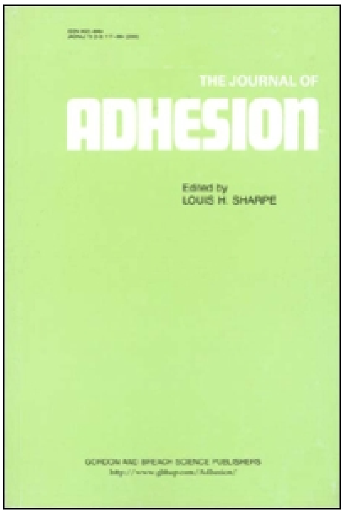

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EFFECTIVE PROPERTIES OF POROUS AND COMPOSITE MATERIALS

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EFFECTIVE PROPERTIES OF POROUS AND COMPOSITE MATERIALS

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Based on a previously modified version of Bruggerman's method, a dependence of the effective diffusion coefficient in porous media on the porosity is deduced and compared with available experimental data. Based on the same method, a dependency of the effective elastic coefficients of composite materials on the volume fraction of inclusions is deduced in the case of different types of inclusions. Comparison with available experimental data shows good agreement between the theory predictions and the experimental data. In the case of the elastic properties of laminated composite materials, application of the same method yields results identical to those obtained using the averaging procedure. A theory of effective viscosity of concentrated suspensions is applied for calculations of dependency of effective viscosity on applied shear rate using available experimental data.

Keywords: Effective elastic properties; Diffusion and viscosity; Composite materials; Porous media; Suspensions

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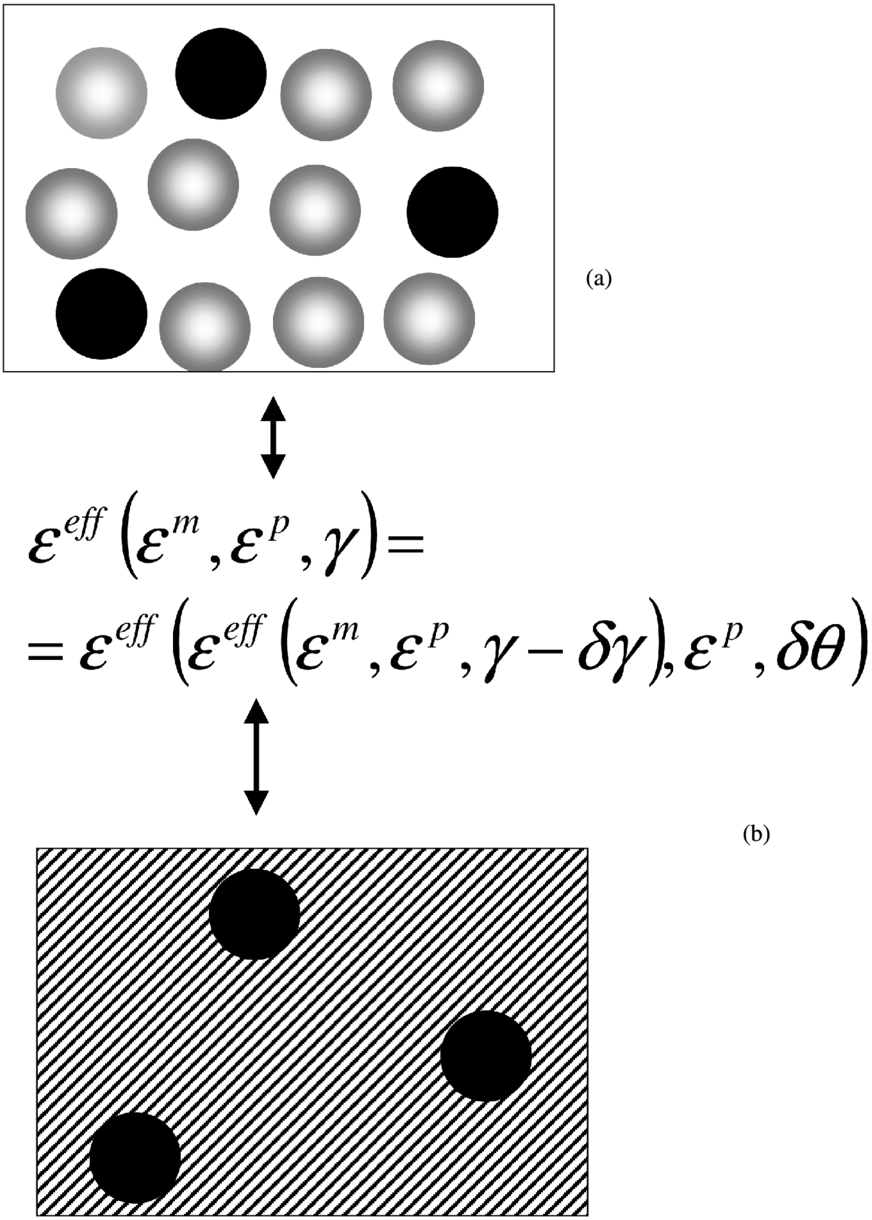
1 INTRODUCTION

