), we arrive at

$$A(\eta_0) = \frac{d\eta}{d\gamma^*} \bigg|_{\gamma^* = 0} = 2.5 \eta_0 F.$$  \hspace{1cm} (18)

Solution of equation (14) with the boundary condition (15) and accounting for relationship (18), yields

$$\eta = \eta_0 \left(1 - \frac{\gamma}{\gamma_{\text{max}}}\right)^{-2.5F},$$  \hspace{1cm} (19)

where $\gamma$ is the concentration of the dispersed phase in the suspension. The formula (19) is the desired theoretical dependence of the effective suspension viscosity on the concentration of the dispersed phase.

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Fig. 2. Dependences of viscosity on the dispersed phase concentration in accordance with equation (19) for $\gamma_{\text{max}} = 1$: (1) $\gamma_{\text{max}} = 1$, $F = 1$; (2) $\gamma_{\text{max}} = 0.73$, $F = 0.61$; (3) $\gamma_{\text{max}} = 0.65$, $F = 0.67$; (4) $\gamma_{\text{max}} = 0.56$, $F = 0.72$.

2. COMPARISON WITH THE EXPERIMENTAL DATA

The results on the determination of the dependence of the viscosity on suspension concentration were reviewed in [8, 9].

The experimental data and the curves plotted from the relationship (19) at different values of parameters $\gamma_{\text{max}}$ and $F$ are compared in Fig. 2. Curve 1 was obtained in [2-4].

As follows from Fig. 2 the whole body of the experimental data is described by equation (19) with parameters $\gamma_{\text{max}}$ and $F$, varying within the following ranges: $0.56 \leq \gamma_{\text{max}} \leq 0.73, 0.61 \leq F \leq 0.72$. Note that the parameter $F$ virtually remains constant, even when cluster packing density changes significantly.

The packing density $\gamma_{\text{max}} = 1$ for curve 1 corresponds to the case where each cluster consists of only one particle. The packing density $\gamma_{\text{max}} = 0.73$ for curve 2 corresponds to the density of hexagonal packing. The packing densities $\gamma_{\text{max}}$ equal to 0.65 (for curve 3) and 0.56 (for curve 4) are close to body centered cubic and simple cubic packings, respectively.
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REFERENCES

Effective viscosity and permeability of porous media

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Abstract

The effective properties of porous media composed of equally sized spherical particles are investigated. Flow inside porous media is modeled using Brinkman's equations, which include two semi-empirical coefficients: an effective viscosity and a resistance coefficient (1/penetritility). The differential method is used to deduce the dependencies of these coefficients on both porosity and the particle size. The deduced dependency of permeability on porosity is found to agree reasonably well with known dependencies obtained by computer simulations of flow in random porous media. © 2001 Elsevier Science B V. All rights reserved.

Keywords Permeability, Porous bodies, Modelling

Nomenclature

- $P$ pressure
- $\dot{u}$ velocity
- $\bar{U}$ constant velocity far from the particle
- $K$ hydrodynamic resistance
- $N$ number of particles
- $L$ characteristic length scale
- $V$ volume
- $a$ radius of particles
- $Z(y) = \frac{K_d a^2}{\eta_0}$ function defined by Eq. (8)
- $A_n$ function defined by Eq. (8)
- $R$ distance from the fixed particle centre
- $\mathbf{s}$ Cartesian co-ordinates
- $n_i = \frac{x_i}{r}, n_j = \frac{x_j}{r}, n_k = \frac{x_k}{r}$ force

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1. Introduction

Viscous flow of a liquid in a porous medium is frequently modelled using Darcy's equations

$$\nabla p = -K \eta (\gamma \hat{u})$$  \hspace{0.5cm} (1)

where $K_0$ is the porous medium hydrodynamic resistance ($1/K_0$ is the porous medium permeability), $\gamma$ is the particle volume concentration ($\phi = 1 - \gamma$ is porosity), $p$ and $\hat{u}$ are the pressure and average velocity, respectively. Eq. (1) should also be coupled with the incompressibility equation

$$\text{div} \ \hat{u} = 0$$  \hspace{0.5cm} (2)

This model suffers from a well-known disadvantage that it is impossible to match flows inside and outside the porous medium. To overcome this difficulty two different approaches have been suggested: a slippage at the boundary between flows inside and outside the porous medium approach [1] and Brinkman's equations [2]. In the former approach, an empirical slippage coefficient is defined, whereas in Brinkman's approach two, physically meaningful, coefficients are introduced: an effective viscosity, $\eta_0$ (which is obviously different from the liquid viscosity $\eta_0$) and the porous medium resistance coefficient, $K_0$. Brinkman's equations have the following form

$$\nabla p = \eta_0 (\gamma \hat{u}) \Delta \hat{u} - K_0 (\gamma \hat{u})$$  \hspace{0.5cm} (3)

Eq (2) should also be considered. Let $L_0$ be a characteristic length scale for Eq (3). This length scale can be determined in the following manner: both terms in the right-hand
side of Eq. (3) have to be of the same order of magnitude. This requirement gives \( \gamma / L = K_\alpha \) or \( \gamma / L = \sqrt{\eta a / \rho_\alpha} \), where \( L \) is referred to as the 'Brinkman's length'. If the distance \( L \) in the depth of the porous medium and remote from the porous medium-liquid interface satisfies the following inequality \( L >> L_\alpha \), the viscosity term \( \eta \) in the right hand side of Eq. (3) can be neglected and Brinkman's equations coincide with Darcy's equations (1) This consideration shows that hydrodynamic resistance in both equations are equal, that is \( K_\alpha = K_\alpha \) Kouznetz'-Carmen and Happel-Brenner equations (2) are frequently used to describe the dependency of hydrodynamic resistance on porosity and particle radius.

The porous medium resistance, \( K_\alpha \), vanishes in two cases either when concentration of the particles is zero \( \gamma = 0 \) for a pure liquid, when \( \eta_\alpha = \eta_\alpha \) where \( \eta_\alpha \) is the pure liquid viscosity) or when the particles move with the same average velocity as the liquid (concentrated suspension). In the latter case \( \eta_\alpha = \eta_\alpha \) where \( \eta_\alpha \) is the viscosity of the concentrated suspension. The last observation gives a very important hint, namely, the dependency of \( \eta_\alpha \) on particle concentration should be close to the viscosity of concentrated suspension with the same particle concentration in the case when \( \eta_\alpha \) is small enough. It is well known that the dependency of \( \eta_\alpha \) on particle volume fraction is an increasing function of particle volume fraction \( \gamma \). Consequently, it is reasonable to assume that \( \eta_\alpha \) dependency should also be an increasing function of particle volume fraction. In contrast to this assumption, a decrease of effective viscosity with particle volume fraction \( \gamma \) has been predicted (4).

2. Calculation of viscosity and hydrodynamic resistance in Brinkman's equations using the differential model.

Let us define and consider four different media (see Fig. 1) as follows.

(1) Porous medium 1, denoted as PM1, with a volume fraction of solid particles \( \gamma \)

\[
\gamma = \frac{V_\gamma}{V_\gamma + V_p}
\]  (4)

where \( V_\gamma \) and \( V_p \) are the volumes of the liquid and particles, respectively. As the particles are all spherical, \( V_p = 4/3 \pi a^3 \), where \( a \) and \( n \) are, respectively, the particle radius and the number of particles in this volume. The liquid flow in PM1 is assumed to obey Eqs (2) and (3). The dependencies of effective viscosity \( \eta_\alpha(\gamma) \) and the resistance coefficient \( K_\alpha(\gamma) \) or \( \gamma \) have yet to be determined.

(2) A homogeneous Brinkman's medium, denoted as BM2, where the liquid flow is described by the same Eqs (2) and (3) with exactly the same viscosity \( \eta_\alpha(\gamma) \), resistance coefficient \( K_\alpha(\gamma) \) and volume as for PM1. In contrast to PM1, BM2 is supposed to be a homogeneous medium without any solid particles at all.

Let a small number of particles, \( \delta \nu \), be added to both porous medium 1 (PM1) and Brinkman's medium 2 (BM2). This addition results in a new porous medium, denoted as PM3 and a porous medium from BM2, denoted as PM4 (Fig. 1). Media PM3 and PM4 have a greater volume, \( V_\gamma + V_p + \delta V_\nu \) as compared with PM1 and BM2, where \( \delta V_\nu = 4/3 \pi a^3 \delta n \).
In the development that follows only small quantities of the first order are retained.

The particle volume fraction in PM3, \( \gamma + \delta \gamma \), is

\[
\frac{\gamma + \delta \gamma}{\gamma + \delta \gamma} = \frac{V_p + \Delta V_p}{V_1 + \Delta V_1 + \Delta V_p} \left( \frac{V_p}{V_1 + V_p + \Delta V_p} \right)
\]

\( \approx \frac{V_p}{V_1 + \Delta V_1 + \Delta V_p} \left( 1 + \frac{\Delta V_p}{V_p} \right) = \gamma + (1 - \gamma) \delta \mu \)  

(5)

where \( \delta \mu = \Delta V_p/V_1 \) is the particle volume fraction inside the PM4.

The liquid flow in PM3 is described by Eqs (2) and (3) but at concentration \( \gamma + \delta \gamma \) instead of \( \gamma \), i.e., Eq (3) transforms into

\[
\text{grad } p = \eta_n(\gamma + \delta \gamma) \Delta \mu - K_n(\gamma + \delta \gamma) \Delta \mu
\]

(6)

The particle concentration in PM4, \( \delta \mu \), according to Eq (5) can be expressed as

\[
\delta \mu = \frac{\delta \gamma}{1 - \gamma}
\]

(7)

It is recalled that BM2 is supposed not to have any particles at all and to be a homogeneous medium. Addition of a small number of particles with concentration \( \delta \mu \) results in a small change both viscosity, \( \delta \eta_n \), and resistance coefficient, \( \delta K_n \), in PM4. The latter small changes are obviously proportional to \( \delta \mu \), i.e., we can write

\[
\delta \eta_n = A_n(\eta_n, K_n) \delta \mu, \delta K_n = A_k(\eta_n, K_n) \delta \mu
\]

(8)

where \( A_n(\eta_n, K_n) \) and \( A_k(\eta_n, K_n) \) are two unknown functions. The main objective becomes one of calculating these two unknown functions.

Let us suppose that these two functions have been already determined. In this case the liquid flow in PM4 would be described by the following equations

\[
\text{grad } p = [\eta_n(\gamma) + A_n(\eta_n, K_n) \delta \mu] \Delta \mu - [K_n(\gamma) + A_k(\eta_n, K_n) \delta \mu] \Delta \mu
\]

(9)

The main assumption of the differential method is as follows: the viscosity and resistance coefficient in porous medium 3 and porous medium 4 are equal. Using this condition from Eqs (6) and (9) we obtain:

\[
\eta_n(\gamma + \delta \gamma) = \eta_n(\gamma) + A_n(\eta_n, K_n) \delta \mu
\]

\[
K_n(\gamma + \delta \gamma) = K_n(\gamma) + A_k(\eta_n, K_n) \delta \mu
\]

A simple rearrangement of the latter equations using Eq. (7) results in the following system of two differential equations

\[
\frac{d\eta_n}{d\gamma} = \frac{A_n(\eta_n, K_n)}{(1 - \gamma)}
\]

(10)

with the obvious boundary conditions

\[
\eta_n(0) = \eta_n, K_n(0) = 0
\]

(11)

This system of two ordinary differential Eqs. (10) with two boundary conditions (11) can be solved directly.

3. Determination of two unknown functions \( A_n(\eta_n, K_n) \) and \( A_k(\eta_n, K_n) \)

According to its definition, BM2 is a homogeneous medium and Eqs (2) and (3) describe the liquid flow in this medium. After addition of a small number of particles, \( \delta \eta_n \), to BM2 it transforms into PM4. The most important observation is that the volume fraction of particles in PM4, \( \delta \mu \), is very small and, hence, particles are located far from each other and their hydrodynamic interaction can be neglected. In other words, in PM4 one may consider flow in a homogeneous medium around an isolated particle.