Bruggerman's method (referred to also as the differential method, which is a version of the mean field theory) has been successfully applied to calculations of the effective dielectric permeability of suspensions and emulsions [1]. The comparison of different theoretical predictions with available experimental data is given in Dukhin and Shilov [1]. The comparison shows that Bruggerman's equation gives the best agreement with the available experimental data.

However, a clear mathematical base of this method has not been presented either in the original paper [2] or in the subsequent publications (see, for example, Christensen [3]). That did not allow further applications of this very promising method. A modified version of Bruggerman's method has been presented in Starov *et al.* [4]. The modified method allows (1) further applications of this method to the calculation of effective properties of a variety of porous/dispersed media and (2) a generalisation of the theory in the case when particles/droplets form clusters. The new method has been applied to the calculation of effective viscosity of suspensions [4] and emulsions [5], permeability of porous media [6] and effective elastic properties of rubber/polymer sheets with cracks [7].

The idea of the modified Bruggerman's method is illustrated below using the calculation of the dependency of an effective dielectric permeability of emulsions/suspensions on the volume fraction of particles/droplets, γ (Figure 1). This example (see below) shows that the application of the modified method [4] results in exactly the same Bruggerman's equation as in Bruggerman [2]. Below we consider emulsions, although the same consideration can be applied to suspensions.

Let ε^m, ε^p be the dielectric permeability of the dispersion phase and droplets, respectively; $\varepsilon^{eff}\,(\varepsilon^m, \varepsilon^p, \gamma)$ is the effective dielectric permeability of the emulsion. Let us mark randomly a small number, $\delta\gamma$, of droplets (Figure 1d). This rest of the emulsion containing nonmarked droplets is replaced by an effective medium with the effective dielectric permeability $\varepsilon^{eff}(\varepsilon^m, \varepsilon^p, \gamma - \delta\gamma)$. The volume fraction of the marked droplets in the new emulsion (Figure 1b) is $\delta\theta$. This volume fraction is different from $\delta\gamma$ because droplets do not overlap (see Appendix A2 for details). The latter means that the dielectric permeability of the emulsion B (Figure 1) is $\varepsilon^{eff}(\varepsilon^{eff}(\varepsilon^m, \varepsilon^p, \gamma - \delta\gamma), \varepsilon^p, \delta\theta)$. The main advantage of the latter expression is that the volume fraction of the marked droplets is small so that the known equation for the dielectric permeability of suspensions at low volume fraction [8] can be used for calculations.



$$\varepsilon^{eff}\left(\varepsilon^{m},\varepsilon^{p},\gamma\right)=$$
$$=\varepsilon^{eff}\left(\varepsilon^{eff}\left(\varepsilon^{m},\varepsilon^{p},\gamma-\delta\gamma\right),\varepsilon^{p},\delta\theta\right)$$

FIGURE 1 Schematic explanation of modified Bruggerman's method [4] (see text for details).

Obviously the dielectric permeability should not depend on the way of its calculation, *i.e.*, the dielectric permeability of emulsions A and B (Figure 1) should be equal. It yields the following equation for the determination of the dependency of the effective dielectric permeability of the emulsion on the volume fraction of droplets:

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

The following steps should be made to solve the latter equation:

1. Taylor's expansion of the righthand side;
2. Utilization of the known solution [8] for the dependency of the dielectric permeability on the volume fraction of droplets in the case of small volume fractions.

This procedure results in a differential equation for the determination of $\varepsilon^{eff}(\varepsilon^m, \varepsilon^p, \gamma)$. Solution of this equation coincides with Bruggerman's equation [2] for the dependency of the dielectric permeability on the volume fraction of droplets.

The above described modified version of the Bruggerman's method is used below for the calculation of the effective properties of porous and dispersed media.

2 CALCULATION OF THE DEPENDENCY OF THE EFFECTIVE DIFFUSION COEFFICIENT ON POROSITY

Figure 2 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 application of the modified Bruggerman'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). That is, as the first step, the effective coefficient of the molecular diffusion in the porous medium built up by impermeable spherical particles in the case of the high porosity should be calculated. It is done below using the cell model (Figure 3).

The unit cell of radius, R, is presented in Figure 3. It includes an impermeable spherical particle of radius, a, which is positioned in the centre of the cell, and the dispersion medium around. The cell is surrounded by the effective medium with unknown effective diffusion coefficient, D^{eff}. The radius of the cell, R, is chosen according to the

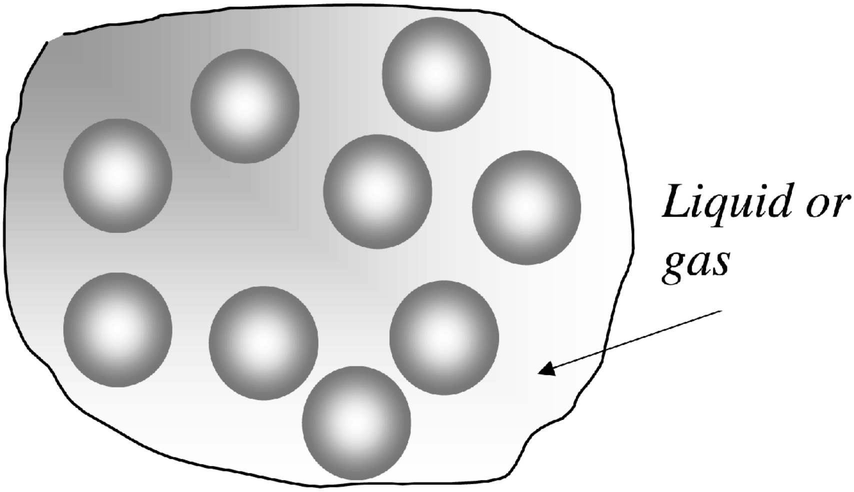


FIGURE 2 Porous medium built up by impermeable particles. An admixture diffuse in liquid or gas/vapor between particles.

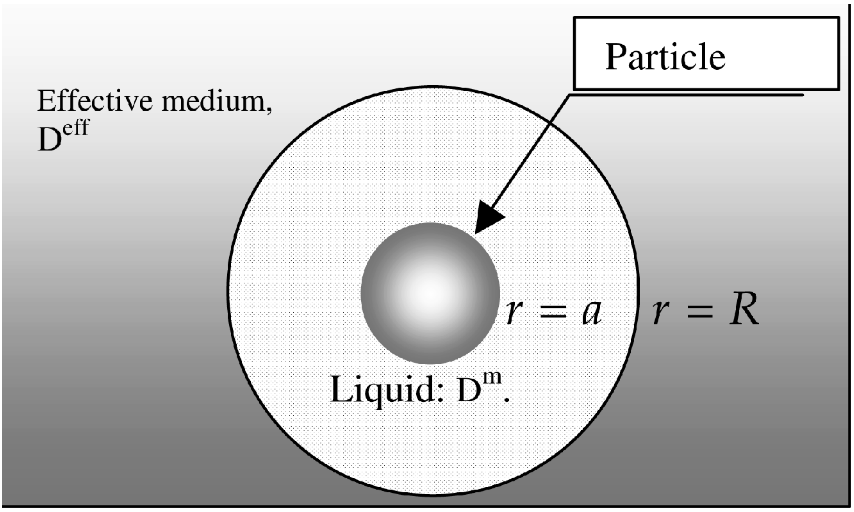


FIGURE 3 Cell method for calculation of effective diffusion coefficient. Spherical impermeable particle of radius **a** is positioned inside a spherical cell of radius ***R***. The cell is surrounded by a medium with the effective diffusion coefficient D^{eff}.