Let us consider an isolated particle placed in BM2 subjected to two different flow regimes: (a) homogeneous flow with constant velocity \( U \), and (b) extensional flow (in both cases remote from the particle). Consideration of both flows is close to that in [5]. Consideration of flow (a) gives us the unknown function \( A_n(\eta_n, K_n) \). Consideration of flow under condition (b) above gives a viscosity change, which determines the unknown function \( A_k(\eta_n, K_n) \). Detailed derivations are presented in Appendix A (Eq. A(16)) and Appendix B (Eq. B(23)), respectively. Substitution of these dependencies into Eq. (10) results in
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The equations and derivations provided are as follows:

\[ \frac{dK}{dy} = \frac{9}{2a^2} \left( 1 + \zeta \frac{\sqrt{\eta} + a^2 \frac{K_b}{\eta}}{1 - \gamma} \right) \]

\[ \frac{d\eta}{dy} = \frac{K_{0\eta}^2}{6} \left( 1 - \gamma \right) \left( 1 + \frac{\sqrt{\eta} + a^2 \frac{K_b}{\eta}}{1 - \gamma} \right) \]

with boundary conditions (11).

Let us introduce two dimensionless functions

\[ Z(\gamma) = K_{0\eta}^2/\eta \quad \eta(\gamma) = \eta_0/\eta_0 \]

Using these functions the system (12-13) with boundary conditions (11) can be rewritten as

\[ \frac{dZ}{dy} = \frac{9}{2} \left( 1 - \gamma \right) \left( \frac{\sqrt{\eta} + a^2 \frac{K_b}{\eta}}{1 - \gamma} \right) \]

\[ \frac{d\eta}{dy} = \frac{Z}{6} \left( 1 - \gamma \right) \left( 1 + \frac{\sqrt{\eta} + a^2 \frac{K_b}{\eta}}{1 - \gamma} \right) \]

with boundary conditions

\[ Z(0) = 0 \]

\[ \eta(0) = 1 \]

4. Discussion

At low particle fraction, \( \gamma \), the dimensionless resistance coefficient \( Z(\gamma) \) becomes small and Eqs. (14) and (15) can be rewritten as

\[ \frac{dZ}{dy} = \frac{9}{2} \left( 1 - \gamma \right) \]

\[ \frac{d\eta}{dy} = \frac{Z}{6} \left( 1 - \gamma \right) \]

The latter system of equations with boundary conditions (11) has the following solutions (reverting to dimensional variables)

\[ \eta_0(\gamma) = \eta_0(1 - \gamma)^{-\frac{a^2}{2}} \]

\[ K_0(\gamma) = \frac{9}{2a^2} \eta_0(1 - \gamma)^{-\frac{a^2}{2} - 1} \]

Eqs. (19) and (20) determine the dependence of effective viscosity and resistance coefficient of Brinkman's medium on the volume fraction of particles, \( \gamma \), in the case of low particle volume fraction. Both dependences are increasing functions of particle concentration, \( \gamma \).

Dependency (19) coincides with the dependency of the viscosity of concentrated suspensions [6] as it has been predicted in Section 1.

It is easy to see that Eq. (20) can be rewritten as

\[ K_0(\gamma) = \frac{9}{2a^2} \eta_0(1 - \gamma)^{-\frac{a^2}{2} - 1} \]

The latter equation gives the dependency of the hydrodynamic resistance on the particle volume fraction, \( \gamma \), if \( \gamma \) is small. According to Eq. (21) the hydrodynamic resistance becomes negative if the effective viscosity is lower than the liquid viscosity, which is obviously impossible.

Let us introduce the dimensionless permeability

\[ k = 1/Z = \eta_0/K_{0\eta} \] and investigate its dependence on porosity \( \varphi \).

According to Eq. (21) at high porosity, \( \varphi \to 1 \)

\[ k(\varphi) = \frac{9}{2} \varphi^{-\frac{a^2}{2}} \]

This dependency is shown by curve 4 in Fig. 2. At low porosity, \( \varphi \to 0 \), according to Appendix C,

\[ k = 1/\eta_0 \] and \( \eta = C_0 \varphi^{-\frac{a^2}{2}} \), hence

\[ k = \frac{C_0 \varphi^{-\frac{a^2}{2}}}{C_0 \varphi^{-\frac{a^2}{2}}} \]

This dependency is shown by curve 5 in Fig. 2. Curve 3 in the same figure represents the permeability dependence on porosity calculated according to Eqs. (14) and (15). Curves 1 and 2 in Fig. 2 give the permeability calculated according to Happel–Brenner and Kozeny–Carmen equations [3], respectively. Points and squares show permeability obtained by direct computer simulations of liquid flow in a random three-dimensional [7] and a two-dimensional porous medium [8], correspondingly. In both papers [7] and [8] simulated porous medium consist of penetrating particles, which form clusters at high concentrations. It is recalled that according to the model adopted here that particles can not penetrate into each other and do not form clusters. It appears that mutual
particle penetration and clustering is more important in the case of three-dimensional porous media [7]. This results in a close agreement of our prediction (curve 3, Fig. 2) with permeability dependency in the case of two-dimensional porous medium (squares [8]).

The relative viscosity at high porosity (e.g. at \( \Phi \to 1 \)) according to Eq (19) can be rewritten as

\[
\log_{10} \eta = -2.5 \log_{10} \Phi, \quad \Phi \to 1
\]

(24)

The latter dependency is shown as asymptote 3 in Fig. 3. At low porosity, \( \Phi \to 0 \), according to Appendix C the relative viscosity is

\[
\log_{10} \eta = -4.130 \log_{10} \Phi - 0.2249, \quad \Phi \to 0
\]

(25)

The latter dependency is shown by asymptote 3 in Fig. 3. Curve 1 represents the relative viscosity dependency on porosity calculated according to Eqs (14) and (15).

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Appendix A. Uniform Flow

Force applied to a single spherical particle in Brinkman's medium and calculation of the function \( \Delta u(\Phi, K) \)

Let us consider a single spherical particle with radius \( a \) placed in a uniform flow inside homogeneous Brinkman's homogeneous medium, denoted previously as BM2. Far from the particles the following boundary conditions should be satisfied

\[
\hat{s}_1|_{r=a} = \vec{U} = (0,0,0)
\]

(11)

that is, \( U_1 = U_2 = 0 \), \( U_3 = U \)

In the case under consideration a force similar to the Stock's force is exerted on the particle and our aim is to calculate this force.

The flow obeys Brinkman's Eq (3) and the incompressibility condition (2).

If we apply a rot operation to Eq (3), then we obtain

\[
\eta
\]

(26)

\[
\quad \rho
\]

Fig. 3. Dependence of relative viscosity \( \eta = \rho_n/\rho \) of porous medium on the porosity \( \Phi = 1 - \rho \) (log-log co-ordinates). 1. Solution of Eqs. (14) and (15), 2, high porosity asymptote, \( \Phi \to 1 \), according to Eq. (24); 3, low porosity asymptote, \( \Phi \to 0 \) according to Eq. (25).
\[ \eta_3 \Delta \text{rot } \vec{u} - K_n \text{rot } \vec{u} = 0 \]  
\text{(A2)}

In the same way as in ref. [5] the velocity vector can be presented in the following form
\[ \vec{d} = \vec{\Omega} + \text{rot rot} (f(r) \vec{\Omega}) \]  
\text{(A3)}

where \( f(r) \) is a new unknown function, \( r = |r| \) is the radial distance from the origin (the origin is selected in the particle centre). Hence,
\[ \text{rot} \vec{d} = \text{rot rot} \text{rot} (f \vec{\Omega}) = \text{grad div} \text{rot rot} (f \vec{\Omega}) - \Delta \text{rot} (f \vec{\Omega}) \]
\[ = - \Delta \text{rot} (f \vec{\Omega}) \]
\text{or}
\[ \text{rot} \vec{d} = \sum_{j=1}^{3} \sum_{k=1}^{3} \epsilon_{jkh} x_j x_k = \sum_{j=1}^{3} \epsilon_{jkh} x_j \Delta \text{rot} f = - \Delta \sum_{j=1}^{3} \epsilon_{jkh} x_j \]

where \( \epsilon_{jkh} \) is the anti-symmetric unit tensor (\( \epsilon_{123} = 1, \epsilon_{132} = -\epsilon_{123} = -1 \)).

Substitution of the latter expression in Eq (A2) gives the following equation for determination of unknown function \( f(r) \)
\[ 0 = \left( \Delta f(r) - \frac{K_n}{\eta_3} \Delta f(r) \right) \sum_{j=1}^{3} \epsilon_{jkh} x_j x_k \]
\text{(A4)}

It is obvious, that \( \sum_{j=1}^{3} \epsilon_{jkh} x_j x_k = 0 \) everywhere, hence Eq (A4) yields

\[ \psi = r \phi/(\sqrt{\eta_3 K_n}) \]  
\text{(A5)}

After substitution \( f = \phi/r \), where \( \phi(r) \) is a new unknown function, and integration Eq. (A5) can be written in the following form
\[ \frac{\phi''(r)}{\eta_3 r} - \frac{K_n \phi'(r)}{\eta_3} = \text{const} \]
\text{(A6)}

An integration constant should be set to zero because the fluid velocity remains finite far from the particle. Eq (A6) has the following solution
\[ \psi = G + Q r + M \exp \left( \frac{K_n}{\eta_3} r \right) + N \exp \left( - \frac{K_n}{\eta_3} r \right) \]
\text{(A7)}

where \( G, Q, M \) and \( N \) are integration constants.

Taking into account boundary condition (A1) the latter equation gives
\[ f = \frac{G}{r} + Q + M \exp \left( \frac{K_n}{\eta_3} r \right) \frac{1}{1 + \sqrt{\frac{K_n}{\eta_3}} \ln r} \]  
\text{(A8)}

Eq (A3) can be rewritten as
\[ u_i = \bar{u}_i + \text{grad div } f \bar{u}_i - \Delta \bar{u}_i \quad i = 1, 2, 3 \]  
\text{(A9)}

From Eqs (A8) and (A9) we can conclude

\[ u_i = \bar{u}_i + \left( \frac{3}{r^2} \sum_{j=1}^{3} n_j \bar{u}_j - \frac{1}{r^2} \bar{u}_i \right) G + N \exp \left( \frac{K_n}{\eta_3} r \right) \sum_{j=1}^{3} n_j \bar{u}_j - \frac{K_n}{\eta_3} \exp \left( - \frac{K_n}{\eta_3} r \right) \bar{u}_i \]

\[ - \frac{K_n}{\eta_3} \exp \left( - \frac{K_n}{\eta_3} r \right) \bar{u}_i + \frac{K_n}{\eta_3} \exp \left( \frac{K_n}{\eta_3} r \right) \sum_{j=1}^{3} n_j \bar{u}_j 
- \frac{3 \exp \left( - \frac{K_n}{\eta_3} r \right)}{r^2} \sum_{j=1}^{3} n_j \bar{u}_j \bar{u}_j \]

\[ \bar{u}_i \]  
\text{(A10)}
The latter equations and non-slip conditions at the particle surface \( r = \alpha \) determine value of constants \( G \) and \( N \):

\[
N = \frac{3}{2} \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha, \quad G = \frac{\alpha^2 - \frac{3}{2} \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha}{\frac{3}{2} \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha} - \frac{3 \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha}{\alpha^2 K_\beta}
\]

(A11)

All functions under consideration below (components of velocity vector, viscous stress tensor and pressure) are presented as \( F = F^{\text{elm}} + F^{\text{mil}} \), where \( F^{\text{elm}} \) is caused by the flow far from the particle and \( F^{\text{mil}} \) is caused by the presence of the particle. Below we are interested only in values caused by the particle and, hence, at first order terms Superscript (1) is omitted.

The pressure can be calculated after substitution in Eq (3) the velocity expression via function \( f(r) \) (Eq (A3))

\[
\text{grad} \ p = \text{grad} (\eta_\alpha \Delta v fU - K_\beta \Delta v \Delta fU) = - (\eta_\alpha \Delta v fU - K_\beta \Delta v \Delta fU)
\]

And after integration:

\[
p = \eta_\alpha \Delta v fU - K_\beta \Delta v \Delta fU
\]

Using Eq (A10) the latter equation gives

\[
p = \left( K_\beta - \eta_\alpha \right) \sum_{i=1}^{N} \Delta v_i \Delta U_i
\]

(A12)

where constants \( G \) and \( N \) are given by Eq (A11).

Let us rewrite the velocity vector (A10) and pressure (A12) using spherical co-ordinate system with polar axe along the direction of the velocity vector, \( \vec{U} \). This gives

\[
\vec{u} = U \cos \theta \left( N \eta_\alpha \frac{2 \exp \left( - \frac{K_\beta}{2} \right)}{\eta_\alpha} \exp \left( - \frac{K_\beta}{2} \right) \right) \frac{\exp \left( - \frac{K_\beta}{\eta_\alpha} \right)}{r^2} \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}} - \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}} \frac{\exp \left( - \frac{K_\beta}{\eta_\alpha} \right)}{r^2} \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}}
\]

\[
\vec{u} = - U \sin \theta \left( N \eta_\alpha \frac{2 \exp \left( - \frac{K_\beta}{2} \right)}{\eta_\alpha} \exp \left( - \frac{K_\beta}{2} \right) \right) \frac{\exp \left( - \frac{K_\beta}{\eta_\alpha} \right)}{r^2} \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}} - \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}} \frac{\exp \left( - \frac{K_\beta}{\eta_\alpha} \right)}{r^2} \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{3}{2} + \frac{\eta_\alpha}{r^2}}
\]

\[
p = \left( K_\beta + \eta_\alpha \right) U \cos \theta
\]

Components of the stress tensor at the particle surface, \( r = \alpha \) can be deduced using the latter expressions as

\[
\sigma_{\alpha} = \left( K_\beta + \frac{3}{2} \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha \right) U \cos \theta
\]

\[
\sigma_{\alpha} = \left( K_\beta + \frac{3}{2} \exp \left( \frac{K_\beta}{\eta_\alpha} \right) \alpha \right) U \sin \theta
\]

(A13)

where \( \sigma_{\alpha}, \sigma_{\alpha} \) are components of the stress tensor in polar co-ordinate system. The force, \( F_{\alpha} \), exerted to the spherical particle according to [3] can be calculated as:

\[
F_{\alpha} = \int_{\Sigma} \left( \sigma_{\alpha} \cos \theta - \sigma_{\alpha} \sin \theta \right) d\Sigma,
\]

(A14)

where \( \Sigma \) is the particle surface, \( d\Sigma \) is the surface element Eqs (A13) and (A14) yield

\[
F_{\alpha} = 6 \pi \mu \eta_\alpha \left( 1 + a \right) \alpha \left( \frac{K_\beta}{\eta_\alpha} \right) \left( \frac{K_\beta}{\eta_\alpha} \right) ^{\frac{2}{3} + \frac{\eta_\alpha}{r^2}}
\]

(A15)

Additional resistance cause by the presence of \( \delta a \) particles inside Brinkman's medium 4 is

\[
\delta \kappa_{\alpha} = \frac{F_{\alpha} \delta a}{V} = \frac{3F_{\alpha} \delta a}{4\pi \alpha^2} = \frac{3F_{\alpha} \delta a}{4\pi \alpha^2 (1 - \gamma)}
\]

(A16)

After substitution of Eq (A15) into the latter equation the result is

\[
\delta \kappa_{\alpha} = 3F_{\alpha} \delta a
\]

(A17)

The latter equation shows that

\[
\eta_\alpha \Delta v fU - K_\beta \Delta v \Delta fU = \eta_\alpha \Delta v fU - K_\beta \Delta v \Delta fU
\]

\[
\delta \kappa_{\alpha} = 3F_{\alpha} \delta a
\]
Appendix B. Extensional flow, calculation of function \( A_x, K_x \).

An extensional flow in the Brinkman's medium 2 around a single sphere of radius \( a \) is considered below. Origin coincides with the particle centre.

Far from the particle the flow is given by

\[
\sum_{j=1}^{3} \varepsilon_j \varepsilon_j = \mathbf{0}
\]  

(B1)

where \( \varepsilon_j \) is a symmetric tensor, \( \sum_{j=1}^{3} \varepsilon_{j} = 0 \). Brinkman's Eq (3) and the equation of incompressibility (2) describe the flow around the sphere. On the particle surface non-slip conditions are

\[
\dot{\mathbf{v}}_{p-w} = 0
\]  

(B2)

In the same way as in Appendix A the velocity vector can be presented in the following form

\[
\mathbf{u} = a \times \mathbf{x} + \text{rot}([\text{rot}(a \times \mathbf{V})])
\]  

(B3)

where an unknown function \( f(r) \) depends on radial distance \( r \) only, \( a \times \mathbf{x} = \sum_{j=1}^{3} a_j \varepsilon_j \). Applying \( \text{rot} \) to both sides of Eq (3) yields

\[
\eta_0 \text{rot} \mathbf{u} - K_0 a \cdot \text{rot} \mathbf{u} = 0
\]  

(B4)

From Eq (B3) we find

\[
\text{rot} \mathbf{u} = \text{rot}([\text{rot}(a \times \mathbf{V})]) = \Delta \text{rot}(a \times \mathbf{V})
\]

\[
= - \nabla \Delta \text{rot}(a \times \mathbf{V})
\]

The velocity field \( \mathbf{u} = a \times \mathbf{x} + \nabla \theta \), where \( \theta = -a \times \mathbf{x} + \nabla \cdot \theta \), is related to the gradient of \( \theta \). The term \( 2 \nabla \theta \times \mathbf{a} \times \mathbf{x} \) is the extensional flux that must be included in the balance of momentum.

Substitution of the latter equation into Eq (B4) gives

\[
- \eta_0 \Delta \text{rot}(a \times \mathbf{V}) + K_0 \Delta \text{rot}(a \times \mathbf{V}) = 0
\]  

(B5)

Using the antisymmetric unit tensor \( \varepsilon_{ik} \) (\( \varepsilon_{12} = 1 \), \( \varepsilon_{13} = -6 \), \( \varepsilon_{23} = -6 \)) in Eq (B5) we arrive (in the same way as in Appendix A) to the following equation for \( f(r) \) determination

\[
\eta_0 \Delta f^* - K_0 \Delta f^* = 0
\]  

(B6)

where \( \Delta \) means a derivative in respect to \( r = |\mathbf{r}| \). After substitution \( f = \psi f \) (where \( \psi f \) is a new unknown function) we obtain from Eq (B6)

\[
\left( \frac{\psi^* f}{r} - K_0 \frac{\psi^* f}{r} \right) = 0
\]  

(B7)

Eq (B7) has the following solution

\[
f = \frac{Q}{r} + G \exp \left( \frac{K_a}{\eta_0} \frac{r}{a} \right)
\]

\[
+ \frac{N \exp \left( \frac{K_a}{\eta_0} \frac{r}{a} \right)}{r} + B a^3 + B r^3
\]

where \( Q, G, M \) and \( N \) are integration constants.

In order to satisfy boundary conditions far from the particle (B1) constants \( M, A \) and \( B \) must be set to zero and constant \( G \) can be easily determined, thus gives

\[
f = \frac{Q}{r} + N \exp \left( \frac{K_a}{\eta_0} \frac{r}{a} \right) + \frac{1}{r} \exp \left( \frac{K_a}{\eta_0} \right)
\]

(B8)

Eq (B3) can be rewritten as

\[
\mathbf{u} = a \times \mathbf{x} + \nabla \theta = \nabla \theta + \text{rot}([\text{rot}(a \times \mathbf{V})])
\]

(B9)

Using latter two equations we obtain

\[
\theta = -15 a + N + \left[ \frac{Q}{r} - \exp \left( \frac{K_a}{\eta_0} \right) \right] + \frac{N}{r} \exp \left( \frac{K_a}{\eta_0} \right) + \frac{1}{r} \exp \left( \frac{K_a}{\eta_0} \right)
\]

\[
= -15 a + N + \left[ \frac{Q}{r} - \exp \left( \frac{K_a}{\eta_0} \right) \right] + \frac{N}{r} \exp \left( \frac{K_a}{\eta_0} \right) + \frac{1}{r} \exp \left( \frac{K_a}{\eta_0} \right)
\]

(B10)
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Non-slip conditions at the particle surface result in the following values of integration constants $N$ and $Q$

\[
N = -\frac{2}{3} \exp\left(\frac{K_{\alpha} a}{\eta_{b}}\right)a^3
\]

\[
Q = \frac{a^2}{\left(1 + \frac{K_{\alpha} a}{\eta_{b}}\right)^{\frac{3}{2}}} \left( a \sqrt{\frac{K_{\alpha}}{\eta_{b}}} + 6 + 15 \frac{\eta_{b}}{K_{\alpha} a} + 15 \frac{\eta_{b}}{K_{\alpha} a^2} - 15 \frac{\eta_{b}}{K_{\alpha} a^3} \exp\left(\frac{K_{\alpha} a}{\eta_{b}}\right) a^2 \right).
\]

Let us calculate a correction to the viscous stress tensor at low concentration of particles. For any function $g$, we introduce an average value as

\[
\langle g \rangle = \frac{1}{V} \int_{V} g \, dV,
\]

where $V$ is the volume of the big sphere with centre coincides with the particle centre. The volume $V$ does not include any other particles (low particles concentration) Integration of the viscous stress tensor over the volume $V$ results in

\[
\langle \sigma_{ij} \rangle = \frac{1}{V} \int_{V} \left( \sigma_{ij} + \eta \left( \frac{\partial \sigma_{ij}}{\partial t} + \frac{\partial \sigma_{ij}}{\partial x_j} \right) \right) \, dV.
\]

The expression under the integral in the right

\[
\langle \sigma_{ij} \rangle = \langle \sigma_{ij} \rangle + \eta \left( \frac{\partial \sigma_{ij}}{\partial t} + \frac{\partial \sigma_{ij}}{\partial x_j} \right) \]

\[
+ \frac{1}{V} \int_{V} \left( \sigma_{ij} + \eta \left( \frac{\partial \sigma_{ij}}{\partial t} + \frac{\partial \sigma_{ij}}{\partial x_j} \right) \right) \, dV.
\]

The expression under the integral in the right

\[
\langle \sigma_{ij} \rangle = \frac{1}{V} \int_{V} \left( \sigma_{ij} + \eta \left( \frac{\partial \sigma_{ij}}{\partial t} + \frac{\partial \sigma_{ij}}{\partial x_j} \right) \right) \, dV.
\]
hand side of the latter equation is zero outside the particle and differs from zero inside the particle. A direct calculation of such an integral inside the particle requires investigations of the stress tensor inside the particle. However, it is possible to avoid this problem by a transformation of the integral over volume to the integral over comprising surfaces inner surface of the volume V, \( \Sigma \), which does not go through any other particle.