following condition,

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

where $\varphi = 1 - \gamma$ is the porosity and γ is the volume fraction of the particles. The concentration and the flux of the molecular substance that diffuses 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 the particle should vanish (impermeable particle). The concentration profile both inside the cell and outside obeys the Laplace equation. The solutions of the corresponding problem (see Appendix A1) result in the following equation:

$$D^{eff} = \left(1 - \frac{3\gamma}{\gamma + 2}\right)D^m, \tag{1}$$

where D^m is the diffusion coefficient in the interparticle space and D^{eff} is the effective diffusion coefficient in the porous medium. Equation (1) coincides with that deduced in Maxwell [9] in a different way.

In the case of very low volume fraction of particles ($\delta\gamma \ll 1$), Equation (1) yields:

$$D^{eff} = D^m + A^{diffusion}(D^m)\delta\gamma, \tag{2}$$

$$A^{diffusion}(D^m) = -1.5D^m. \tag{3}$$

As the next step below a modification of the Bruggerman's method introduced in Starov *et al.* [4] and briefly described here in the ***INTRODUCTION*** is used.

Let us randomly mark a small number of particles in the porous medium (with volume fraction $\delta\gamma \ll 1$). 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. Thus, the effective diffusion coefficient can be expressed in two different ways: (1) using the equation

$$D^{eff} = D(D^m, \gamma), \tag{4}$$

where $D(D^m, \gamma)$ is the dependency to be determined; and (2) using the "marked" particles with volume fraction $\delta\theta$ (which is different from $\delta\gamma$), surrounded by the effective porous medium with "non-marked" particles with volume fraction $\gamma - \delta\gamma$. The diffusion coefficient inside this part of the effective porous medium is $D(D^m, \gamma - \delta\gamma)$. The latter two definitions should give the same dependency of the effective diffusion coefficient in the whole porous medium. It yields the following equation for calculation of $D(D^m, \gamma)$:

$$D(D^m, \gamma) = D(D(D^m, \gamma - \delta\gamma), \delta\theta). \tag{5}$$

Geometrical considerations (see Appendix A2) give $\delta\theta = \delta\gamma / 1 - \gamma$. Substitution of the latter expression into Equation (5) and using first two terms of Taylor's series in the righthand site (small parameters $\delta\gamma$ and $\delta\theta$) results in the following differential equation (see Appendix A2 for details):

$$\frac{dD^{eff}}{d\gamma} = \frac{A^{diffusion}(D^{eff})}{1-\gamma}, \tag{6}$$

with the boundary conditions

$$D^{eff}|_{\gamma=0} = D^m. \tag{7}$$

Solution of Equations (3), (6), and (7) results in

$$D^{eff} = D^m(1-\gamma)^{3/2}. \tag{8}$$

The comparison of the latter dependency in Equation (8) (dashed curve) with the known theoretical relations (continuous lines) and available experimental data [10] is presented in Figure 4. Comparison shows that the relation in Equation (8) agrees well with the known experimental data.

3 ELASTIC PROPERTIES OF COMPOSITE MATERIALS WITH DIFFERENT TYPES OF INCLUSIONS

Below our modified method is applied to the calculations of effective elastic properties of composite materials.

The differential equation for dependency of the effective elastic properties of composite materials on volume fractions of several different types of inclusions is deduced below. The volume fraction of inclusions of type k, γ^k, is defined as

$$\gamma^k = \frac{V^k}{V}, \tag{9}$$

where V is the volume of the composite material and V^k is the volume of inclusions of type k $(k = 1, 2, \ldots, M)$.