Using Eqs. (A1)-(A3) and definition of the stress tensor we can rewrite the stress tensor as

\[
\sigma_{ij} = \frac{1}{2n} \sum_{k=1}^{n} \left( \frac{\partial \rho_{i}}{\partial x_{k}} + \frac{\partial \rho_{k}}{\partial x_{i}} \right) - \frac{\rho_{i}}{2V} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma
\]  

(B15)

Substitution of Eq. (B15) into (B14) gives

\[
\langle \rho_{i} \rangle = \langle \rho_{i} \rangle \left( \frac{\partial \rho_{i}}{\partial x_{k}} + \frac{\partial \rho_{k}}{\partial x_{i}} \right) + \frac{1}{2V} \sum_{k=1}^{n} \left( \sigma_{ik} n_{j} + \sigma_{jk} n_{i} \right)
\]

(B16)

where \( \langle \rho_{i} \rangle \) is the average pressure which must be determined by a linear combination of components of the tensor \( \sigma_{ij} \), the latter scalar is equal to \( \sigma_{ij} = 0 \) in order to calculate the integral in (B16) the following relations which are valid at integration over spherical surface, are used

\[
\frac{1}{2} \int_{\Sigma} \rho_{i} n_{j} \, d\Sigma = \frac{1}{2} \sum_{k=1}^{n} \rho_{k} n_{i} n_{j} \, d\Sigma = \frac{1}{2} \sum_{k=1}^{n} \left( \rho_{k} n_{i} n_{j} + \rho_{k} n_{j} n_{i} \right)
\]  

(B17)

where \( n_{i} = x_{i}/r \), \( d\Sigma \) is the differential on the spherical surface Eq. (B16) may be rewritten in the following way

\[
\langle \rho_{i} \rangle = \langle \rho_{i} \rangle \left( \frac{\partial \rho_{i}}{\partial x_{k}} + \frac{\partial \rho_{k}}{\partial x_{i}} \right) + \frac{1}{2V} \sum_{k=1}^{n} \left( \sigma_{ik} n_{j} + \sigma_{jk} n_{i} \right)
\]

(B18)

For calculation of the integral (B18) we will use stress tensor given by Eq. (B15) and the velocity vector given by Eq. (B10). In the final equation we keep terms proportional to \( 1/r^{2} \) and omit those tends faster to zero

\[
\langle \rho_{i} \rangle = \frac{1}{2V} \sum_{k=1}^{n} \left( \sigma_{ik} n_{j} + \sigma_{jk} n_{i} \right) + \frac{1}{2V} \frac{1}{r} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma
\]

(B19)

The value \( \langle \rho_{i} \rangle \) disappears because the average pressure is equal to zero \( \langle \rho_{i} \rangle \) is a scalar, which must be determined by a linear combination of components of the tensor \( \sigma_{ij} \), the latter scalar is equal to \( \sigma_{ij} = 0 \) in order to calculate the integral in (B16) the following relations which are valid at integration over spherical surface, are used

\[
\int \rho_{i} n_{j} \, d\Sigma = \int \sum_{k=1}^{n} \rho_{k} n_{i} n_{j} \, d\Sigma = \frac{1}{2} \sum_{k=1}^{n} \left( \rho_{k} n_{i} n_{j} + \rho_{k} n_{j} n_{i} \right)
\]

(B17)

where \( \rho_{i} = x_{i}/r \), \( d\Sigma \) is the differential on the spherical surface Eq. (B16) may be rewritten in the following way

\[
\langle \rho_{i} \rangle = \langle \rho_{i} \rangle \left( \frac{\partial \rho_{i}}{\partial x_{k}} + \frac{\partial \rho_{k}}{\partial x_{i}} \right) + \frac{1}{2V} \sum_{k=1}^{n} \left( \sigma_{ik} n_{j} + \sigma_{jk} n_{i} \right)
\]

(B18)

The latter equation can be rewritten as

\[
\langle \rho_{i} \rangle = \frac{1}{2V} \frac{1}{r} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma
\]

(B19)

Where

\[
\int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma = 2\pi r \frac{1}{V} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma
\]

(B20)

After substitution of integration constants \( N \) and \( Q \) from Eq. (B11) we find using Eqs. (B13), (B18), (B19),

\[
\int \frac{1}{2V} \frac{1}{r} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma = \frac{1}{2V} \frac{1}{r} \int_{\Sigma} \sigma_{ij} n_{i} n_{j} \, d\Sigma
\]

\[
K_{a} \left( \frac{a^{2}}{n_{b}} \sqrt{\frac{3}{\pi}} + 6a^{2} \frac{1}{5} \sqrt{\frac{3}{\pi}} + 15 \frac{1}{\sqrt{\pi}} + n_{b} \sigma_{i} \right)
\]

(B21)

In the case under consideration, \( \sigma_{i} = (a/3)^{2} \sigma_{i} \), hence, from Eqs. (B18)–(B21) we conclude

\[
\langle \rho_{i} \rangle = \pi \sigma_{i} 2\pi q
\]

(B21)

where

\[
K_{a} \left( \frac{a^{2}}{n_{b}} \sqrt{\frac{3}{\pi}} + 6a^{2} \frac{1}{5} \sqrt{\frac{3}{\pi}} + 15 \frac{1}{\sqrt{\pi}} + n_{b} \sigma_{i} \right)
\]

(B21)
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\[ K_s (a^3 \frac{K_s}{\eta_b} + 6a^2 + 15 \frac{\eta_b}{K_s} a + 15 \frac{\eta_b}{K_s} \beta \mu) \]

Comparison of Eqs. (B22) and (9) gives

\[ A_s = \frac{K_s (a^3 \frac{K_s}{\eta_b} + 6a^2 + 15 \frac{\eta_b}{K_s} a + 15 \frac{\eta_b}{K_s} \beta \mu)}{6 (1 + \frac{K_s}{\eta_b} a)} \]

(B23)

If \( \sqrt{K_s/\eta_b} \rightarrow 0 \) then the latter equation gives \( A_s = 5/2 \), which coincides with Einstein’s equation

Appendix C. Solution of the system of the differential Eqs. (14)–(15).

The resulting system of the differential equations is (14)–(15) with boundary conditions (16) is under consideration below. Dividing Eq. (14) by Eq. (15) gives

\[ \frac{dZ}{\eta} = \frac{1 + \frac{Z}{\eta} + \frac{Z^2}{\eta^2}}{\frac{Z}{\eta} + 6 + \frac{Z}{\eta} + \frac{Z^2}{\eta^2}} \]

(C1)

After substitution \( Z = H(\eta) \times \eta \), where \( H(\eta) \) is a new unknown function the differential Eq. (C1) becomes

\[ \frac{dH}{d\eta} = \frac{2(\epsilon^2 + 6\epsilon + 15\gamma + 15)}{\eta (\epsilon^2 - 6\epsilon - 12\gamma + 15\gamma^2 + 54\gamma + 27)} \]

(C2)

Eq. (C2) can be directly integrated

\[ \ln \eta + C = \int \frac{2(\epsilon^2 + 6\epsilon + 15\gamma + 15)}{\eta (\epsilon^2 - 6\epsilon - 12\gamma + 15\gamma^2 + 54\gamma + 27)} d\eta \]

(C3)

where \( C \) is an integration constant. Polynomial function as the denominator can be presented as

![Graph showing dependence of \( \eta \) on porosity \( \phi \).](image)

Fig. 4 Dependence of \( \eta \) on porosity \( \phi \) (calculated according to Eqs. (16) and (15)). Broken horizontal line corresponds to 0.5937

\[ -t^2 - 6t^2 - 12t^2 + 15t^2 + 54t + 27 = -\left( t^2 + 1 + 63209 \right) \]

\[ \times (t + 0.67371)(t - 1.69389) \]

\[ \times (-t^2 - 5.58797t - 12.9656) \]

Using the latter representation the integral in the right hand side of Eq (C3) can be directly calculated. The result is

\[ \ln \eta + C = \int \frac{2(t^2 + 6t^2 + 15\gamma + 15)}{\eta (t^2 - 6t^2 - 9t^2 + 18t^2 + 54t + 27)} dt \]

\[ = 0.0457026 \arctan(0.220129) \]

\[ - 0.10585 \ln(12.9656 + 5.58797t) \]

In the derivation of the latter two equations Mathematica symbolic manipulation is used. The latter equation and Eq. (C5) results in

\[ \ln \eta + C = 0.0457026 \arctan(0.220129) \]

\[ - 0.10585 \ln(12.9656 + 5.58797t) \]

(C4)

The integration constant \( C \) can be calculated using condition

\[ d_{\eta=1} = 0 \]

(C5)
which can be directly deduced from boundary conditions (16) Eq (C4) and boundary condition (C4), which gives $C = -1.368995$

Below the case when the concentration of the particles, $Y$, tends to 1 is investigated. It is clearly seen from Eq (C4) that $t$ ranges between 0 and value 1.89389. It happens because $t$ starts from 0 at $y = 1$ and cannot pass value $t_m = 1.89389$ (this value arises in the third term $-1.10385 \ln(1.89389 - 1)$). Eq (C8). Consequently, at $\eta$ tends to infinity $\sqrt{Z/\eta - t_m}$ Eq (15) after substitution $Z = t_m^2 \eta$ yields

$$\frac{d\eta}{d\gamma} = \frac{\eta}{(1 - \gamma)} \quad \text{(C6)}$$

where $\lambda = (2 + 6r_a + 15m_1 + 15)(1 + t_m) = 4.139$. Eq (C6) corresponds to the limiting case $\gamma = 1$. Solution of this equation is

$$\eta = C_m(1 - \gamma)^{-4.139} \quad \text{(C7)}$$

where $C_m$ is an integration constant. According to Eq (C7) exact solution should satisfy the following requirement

$$\eta^{1.19} = C_m \text{ at } \varphi = 0 \quad \text{(C8)}$$

Constant $C_m$ is calculated using direct integration of system (14)–(15) (see Fig. 4 for details). The result is $C_m = 0.5957$ and $\log_{10}0.5957 = -0.2249$.

The asymptotic dependence $\log_{10} \eta = -4.139 \log_{10} \varphi + -0.2249$ of the viscosity on porosity is presented in Fig. 3 (asymptote 3).

References

Viscosity of concentrated suspensions: influence of cluster formation

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Abstract

Dispersed particles can form clusters even at low concentrations. Colloidal and hydrodynamic forces are responsible for this phenomenon and these forces determine both structure and size of clusters. We assume that the viscosity of a concentrated suspension is completely determined by cluster size distribution, regardless if clusters form under the action of colloidal, hydrodynamic interactions or applied shear rates. Based on this assumption an equation, which describes dependency of viscosity on a concentration of dispersed particles taking into account cluster formation, is deduced. Under special restrictions the deduced dependency coincides with the well-known Dougherty–Krieger's equation except for a clear physical meaning of parameters entered. Our consideration shows that Dougherty–Krieger's equation has deeper physical background than it has been supposed earlier. Experimental verification of the suggested model shows a good agreement with the theory predictions and proves a presence of clusters even at low concentrations of dispersed particles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cluster size distribution; Viscosity; Concentrated suspensions

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1. Introduction

There is no need to describe the importance of concentrated suspensions for industrial applications as well as a number of theoretical approaches used for description of viscosity dependence on concentration of dispersed particles [1]. Colloidal and hydrodynamic interactions between particles result in a formation of doublets, triplets and higher clusters [1]. Aggregation of particles may be accompanied by destruction of aggregates caused by finite depth of potential well and/or shear stress applied. As a result a steady state distribution of cluster sizes is formed in the suspension. Presence of clusters influences drastically viscosity of concentrated suspensions. Computer simulation is a useful tool for exploring the relationship between interparticle interactions and rheological properties of suspensions. Clustering and restructuring of colloidal systems under shear is observed in a number of computer simulations [2–6]. However, computer simulations cannot substitute analytical modeling, and interactions between these two types of modeling can provide a new insight. Here we present a new analytical method, which allows deduction of the dependence of viscosity on particle concentration taking into account cluster formation. A differential method, a modified version of which is used in the present paper, has not been frequently used in this area. For this reason, the differential method is briefly reviewed below.

The differential method is adjusted for determination of effective properties of non-homogenous media. For the first time the differential method has been suggested in Bruggemann [7] and then it has been applied for determination of viscosity of concentrated suspensions without cluster formation [8,9]. Elastic properties of solid non-homogeneous materials have been investigated [10,11] with the help of the same method. Comparison of calculations of dielectric permeability of suspensions based on the differential method with both experimental measurements and other theories are presented in Duhkin and Shilov [12]. Comparison shows an excellent agreement of the differential method predictions and experimental measurements (Figs. 20 and 24 in [12]) other theory predictions (Table 8 in [12]) including statistic physics treatment [13].

Below a modified version of differential method is used for calculation of
viscosity dependence on concentration in the case when clusters form in a suspension.

2. Theory

Let us consider a suspension of volume $V$, which contains $N$ single particles. The volume fraction of particles, $\gamma$, is

$$\nu = \frac{vN}{V}$$

where $\nu = \frac{4\pi}{3}a^3$, and $a$ are the volume of a single particle and particle radius, respectively. Let $n_i, i = 1,2,3,...$ be a number of clusters of corresponding size in the volume $V$ and $\gamma_{l,\text{max}}, i = 1,2,3,...$ be an averaged packing density of single particles inside corresponding clusters. $n_i$ is a number density of 'clusters of size $i$', i.e. single particles, hence, $\gamma_{l,\text{max}} = 1$.

Volume fraction of clusters containing $i$ particles can be written as

$$\gamma_i = \frac{V_i}{V}, \quad V_i = \frac{i\nu n_i}{\gamma_{l,\text{max}}}, \quad i = 1,2,3,...$$

which satisfy the following mass conservation condition

$$\sum_{i=1}^{\infty} \gamma_i \gamma_{l,\text{max}} = \gamma$$

It is assumed below that the viscosity of the suspension is completely determined by cluster size distribution, i.e. can be described by the following dependency

$$\eta(\eta_0, \gamma) = \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, ...]$$

where $\eta_0$ is the viscosity of the pure liquid.

When all cluster concentrations, $\gamma_i$, are zero, the suspension consists only of the pure liquid and Eq. (4) gives

$$\eta_0 = \Psi(\eta_0, 0,0,0,...)$$

which is used below.

When particle density, $\gamma$, is small then all $\gamma_i$ are small too and Eq. (4) can be written in accordance with Einstein's relation as

$$\Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, ...] = \Psi[\eta_0, 0,0,0,...] + 2.5 \sum_{i=1}^{\infty} \eta_0 A_i \gamma_i$$

where coefficients $A_i, i = 1,2,3,...$ are deviations of friction coefficient of clusters with $i$ particles from the corresponding value for solid particles. Obviously $A_1 = 1$. 

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Loughborough University
Coefficients $A_i$, $i = 1, 2, 3, \ldots$ are referred to below as friction coefficients for abbreviation. The meaning of friction coefficients can be understood using the following example. Let two spherical particles with the same diameter be considered: the first one is a solid particle, the second one is a particle composed of $i$ smaller particles (a model of a cluster). A friction force exerted to each of two particles under consideration will be different if both particles are placed in a liquid flow. Let $A_i$ be a ratio of the friction force in the case of the composed particle (cluster) to the corresponding force exerted to the solid particle. The friction force is changed in the case of the composed particle because of two reasons: (a) a solid surface exposed to the liquid flow is smaller than in the case of the solid particle, (b) the liquid flow partially penetrates inside the composed particle. Two mentioned trends, (a) and (b), change $A_i$, $i = 2, 3, \ldots$ values in different ways: because of the reason (a) these values decrease and increase because of the reason (b). That is, a complex interplay determines $A_i$, $i = 2, 3, \ldots$ values. Friction coefficients can be calculated based on the theory developed in Perepelkin et al. [14].

Deviation of cluster shapes from spherical is an additional cause of change of friction coefficient values [15].

It is obvious that parameters $\gamma_{i, \text{max}}$, $A_i$, $i = 2, 3, \ldots$ are functions of both colloidal, hydrodynamic interactions and applied shear rates. These dependencies are left undetermined in the present consideration.

Let a small amount of clusters, $\Delta n_i \ll n_i$, $i = 1, 2, 3, \ldots$ be marked randomly in the whole volume of suspension. The suspension can be considered as a mixture of the marked clusters surrounded by a suspension of non-marked clusters. Volume concentrations of the marked clusters, $\Delta \mu_i$, $i = 1, 2, \ldots$, are

$$
\Delta \mu_i = \frac{\Delta V_i}{V}, \quad \Delta V_i = \frac{1}{\gamma_{\text{max}}} \Delta n_i, \quad i = 1, 2, 3, \ldots
$$

Concentrations of non-marked clusters in the rest of the suspension are

$$
\gamma_i - \Delta \xi_i = \frac{V_i - \Delta V_i}{V - \sum_{j=1}^\infty \Delta V_j}, \quad i = 1, 2, 3, \ldots
$$

or keeping only first order terms:

$$
\Delta \xi_i = \frac{V_i}{V} - \frac{V_i - \Delta V_i}{V - \sum_{j=1}^\infty \Delta V_j} = \frac{\Delta \mu_i - \gamma_i \sum_{j=1}^\infty \Delta \mu_j}{1 - \sum_{j=1}^\infty \Delta \mu_j} \approx \Delta \mu_i - \gamma_i \sum_{j=1}^\infty \Delta \mu_j, \quad i = 1, 2, 3, \ldots
$$

Marked clusters are surrounded by the rest of the suspension, which is assumed to be a homogenous liquid with viscosity $\Psi[\gamma_i, \gamma_{i+1}, \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots]$. 

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where small volume fractions $\Delta \xi_i, i = 1, 2, 3, \ldots$ in the latter expression are given by Eq. (8). Hence, viscosity of suspension can be expressed in two ways: according to Eq. (4) and considering the suspension as a mixture of marked and non-marked clusters:

$$\eta = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots, \Delta \mu_1, \Delta \mu_2, \Delta \mu_3, \ldots]$$  (9)

The right hand sides of Eqs. (4) and (9) should be equal, this gives

$$\Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] = \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots, \Delta \mu_1, \Delta \mu_2, \Delta \mu_3, \ldots]$$  (10)

A transformation of Eq. (10) is given in Appendix A. As a result the following differential equation is deduced, which describes dependence of viscosity of concentrated suspension, $\eta$, on volume concentration of particles, $\gamma$

$$\frac{d\eta}{d\gamma} = 2.5\eta \sum_{i=1}^{\infty} A_i \gamma_i \frac{d\gamma_i}{d\gamma}$$  (11)

Solution of Eq. (11) should satisfy boundary condition, which follows from Eq. (5)

$$\eta(0) = \eta_0$$  (12)

Let us introduce the following averaged values

$$\bar{A} = \frac{\sum_{i=1}^{\infty} A_i \gamma_i}{\sum_{i=1}^{\infty} \gamma_i}, \quad \bar{\gamma}_{max} = \frac{\sum_{i=1}^{\infty} \gamma_{i,\text{max}} \gamma_i}{\sum_{i=1}^{\infty} \gamma_i}$$  (13)

which are an averaged resistance coefficient and an averaged packing density of all clusters. Using Eq. (3) and definition of $\bar{\gamma}_{max}$ [according to Eq. (13)] we can conclude $\bar{\gamma}_{max} = \frac{\gamma}{\sum_{i=1}^{\infty} \gamma_i}$, or $\sum_{i=1}^{\infty} \gamma_i = \frac{\gamma}{\bar{\gamma}_{max}}$. Substitution of the latter expression and Eq. (13) into Eq. (11) results in

$$\frac{d\eta}{d\gamma} = 2.5\eta \left[ \frac{d\left( \bar{A} \frac{\gamma}{\bar{\gamma}_{max}} \right)}{d\gamma} + \frac{\bar{A} \frac{\gamma}{\bar{\gamma}_{max}}}{1 - \frac{\gamma}{\bar{\gamma}_{max}}} \frac{d\left( \frac{\gamma}{\bar{\gamma}_{max}} \right)}{d\gamma} \right]$$
Let us assume that $\overline{A}$ is independent of volume concentration $\gamma$ but still $\overline{A}$ can depend on applied shear rate. In this case the latter equation takes the following form

$$\frac{d\eta}{d\gamma} = 2.5\eta \left[ \frac{d\overline{A}}{d\gamma} \frac{\gamma}{\overline{\gamma}_{\text{max}}} + \overline{A} \frac{d\left( \frac{\gamma}{\overline{\gamma}_{\text{max}}} \right)}{d\gamma} \right]$$

(14)

with boundary condition [Eq. (12)].

It is important to emphasize that $\overline{\gamma}_{\text{max}}$ is not supposed to retain a constant value, independent of volume concentration $\gamma$.

Solution of Eq. (15) with boundary condition [Eq. (12)] is

$$\eta(\gamma) = \frac{1}{\eta_0} \left( 1 - \frac{\gamma}{\overline{\gamma}_{\text{max}}} \right)^2$$

(16)

Eq. (16) almost coincides with Dougherty-Krieger's equation [16,17]

$$\eta(\gamma) = \frac{1}{\eta_0} \left( 1 - \frac{\gamma}{\gamma_{\text{max}}} \right)^{(\eta_0\gamma_{\text{max}})}$$

(17)

where $[\eta]$ is an intrinsic viscosity. However, it is important to emphasize that: (1) $\gamma_{\text{max}}$ in Dougherty-Krieger's equation [Eq. (16)] is constant, whereas $\overline{\gamma}_{\text{max}}$ cannot be; (2) both parameters $\overline{A}$, $\gamma_{\text{max}}$ are a function of the applied shear rate.

It is easy to conclude that Eqs. (16) and (17) coincide if we adopt

$$\gamma_{\text{max}} = \overline{\gamma}_{\text{max}}, [\eta] = \frac{2.5\overline{A}}{\overline{\gamma}_{\text{max}}}$$

It is necessary to stress here that in spite of a striking similarity of Eqs. (16) and (17) a physical meaning of parameters included in Eq. (16) is quite different from those used in Eq. (17). According to the theory developed above viscosity dependence on concentration is connected with cluster formation and this physical phenomenon is incorporated in Eq. (16).
If particles do not form clusters, that is, \( \gamma_i = \gamma \); \( \gamma_i = 0, i = 2,3,4, \ldots \) and, hence, \( \bar{\gamma}_{\text{max}} = \bar{\alpha} = 1 \) should be adopted in Eq. (16), which gives

\[
\frac{\eta(\gamma)}{\eta_0} = \frac{1}{(1-\gamma)^{2.5}}
\]

(18)

The latter equation coincides with earlier obtained solution for the same case [8,9] when particles do not form clusters.

3. Comparison with selected experimental data

A comprehensive review of experimental data on viscosity of concentrated suspensions is presented in [18]. In Fig. 1 a comparison of experimental data with predictions according to Eq. (18) (curve 1), and Eq. (16) (curves 2–4) is presented. Experimental points used in Fig. 1 are specified in Thomas [18]. Fig. 1 shows that the whole array of experimental data can be described using Eq. (16) at different but reasonable parameters \( \bar{\gamma}_{\text{max}} \) and \( \bar{\alpha} \): curve 4 (\( \bar{\gamma}_{\text{max}} = 0.56 \), close to a simple cubic packing density; \( \bar{\alpha} = 0.72 \)); curve 3 (\( \bar{\gamma}_{\text{max}} = 0.65 \), close to a cubic centered packing density; \( \bar{\alpha} = 0.67 \)); curve 2 (\( \bar{\gamma}_{\text{max}} = 0.73 \), close to hexagonal packing density; \( \bar{\alpha} = 0.61 \)).