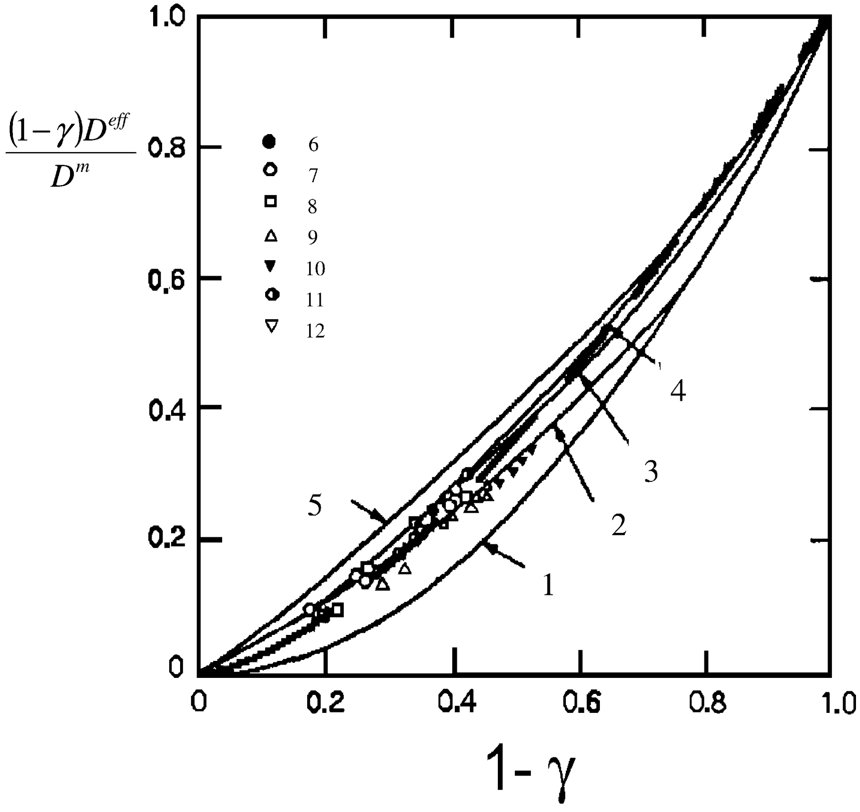


FIGURE 4 Dependence of the effective diffusion coefficient, D^{eff}, on the particle volume fraction, γ. Solid lines correspond to the models of the different authors; experimental data from Kim *et al.* [21], Curie [22], and Hoogschagen [23]. Dashed line according to Equation (8). Solid line according to the following: 1, Wakao and Smith [24]; 2, Ryan *et al.* [25]; 3, Quintard and Whitaker [26–27]; 4, Weissberg [28]; 5, Rayleigh [20]. Experimental data are reproduced from Whitaker [10]: 6, Kim *et al.* [21]; 7, Currie [22]; 8, Currie [22]; 9, Currie [22]; 10, Currie [22]; 11, Hoogschagen [23]; 12, Hoogschagen [23].

Let h^{eff} be an effective elastic coefficient of the composite material, h^m be the elastic coefficient of the matrix, and h^k be the elastic coefficient of inclusions of the type k $(k = 1, 2, \ldots, M)$.

The elastic coefficients h^{eff}, h^m, and h^k can be tensors, vectors (for example, both Young's modulus and Poisson's ratio), or scalars depending on the problem under consideration. It is assumed below that the following relation describes the effective elastic coefficients:

$$h_j^{eff} \; = \; h_j\left[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M\right],\; j = 1, 2, \ldots, N. \qquad (10)$$

Below the subscript j is dropped for an abbreviation.

In the case $\gamma^1 = \gamma^2 = \cdots = \gamma^M = 0$ (no inclusions), Equation (10) results in

$$h^m = h\left[h^m, h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0\right], \qquad (11)$$

which is used below as the boundary condition. In the case $\gamma^i = 0$ $(i = 1, 2, \ldots, k - l, k + 1, \ldots, M)$ (only inclusions of the type k), Equation (10) results in

$$h^{\text{single},k}\left[h^m, h^k, \gamma^k\right] = h\left[h^m, h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0, \gamma^k, 0, \ldots, 0\right], \qquad (12)$$

which is determined below independently.