4. Experimental method

This section presents results of rheological experiments and comparison with theoretical predictions. Yeast suspensions at different cell concentrations are used.

4.1. Suspension

The suspension under investigation was made of active dry baker’s yeast *Saccharomyces cerevisiae* (Lesaffre, France) suspended in physiological solution (8 g/l NaCl). Yeast particles were of 5 μm average diameter. The particle density was 1.13 g/cm³. The volume fraction of the suspension is used below.

4.2. Volume fraction determination

Since yeast cells allow water transfer through the cell membrane, the determination of the volume fraction is not straightforward. The conversion of a dry weight into the volume fraction has been a source of errors in literature on the concentration dependence of yeast viscosity [19]. A particular attention is given here to the determination of the volume fraction, \( \gamma \), of yeast suspensions. Reuss et al. [19] proposed a dye dilution technique to determine a volume fraction as a function of
a dry weight at several osmotic pressures: a fixed quantity of a dye (Naphtol green B) solution is mixed with the yeast suspension. External water is then determined by measuring the dilution effect.

In this study, the determination of the volume fraction is carried out according to the following procedure: two to three drops of concentrated Naphtol green B
solution are added to the thoroughly mixed yeast suspension in a 200-ml \( V_0 \) centrifuge tube, which is centrifuged at 5000 rev./min for 30 min. The volume of the sediment \( V_s \) and the extinction value (710 nm) \( E1 \) of the supernatant are then determined. The sediment is re-suspended in the supernatant of the original suspension in order to ensure constant osmotic pressures. After mixing and centrifuging, volumetric determination of the sediment and measurement of the extinction \( E2 \) are repeated. This procedure gives the following value of the volume fraction

\[
\gamma = \frac{\left( \frac{E1}{E2} \right) V_s - V_0}{\left[ \left( \frac{E1}{E2} \right) - 1 \right] V_0}
\]  

(19)

The results obtained are compared with two other techniques of determination of volume fraction: thermogravimetric (Mettler-Toledo) and conductimetric analysis (Coulter). There is a good agreement with data obtained by the three different methods confirming the validity of the experimental results.

The volume fraction \( \gamma \) is obtained as a linear function of yeast concentration \( C \) (\% dry w/w) expressed as follows:

\[
\gamma = A \times C
\]  

(20)

The values of \( A \) determined by the three different methods are presented in Table 1.

### 4.3. Rheological measurements and observation of cluster formation

Rheological measurements utilized a controlled strain rate rheometer (Rheomat 115 - Contraves) with concentric cylinder geometry. Temperature of the suspension in the rheometer was maintained and controlled at 20℃ in all measurements.

Determination of physical parameters describing the rheological properties of the suspension requires steady state conditions. Experiment shows that at volume

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental values of ( A ) using different experimental methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental methods</td>
<td>( A ) (% dry w/w)(^{-1})</td>
</tr>
<tr>
<td>Dye dilution</td>
<td>2.1</td>
</tr>
<tr>
<td>Conductimetric</td>
<td>1.8</td>
</tr>
<tr>
<td>Thermogravimetric</td>
<td>2.0</td>
</tr>
<tr>
<td>Average:</td>
<td>2.0 ± 0.2</td>
</tr>
</tbody>
</table>
fractions higher than 0.3 the rheological behavior becomes non-Newtonian because viscosity value depends on the shear rate.

Linear increasing–decreasing shear rates sequences 10−1000 s−1 are performed during 2000 s including a step at 1000 s−1 for 200 s to reach a steady state.

For a direct determination of cluster formation a drop of yeast suspension is placed on the support of the sample and is observed by optical microscope (Zeiss). The number of single particles (N1), clusters (N2), triplets (N3), four and more particle clusters (N4 & +) are calculated.

5. Results and discussion

Yeast suspension is selected for comparison because of the following reasons:

1. yeast suspension clearly shows cluster formation;
2. the mechanism of clustering is mostly unknown but in spite of this viscosity measurements are in agreement with deduced dependency. We would like to emphasize once again that any mechanism of cluster formation results in the deduced dependence of suspension viscosity on concentration.

The number of single particles (N1), clusters (N2), triplets (N3), four and more particle clusters (N4 & +) at γ = 0.002 volume concentration are presented in Table 2.

Yeast suspensions at different low concentration were observed under a microscope. Results are presented in Fig. 2a–c. All concentrations used are low enough (γ = 0.002, Fig. 2a) and (γ = 0.02 and γ = 0.04 Fig. 2b,c, respectively). These pictures clearly show that clustering increases with concentration and at 4% volume fraction particles are mostly aggregated and form clusters of different sizes. It is usually assumed at theoretical considerations that suspensions are monodisperse at such low concentrations, which is in an obvious contradiction with our observations.

Fig. 3 presents comparison of the measured relative viscosity vs. volume fraction of yeast suspension (points) and theoretical Eq. (16) (solid line, fitted parameters are \( \gamma_{max} = 0.73 \) and \( A = 1 \)). Base fluid is physiological suspension (8 g/l NaCl).

It is worth noting that according to our derivation parameters \( \gamma_{max} \) and \( A \) are complex functions of: (a) interparticle interaction potential; and (b) hydrodynamic interactions between clusters. Both interactions are unknown in the case of yeast.

<p>| Number of single particles and clusters at γ = 0.002 volume concentration |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>N1</th>
<th>N2</th>
<th>N3</th>
<th>N4 &amp; +</th>
<th>N1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Result</td>
<td>100</td>
<td>6</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
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Fig. 2. Photographs of yeast suspensions at different concentrations. (a) \( \gamma = 0.002 \), (b) \( \gamma = 0.02 \), (c) \( \gamma = 0.04 \).
suspensions. In spite of this reasonable agreement with experimental data is achieved using a fitting procedure with these two parameters.

6. Conclusions

A new method is suggested for derivation of viscosity dependence on the concentration of dispersed particles, taking into account cluster formation. We assume that the viscosity of a concentrated suspension is completely determined by cluster size distribution, regardless if clusters form under the action of colloidal, hydrodynamic interactions or applied shear rates. Based on this assumption, an equation which describes dependency of viscosity on a concentration of dispersed particles taking into account cluster formation, is deduced. Under special restrictions the deduced dependency coincides with the well-known Dougherty-Krieger's equation except for a clear physical meaning of entering parameters. Our consideration shows that Dougherty-Krieger's equation has deeper physical background than it has been supposed earlier. Observations of yeast suspensions prove a presence of clusters even at low concentrations of dispersed particles. Viscosity dependency of yeast suspension on concentration is in good agreement with the deduced theoretical equation and gives reasonable value of parameters.

Acknowledgements

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Appendix A

Below mathematical transformations of Eq. (10) are presented which do not include any additional assumptions.

Everywhere below only first order terms are taken into consideration. Using Eq. (6) the right hand side of Eq. (10) can be re-written as

\[
\Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \Delta \mu_1, \Delta \mu_2, \Delta \mu_3, \ldots
\]

\[
= \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots], 0, 0, 0, \ldots \Delta \mu_i
\]

\[
+ 2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots], 0, 0, 0, \ldots \Delta \mu_i
\]

\[
= \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots]
\]

\[
+ 2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots] \Delta \mu_i
\]

(A1)

Further transformation of right hand side of Eq. (A1) keeping only first order terms gives

\[
\Psi[\eta_0, \gamma_1 - \Delta \xi_1, \gamma_2 - \Delta \xi_2, \gamma_3 - \Delta \xi_3, \ldots]
\]

\[
= \Psi(\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots) - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \Delta \xi_i
\]

(A2)

Using Eqs. (A1) and (A2), Eq. (10) becomes

\[
2.5 \sum_{i=1}^{\infty} A_i \Psi[\eta_0, \gamma_1, \gamma_2, \gamma_3, \ldots] \Delta \mu_i - \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \Delta \xi_i = 0
\]

Substitution of expressions for \(\Delta \xi_i\) from Eq. (8) into the latter equation and collecting all terms proportional to \(\Delta \mu_i\) gives

\[
\sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j - \frac{\partial \Psi}{\partial \gamma_i} + 2.5 A_i \Psi = 0, \quad i = 1, 2, 3, \ldots
\]

(A3)
Let Eq. (A3) be multiplied by \( \gamma_j \) and summarized over \( j = 1,2,3\ldots \) this gives

\[
\sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j = \frac{2.5 \sum_{j=1}^{\infty} \eta A_j \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j}
\]

Substitution of the latter expression for \( \sum_{j=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_j} \gamma_j \) into Eq. (A3) gives

\[
\frac{\partial \Psi}{\partial \gamma_i} = 2.5 \eta A_i + \frac{2.5 \sum_{j=1}^{\infty} \eta A_j \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j}
\]

(A4)

It is obvious that

\[
\frac{d\eta}{d\gamma} = \sum_{i=1}^{\infty} \frac{\partial \Psi}{\partial \gamma_i} \frac{d\gamma_i}{d\gamma}
\]

where \( \gamma \) is the volume fraction of particles. After multiplying Eq. (A4) by \( \frac{d\gamma_i}{d\gamma} \) and summation over \( i = 1,2,3\ldots \) Eq. (A4) becomes

\[
\frac{d\eta}{d\gamma} = 2.5 \eta \sum_{i=1}^{\infty} \left[ A_i + \frac{\sum_{j=1}^{\infty} A_j \gamma_j}{1 - \sum_{j=1}^{\infty} \gamma_j} \right] \frac{d\gamma_i}{d\gamma}
\]

(A5)

References

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ISPMS
Effective elastic properties of a rubber/polymer sheet with cracks

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In this paper equations for calculation of dependence of the effective elastic coefficients on the concentration of cracks are deduced based on modified Bruggerman’s approach. It is shown that the values of modulus $E_{\text{eff}}$ and $v_{\text{eff}}$ calculated using these equations are in good agreement with experimental data.

1. Introduction

The Bruggeman’s method has been successfully applied for calculation of effective dielectric constants of suspensions and emulsions [1]. In [2] the modified version of the Bruggeman’s method has been suggested and applied for calculation of effective viscosity of suspensions. The same method has been used for calculation of viscosity and permeability of porous media in [3]. Expressions of the Young’s modulus and Poisson’s ratio in the case of a single crack in a rubber sheet have been deduced in [4]. Experimental measurements of the dependence of the effective Young’s modulus and Poisson’s ratio on the concentration of cracks have been undertaken in [5, 6] as well as comparison of experimental dependencies with theoretical calculations of authors based on the Bruggeman’s method. However, the final equations are given in [5, 6] as a matter of fact without derivation. The latter does not allow making further generalization and estimating a correctness of the results obtained. In this paper equations for calculation of dependence of the effective elastic coefficients on the concentration of cracks are deduced based on modified Bruggeman’s approach [2, 3]. A polymer sheet with cracks is a model of a flat porous membrane, the latter determines importance of the problem under consideration. Everywhere below only a rubber sheet is mentioned for the sake of briefness.

2. Calculation of effective elastic properties

In this section the effective elastic properties of a flat sheet of rubber with cracks is considered (see Fig. 1). Let $M \gg 1$ is the number of cracks per area $S$. All cracks are randomly oriented and $l_i$ is the length of the crack, $i = 1, 2, \ldots, M$. Cracks are assumed not to intersect each other. The latter is always satisfied in the case of porous polymer membranes.

Density of cracks, $\lambda$, is introduced in the following way:

$$\lambda = \frac{1}{\sum_{i=1}^{M} \frac{l_i^2}{S}} \quad (1)$$

According to the above definition $\lambda$ is always positive and ranges between zero and infinity. Higher value of $\lambda$ corresponds to higher concentration of cracks per unit area.