Dependences $A^{\text{single},k}(k = 1, 2, \ldots, M)$ are defined as

$$A^{\text{single},k}(h^m, h^k) = \left.\frac{\partial h^{\text{single}}[h^m, h^k, \delta\gamma^k]}{\partial \delta\gamma^k}\right|_{\delta\gamma^k = 0}, (k = 1, 2, \ldots, M). \qquad (13)$$

Application of our modified method (see Appendix A3 for details) results in the following system of partial differential equations:

$$\frac{\partial h^{eff}}{\partial \gamma^k} = A^{\text{single},k}(h^{eff}, h^k) + \frac{\sum_{i=1}^{M} A^{\text{single},i}(h^{eff}, h^i)\gamma^i}{1 - \sum_{i=1}^{M} \gamma^i}, k = 1, 2, \ldots, M. \qquad (14)$$

The effective elastic coefficients of the composite material, h^{eff}, can be calculated as solutions of the system of nonlinear partial differential Equations (14) with the boundary conditions

$$h^{eff}\Big|_{\gamma^1 = \gamma^2 = \cdots = \gamma^m = 0} = h^m. \qquad (15)$$

In the case of only one type of inclusion the latter system reduces to one ordinary differential equation.

4 APPLICATION TO THE CALCULATION OF ELASTIC PROPERTIES OF THE LAMINATED COMPOSITE MATERIALS

In this section the elastic properties of the laminated composite materials (Figure 5) are considered using the deduced system of differential Equations (14). Earlier, the same problem has been solved using the averaging method [11] where the analytical expressions for the elastic

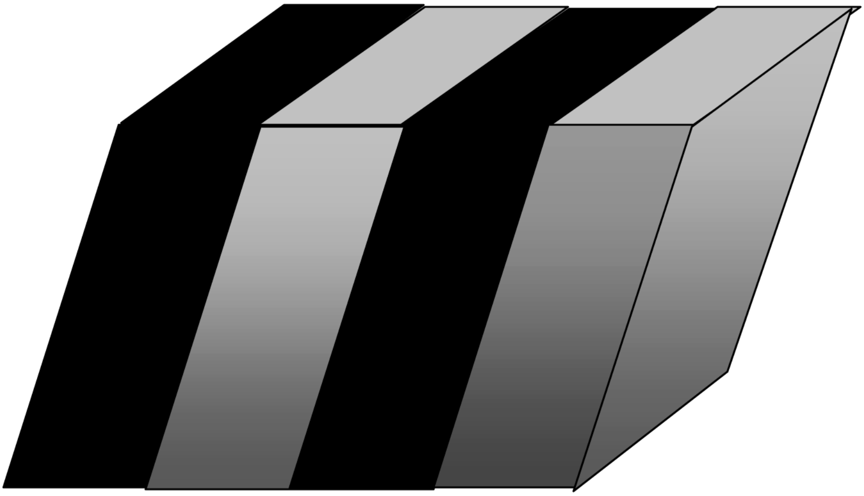


FIGURE 5 Laminated composite material.

properties have been obtained. The main result of this section is as follows: the analytical solution presented in Khorshun *et al.* [11] is the solution of our system of differential equations deduced using the modified Bruggerman's method. That is, both methods give identical results in the case of laminated composite materials.

Let the axes of symmetry be directed perpendicular to the layers of the laminated composite material. The equations of equilibrium are considerably simplified in this case. Derivatives of both the stress tensor and the fluctuation of displacements $u_i - \sum_{j=1}^{3} \langle \varepsilon_{ij} \rangle x_j$ vanish in any direction tangential to the layers, where $\bar{u}$ is the displacement and $\langle \varepsilon_{ij} \rangle$ 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 moduli [11].

Let h^m be the elastic moduli of the matrix, $h^1, h^2, \ldots, h^M$ be the elastic moduli of layers of type $1, 2, \ldots, M$ and $\gamma^1, \gamma^2, \ldots, \gamma^M$ be the volume fractions of layers of type $1, 2, \ldots, M$.