Let $E_0$ and $v_0$ are the Young’s modulus and the Poisson’s ratio of rubber without cracks. It is assumed below that dependencies of the Young’s modulus $E_{\text{eff}}$ and the Poisson’s ratio $v_{\text{eff}}$ of the rubber sheet with cracks are given by the following dependencies on the density of cracks, $\lambda$:

$$E_{\text{eff}} = E(E_0, v_0, \lambda) \quad (2)$$

and

$$v_{\text{eff}} = v(E_0, v_0, \lambda) \quad (3)$$
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In the case $\lambda = 0$ (no cracks) Eqs. (2) and (3) reduce to

$$E_0 = E(E_0, \nu_0, 0)$$  \hspace{1cm} (4)

and

$$\nu_0 = \nu(E_0, \nu_0, 0)$$  \hspace{1cm} (5)

If density of cracks is small, $\delta \lambda \ll 1$, then Eqs. (2) and (3) can be rewritten as:

$$E^{\text{eff}} = E_0 + A^2(E_0, \nu_0)\delta \lambda$$  \hspace{1cm} (6)

and

$$\nu^{\text{eff}} = \nu_0 + A'(E_0, \nu_0)\delta \lambda,$$  \hspace{1cm} (7)

where $A^2$, $A'$ are two new unknown functions which are determined below.

Let $\delta M$ cracks in the rubber sheet are marked and the rest of cracks are non-marked, $\delta M \ll M$. The density of marked cracks, $\delta \rho$, is

$$\delta \rho = \frac{\delta M^2}{M S}.$$  \hspace{1cm} (8)

The density of non-marked cracks is

$$\lambda = \delta \lambda = \frac{M - \delta M^2}{M S}.$$  \hspace{1cm} (9)

Equations (1), (8), (9) result in

$$\delta \rho = \delta \lambda.$$  \hspace{1cm} (10)

Sheet of rubber with cracks can be considered as a mixture of the marked cracks surrounded by sheet of rubber.
with non-marked cracks. So effective coefficients $E^\text{eff}$ and $v^\text{eff}$ can be expressed in two different ways (i) according to Eqs. (2), (3) and (ii) using “marked cracks” (with density $\delta\lambda$) surrounded by the medium with “non-marked” cracks (with the density $\lambda - \delta\lambda$). The latter is a medium with unknown Young’s modulus and Poisson’s ratio $E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda)$.

Two mentioned definitions should give equal values of the elastic coefficients. The latter results in the following system of equations for their definition:

$$E(E_0, v_0, \lambda - \delta\lambda) =$$

$$= E(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda), \delta\lambda)$$

and

$$v(E_0, v_0, \lambda) =$$

$$= v(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda), \delta\lambda).$$

Equations (11) and (12) are expanded below into Taylor’s series using the small parameter $\delta\lambda$ and $\delta\delta$ and keeping only first order terms. Transformations of Eq. (12) are presented below because Eq. (11) can be transform completely into the same way:

$$v(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda), \delta\lambda)$$

and

$$v(E_0, v_0, \lambda) =$$

$$= v(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda), \delta\lambda).$$

Equation (13) can be simplified using Eqs (3), (5)

$$v(E(E_0, v_0, \lambda), v(E_0, v_0, \lambda), 0) =$$

$$= v(E_0, v_0, \lambda) = v^\text{eff}.$$ (14)

Combination of Eqs. (3), (7) results in

$$\frac{\partial v}{\partial \delta\lambda}(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda - \delta\lambda), \delta\lambda)$$

and

$$\frac{\partial v}{\partial \delta\delta}(E(E_0, v_0, \lambda), v(E_0, v_0, \lambda)) =$$

$$= a^\text{eff}(E_0, v_0, \lambda, v(E_0, v_0, \lambda)) = a^\text{eff}(E^\text{eff}, v^\text{eff}).$$ (15)

Equation (3) gives

$$\frac{\partial v}{\partial \delta\lambda}(E(E_0, v_0, \lambda), v(E_0, v_0, \lambda))$$

and

$$\frac{\partial v}{\partial \delta\delta}(E(E_0, v_0, \lambda - \delta\lambda), v(E_0, v_0, \lambda))$$

Equation (13) can be simplified using Eqs. (12), (14)–(16) as

$$0 = A(E^\text{eff}, v^\text{eff})\delta\lambda - \frac{dv^\text{eff}}{d\lambda} - \delta\lambda.$$ (17)

Equations (17), (10) yield

$$\frac{dv^\text{eff}}{d\lambda} = A(E^\text{eff}, v^\text{eff}).$$ (18)

Using similar transformations, Eq. (11) is transformed into

$$\frac{dE^\text{eff}}{d\lambda} = A^\text{eff} (E^\text{eff}, v^\text{eff}).$$ (19)

Equations (4), (5) give the following boundary conditions

$$v^\text{eff}|_{\lambda = 0} = v_0$$ (20)

and

$$E^\text{eff}|_{\lambda = 0} = E_0$$ (21)

In [4] the following expressions of both the Young’s modulus and the Poisson’s ratio have been deduced at low cracks density, $\delta\lambda \ll 1$

$$E^\text{eff} = E_0 \left(1 - \frac{1}{4} \pi \delta\lambda\right),$$

$$v^\text{eff} = v_0 \left(1 - \frac{1}{4} \pi \delta\lambda\right).$$

Comparison of the latter two equations with Eqs (6) and (7) gives

$$A^\text{eff}(E_0, v_0) = -\frac{\pi}{4} E_0$$

and

$$A^\text{eff}(E_0, v_0) = -\frac{\pi}{4} v_0.$$ (22)

Using the latter two equations, the system of differential equations (18), (19) can be rewritten as

$$\frac{dE^\text{eff}}{d\lambda} = -\frac{E^\text{eff}}{4},$$

$$\frac{dv^\text{eff}}{d\lambda} = -\frac{v^\text{eff}}{4}.\text{ (23)}$$

System (22) with boundary conditions (20), (21) has the following solution

$$E^\text{eff} = E_0 e^{-\frac{1}{4} \pi \lambda},$$

$$v^\text{eff} = v_0 e^{-\frac{1}{4} \pi \lambda}.\text{ (24)}$$

3. Comparison with available experimental data

In Fig. 1 an example of a rubber sheet with cracks is shown, which has been used for experimental investiga-
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Fig. 2 Dependence of the Young's modulus on the concentration of cracks, λ. Solid line according to Eq (25). Experimental data from [5, 6]

Fig. 3 Dependence of the Poynting's ratio on the concentration of cracks, λ. Solid line according to Eq (26). Experimental data from [5, 6]

...ions in [5, 6]. Dependencies of Eeff and νeff on density of cracks are calculated according to Eqs (23), (24) and compared with experimental data from [5, 6] Figures 2 and 3 show results of comparison, which are sufficiently good.

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МИНИСТЕРСТВО ОБЩЕГО И ПРОФЕССИОНАЛЬНОГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ
МОСКОВСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ ПИЩЕВЫХ ПРОИЗВОДСТВ

ИНДУСТРИЯ ПРОДУКТОВ ЗДОРОВОГО ПИТАНИЯ - ТРЕТЬЕ ТЫСЯЧЕЛЕТИЕ
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VISCOSITY OF CONCENTRATED SUSPENSIONS TAKING INTO ACCOUNT CLUSTERS FORMATION BY DISPERSE PARTICLES

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It is well known that particles in suspensions at low shear stresses form clusters under the action of colloidal and hydrodynamic forces. An attempt to describe a dependence of an effective viscosity on concentration in concentrated suspensions under those conditions is undertaken in this paper. Dispersed particles are supposed to form clusters of different sizes but with the same packing density of dispersed particles $\gamma_{\text{max}}$ inside each of cluster. Obviously clusters in suspensions have a different packing density that is $\gamma_{\text{max}}$ is an average characteristic of a suspension under consideration, and $\gamma_{\text{max}}$ depends on an intensity of colloidal forces between dispersed particles. Clusters concentration in suspension equals to $\gamma^e = \gamma / \gamma_{\text{max}}$.

Differential method is used to solve the problem. The method can be explained in the following way. Let us consider a suspension with a concentration of a dispersed phase $\gamma$, and dispersed particles have formed clusters. This suspension is referred to as SUSPENSION 1. Let us introduce a new homogeneous liquid (LIQUID 2) with the same volume and viscosity as SUSPENSION 1. Let a small volume of clusters be added both in SUSPENSION 1 and LIQUID 2. As a result new SUSPENSION 3 and SUSPENSION 4 respectively are prepared. A concentration of clusters in SUSPENSION 4 is small, hence, a modified linear Einstein relation can be used to calculate a new viscosity in SUSPENSION 4.

$$\eta(\gamma^e + \Delta \gamma^e) = \eta(\gamma^e) (1 + 2.5P \gamma^e),$$

here an empirical parameter $P$ takes into account deviation of a hydrodynamic drag force exerted to a cluster as compared with a rigid particle. It is easy to see that parameter $P$ must be less than 1. The main assumption of differential method is viscosities of SUSPENSION 3 and SUSPENSION 4 are equal. Using that assumption a differential equation for determination of viscosity on concentration can be derived. Solution of that equation is

$$\eta(\gamma) = (1 - \gamma / \gamma_{\text{max}})^{-2.5P}.$$  \hspace{1cm} (1)

The latter equation is close (but not coincides) to Dougherty-Krieger equation, but in contrast with their equation all parameters in our equation (1) have a clear physical meaning. We compared predictions according to equation (1) with know experimental data on dependence of viscosity of concentrated suspensions on concentration. The comparison shows (i) parameter $P$, as expected, is less than 1 and equals approximately to 0.65; (ii) a number of experimental dependences (about 20) is described by equation (1) when a packing density in clusters $\gamma_{\text{max}}$ changes from the most dense (hexagonal) to a simple cubic.
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ABSTRACTS
VISCOSITY OF CONCENTRATED SUSPENSIONS: INFLUENCE OF CLUSTER SIZE DISTRIBUTION

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Particles in colloidal suspensions form clusters under the action of colloidal and hydrodynamic interactions. All essential properties of suspensions depend on cluster size distribution and packing density of individual particles inside clusters. We do not specify nature of forces, which result in cluster formation, that is, $\gamma_k(\gamma, \tau)$, $k = 1, 2, \ldots$, volume fractions of cluster containing $k$ particles are considered as given functions, where $\gamma$ is the volume fraction of individual particles and $\tau$ is the applied shear rate. It is assumed that the viscosity of the suspension can be described by the following dependency $\eta = \eta(\eta_0, \gamma_1, \gamma_2, \ldots, \gamma_k, \ldots)$ where $\eta_0$ is the viscosity of the pure liquid. Let us randomly select a small amount of clusters of size $k$, $\Delta \gamma_k$, $k = 1, 2, \ldots$, and mark these clusters. The rest of the suspension with non-marked clusters is considered as a homogeneous liquid with a small amount of hydrodynamically non-interacting marked clusters. This approach results in the following differential equation for the viscosity on the particle concentration determination:

$$\frac{d \eta}{d \gamma} = \frac{5}{2} \left[ (\gamma / \bar{\gamma}) \frac{d \bar{\eta}^*}{d \gamma} - \frac{\bar{\eta}^*}{1 - \gamma / \bar{\gamma}} \frac{d (\gamma / \bar{\gamma})}{d \gamma} \right],$$

where $\bar{\gamma} = \sum_{j=1}^{\infty} \gamma_j/r_{2m}/\sum_{j=1}^{\infty} \gamma_j$, and $\bar{\eta}^*$ = $\sum_{j=1}^{\infty} \eta_j/r_{2m}/\sum_{j=1}^{\infty} \gamma_j$ are averaged coefficients; $\lambda_i$, $\gamma_{1m}$, $i = 1, 2, \ldots$ are resistant coefficients, which describe a deviation of a hydrodynamic resistance from the Stokes law and packing density inside clusters of size $i$, respectively. Let us assume that both averaged coefficients, $\bar{\eta}^*$, $\bar{\gamma}$, $r_{2m}$, are independent of particle volume fraction, that is, both of them are functions of applied shear rate $\tau$ only. In this case the above equation results in the following dependency of viscosity on particle concentration:

$$\eta/\eta_0 = (1 - \gamma / \bar{\gamma})^{2\gamma^2},$$

which coincides with the well known Dougherty-Krieger's equation except for a different meaning of parameters entered. Comparison of the latter equation with experimental data shows that the latter equation is capable of describing them reasonably well.
Determination of Effective Properties of the Brinkman’s Medium Formed by Solid Spherical Particles

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Abstract—The problem of effective properties of Brinkman’s medium formed by spherical particles taken in an arbitrary concentration is solved within the framework of a differential model.

In many cases, the slow flow of incompressible liquid in a porous medium is described by Brinkman’s equation

\[ \text{grad } p = -Ku + \mu_1 \Delta u, \quad (1) \]

where \( p \) is the pressure, \( u \) is the flow velocity vector, and \( \mu_1 \) and \( K \) are the viscosity and the resistance coefficient of the porous medium. Equation (1) can be used for describing the flow of a viscous liquid containing fixed spherical particles. The problem of the effective viscosity of Brinkman’s dispersion can be solved based on this equation.

Assume that new fixed spherical particles of the radius \( R \) are placed into the initial Brinkman’s medium; then, at a small volume concentration of these particles, according to [1, 2],

\[ \text{grad } p = -6\pi \mu_1 n Ru + \mu_1 \Delta u - Ku, \quad (2) \]

where \( n \) is the number of additional spheres per unit volume, and \( \mu_1^* \) and \( K^* \) are the new viscosity and the new resistance coefficient of the porous medium. Combination of equations (1) and (2) yields

\[ K^* = K + 6\pi \mu n R. \quad (3) \]

Let us calculate \( \mu_1^* \) and \( K^* \) at an arbitrary concentration of additional particles.

The viscous stress tensor for Brinkman’s liquid has the form

\[ \sigma_{ij} = -p \delta_{ij} + \mu_1 \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (4) \]

where \( x \) is the Cartesian coordinate of the point. The flow equation can be written in the form

\[ \text{div } \sigma + X = 0. \quad (5) \]

Taking into account the liquid incompressibility condition

\[ \text{div } u = 0, \quad (6) \]

the mass force can be represented as

\[ X = -Ku. \quad (7) \]

Let us consider the impermeable-to-liquid solid sphere of the radius \( R \) placed into Brinkman’s medium. Far from the particle, the flow around the sphere has the velocity [2]

\[ \frac{U_1}{U_0} = \frac{0.5x}{r^*}, \quad \frac{U_2}{U_0} = \frac{0.5y}{r^*}, \quad \frac{U_3}{U_0} = \frac{z}{r^*}. \quad (8) \]

where \( U_0 \) is the velocity scale factor, and \( r^* = \sqrt{\mu_1/K} \) is the Brinkman radius.

Let us introduce the current function \( \chi \) in the spherical coordinates using the formulas

\[ u_r = \frac{1}{r^2 \sin \theta} \frac{\partial \chi}{\partial \theta}, \quad u_\theta = \frac{1}{r \sin \theta} \frac{\partial \chi}{\partial r}, \]

where \( r \) and \( \theta \) are the radial and angular coordinates, respectively. Then, Brinkman’s equation (2) takes the form

\[ E^2 \left( E^2 - \frac{K}{\mu_1} \right) \chi = 0. \quad (9) \]

where

\[ E^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} - \frac{\cos \theta}{r^2} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \theta} \]

The solution of equation (9) satisfying the boundary conditions
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Substituting the velocity expressed by (10) into formula (1) and solving the obtained relation with respect to \( p \), we find that

\[
p = \left\{ \frac{1}{2} \alpha_\text{j} n_j n_j + \frac{1}{3} \frac{L n_j n_k n_l}{r^3} \right\}_{r^*} \mu_1.
\]

(13)

Taking into account the expression for the velocity (10), the expression for the viscous stress tensor (4) can be transformed to the form

\[
\sigma_{ij} = \left\{ \frac{1}{2} \alpha_\text{ij} n_j n_j \delta_{ij} - \frac{L n_j n_k n_l}{3 r^3} \delta_{ij} + 2 \alpha_\text{ij} \right. \\
+ \left. \frac{L}{3} \left( \frac{20 \alpha_\text{ij} n_j n_k n_l}{r^3} - \frac{20 \alpha_\text{ij} n_k n_l}{r^3} - \frac{10 \alpha_\text{ij} n_k n_l}{r^3} \right) \delta_{ij} \right\}_{r^*} \mu_1
\]

(14)

where the omitted terms are proportional to \( e^{-r} \).

Now, following [3], let us calculate the first correction to the stress tensor at a close-to-zero concentration of particles comprising the porous medium. Integrating the viscous stress tensor over the large volume \( V \) yields the identity

\[
\langle \sigma_\text{ij} \rangle = - \langle p \rangle \delta_{ij} + \mu_1 \left( \frac{\partial u_\text{j}}{\partial x_j} + \frac{\partial u_\text{i}}{\partial x_i} \right) \\
+ \frac{1}{V} \int_v \sigma_{ij} + p \delta_{ij} - \mu_1 \left( \frac{\partial u_\text{i}}{\partial x_j} + \frac{\partial u_\text{j}}{\partial x_i} \right) \, dV,
\]

(15)

where \( x \) are the Cartesian coordinates.

The average of an arbitrary function \( g \) is \( \langle g \rangle = \frac{1}{V} \int_v g \, dV \). Here, integration is performed over the volume of the sphere, whose radius tends to infinity and the center coincides with the center of the particle. Inside and outside the particle, the element of integration on the right-hand side of (15) is different from and equal to zero, respectively. From equations (5) and (7), it follows

\[
\sigma_{ij} = \frac{\partial (\sigma_{ik} \tilde{x}_k)}{\partial x_j} + \tilde{x}_j \delta_{ij} = \frac{\partial (\sigma_{ik} \tilde{x}_k)}{\partial x_j} - K \tilde{u}_i \tilde{x}_j.
\]

From this relation, using the symmetry property of the stress tensor \( \langle \sigma_\text{ij} \rangle = \langle \sigma_\text{ji} \rangle \) and continuity equation (6), we obtain

\[
\sigma_{ij} = \frac{1}{2} \left( \frac{\partial (\sigma_{ik} \tilde{x}_k)}{\partial x_j} + \frac{\partial (\sigma_{ik} \tilde{x}_k)}{\partial x_k} - K \frac{\partial (\tilde{u}_i \tilde{x}_j)}{\partial x_k} \right).
\]

(16)

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To calculate immediately the integral in (15), there is a need to examine the internal stresses in the inclusion; however, to avoid this obstacle, the integration over the volume may be changed for the integration over the surface of an infinitely spaced sphere passing through the liquid only. From (15) and (16), it follows

$$\langle \sigma_0 \rangle = \mu_r \left( \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \frac{1}{2} \frac{1}{r^2} \sigma_{ik} \delta_{ik} + \frac{1}{2} \frac{1}{r^2} \sigma_{ii} \delta_{ii} \right)$$

+ $\sigma_{ik} \delta_{ik} + \frac{1}{2} \frac{1}{r^2} \sigma_{ii} \delta_{ii} \}.$

Here, the term $\langle p \rangle$ vanishes because the average pressure is identically equal to zero (actually, $\langle p \rangle$ is the scalar determined by the linear combination of components of $\sigma_{ik}$ tensor, and this scalar is $\sigma_{ii} = 0$). In the calculation of integral (17), we use the following relations valid for the case of integration over the sphere:

$$\frac{1}{4\pi} \delta_{ii} \omega = \frac{1}{3} \delta_{ij},$$

$$\frac{1}{4\pi} \delta_{ii} \omega = \frac{1}{15} \delta_{ii} \omega,$$

where $\omega = \frac{n_i \omega}{|r|}$ are the direction cosines, and $d\omega$ is the differential with respect to the sphere surface. Relation (17) can be rewritten in the form

$$\langle \sigma_0 \rangle = \mu_r \left( \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \frac{1}{2} \frac{1}{r^2} \sigma_{ik} \delta_{ik} + \frac{1}{2} \frac{1}{r^2} \sigma_{ii} \delta_{ii} \right)$$

+ $\sigma_{ik} \delta_{ik} + \frac{1}{2} \frac{1}{r^2} \sigma_{ii} \delta_{ii} \}.$

Substituting the expressions for $u_i$, $\sigma_{ij}$ into formula (18) yields

$$\langle \sigma_0 \rangle = 2 \mu_r u_i \frac{\partial u_i}{\partial r^2}.$$

Substituting the expressions for $u_i$, $\sigma_{ij}$ into formula (18) and passing to the limit $r \rightarrow \infty$, it follows from relation (12) that

$$\langle \sigma_0 \rangle = 5 \mu_r \frac{U_0}{r^2} \gamma \alpha_r.$$

Substituting the expressions for $u_i$, $\sigma_{ij}$ into formula (18) and passing to the limit $r \rightarrow \infty$, it follows from relation (12) that

$$\langle \sigma_0 \rangle = 5 \mu_r \frac{U_0}{r^2} \gamma \alpha_r.$$

At $\gamma = 0$, formula (20) transforms into the expression for the averaged stress tensor for the initial liquid $\langle \sigma \rangle = 2 \mu \alpha_r U_0 / r^2$, and, if $\gamma$ is a small but nonzero value, the quantity $\mu_r (1 + 2.5 \gamma)$ in (20) represents the effective viscosity of the medium, which can be designated as $\mu_r^*$. Thus, a $\gamma$ value much smaller than unity, the expression for the effective viscosity $\mu_r^*$, can be written in the form

$$\mu_r^* = \mu_r (1 + \frac{5}{2} \gamma).$$

A comparison of equations (1) and (2) shows that, at small concentrations of additional particles, $K^* = 6 \mu \pi R + K$. When $\mu$ is expressed through $\gamma$, we have

$$K^* = \frac{9 \mu \pi}{2 R^2} \gamma + K.$$

From (21) and (22), according to [4–6], we may obtain the differential model

$$\frac{d\mu_r^*}{d\gamma} = \frac{5 \mu_r^*}{2 (1 - \gamma)},$$

$$\frac{dK^*}{d\gamma} = \frac{9 \mu \pi}{2 R^2} \gamma (1 - \gamma),$$

with the boundary conditions

$$\mu_r^* |_{\gamma = 0} = \mu_r \frac{K^* |_{\gamma = 0}}{K} = K,$$

where $\mu_r$ and $K$ are the viscosity and the resistance coefficient of Brinkman’s liquid free from additional inclusions, and $\mu_r^*$ and $K^*$ are the respective effective coefficients, i.e., the coefficients of the Brinkman’s liq-
uid containing additional fixed spherical inclusions, whose volume concentration is equal to $\gamma$.

The set of differential equations (23) with boundary conditions (24) has the following solution:

$$\mu^* = \mu_1 (1 - \gamma)^{-\frac{5}{2}},$$

$$K^* = \frac{9\pi\mu_1}{7R^2} (1 - \gamma)^{-\frac{5}{2}} - 1 + K.$$  \hspace{1cm} (25)

Thus, formulas (25) define the effective viscosity of Brinkman’s liquid and its flow resistance at arbitrary values of the concentration $\gamma$.

For the initial medium represented by the Newtonian liquid, formula (25) can be rewritten in the form

$$\mu^* = \mu_1 (1 - \gamma)^{-\frac{5}{2}},$$

$$K^* = \frac{9\pi\mu_1}{7R^2} (1 - \gamma)^{-\frac{5}{2}} - 1.$$  \hspace{1cm} (26)

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