An averaged value of an arbitrary function, g, over big volume, V, is introduced as $\langle g \rangle = \frac{1}{V} \int_V g dv$. Let $g(x)$ be equal to g^m inside the matrix and $g^1, g^2, \ldots, g^M$ inside corresponding to layers of type $1, 2, \ldots, M$. All values $g^m, g^1, g^2, \ldots, g^M$ remain constant inside the matrix/layers. The averaging procedure results in $\langle g \rangle = g^m \left(1 - \sum_{i=1}^{M} \gamma^i\right) + \sum_{i=1}^{M} g^i \gamma^i$.

Deformations, ε, and stresses, σ, inside any layer of the type $q (q = 1, 2, \ldots, M)$ and matrix are related according to $\sigma = h^q \varepsilon$ and $\sigma = h^m \varepsilon$, respectively. Averaged deformations, $\langle \varepsilon \rangle$, and stresses, $\langle \sigma \rangle$, are related according to the same law [11]: $\langle\sigma\rangle = h^{eff}\langle\varepsilon\rangle$. The latter relations allow the presentation of the solution in the following form: $h^{eff} = h(h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M)$ [11]. These expressions in the case of laminated composite materials with orthotropic layers and common axes of isotropy, one of which is perpendicular to the layers, have been obtained in Khorshun *et al.* [11] as follows:

$$\begin{aligned}
h^{eff}_{33333} &= \langle h_{3333}\rangle + \langle h_{1133}/h_{1111}\rangle^2/\langle 1/h_{1111}\rangle - \langle {h_{1133}}^2/h_{1111}\rangle\\
h^{eff}_{2222} &= \langle h_{2222}\rangle + \langle h_{1122}/h_{1111}\rangle^2/\langle 1/h_{1111}\rangle - \langle {h_{1122}}^2/h_{1111}\rangle\\
h^{eff}_{1111} &= 1/\langle 1/h_{1111}\rangle\\
h^{eff}_{2233} &= \langle h_{2233}\rangle + \langle h_{1133}/h_{1111}\rangle\langle h_{1122}/h_{1111}\rangle/\langle 1/h_{1111}\rangle\\
&\quad - \langle h_{1133}h_{1122}/h_{1111}\rangle \qquad (16)\\
h^{eff}_{1133} &= \langle h_{1133}/h_{1111}\rangle/\langle 1/h_{1111}\rangle\\
h^{eff}_{2323} &= \langle h_{2323}\rangle\\
h^{eff}_{1212} &= 1/\langle 1/h_{1212}\rangle\\
h^{eff}_{1313} &= 1/\langle 1/h_{1313}\rangle.
\end{aligned}$$

The derivatives $A^{\mathrm{single},k}$ are defined below as follows:

$$A^{\mathrm{single},k}(h^m, h^k) = \left.\frac{\partial h\left(h^m, h^1, h^2, \ldots, h^M, \delta\gamma^1, \delta\gamma^2, \ldots, \delta\gamma^M\right)}{\partial\delta\gamma^k}\right|_{\delta\gamma^1=\delta\gamma^2=\cdots=\delta\gamma^M=0}, (k = 1, 2, \ldots, \mathrm{M}). \qquad (17)$$

Now let the functions $A^{\mathrm{single},k}(h^m, h^k)$ be calculated according to Equations (16) and (17) and substituted into the system of Equations (14). After tiresome calculations (not presented) it is possible to show that Equations (16) being substituted into the system of Equations (14) give their exact solution. This means that the averaging method [11] and the modified Bruggerman's method give identical results in the case of laminated composite materials.

5 CALCULATION OF THE EFFECTIVE ELASTIC MODULI OF COMPOSITE MATERIAL WITH SPHERICAL INCLUSIONS

The system of the differential Equations (14) is applied below for calculations of the effective elastic moduli of the elastic isotropic composite materials with spherical isotropic particles (inclusions) and isotropic matrices. Earlier these moduli have been calculated using the cell method and Bruggerman's method in the case of inclusions of only one type [3]. However, the equations have been presented in Christensen [3] without any derivation. It does not allow one either to estimate the correctness of the obtained results or develop further generalization in more complex cases of inclusions of different types. Below the modified Bruggerman's method is applied to calculation of the elastic properties of the composite materials with several different types of inclusions using Equations (14).

Hooke's law for the particles and the matrix reads

$$\sigma_{ij} = k^p \left(\sum_{n=1}^{3} \varepsilon_{nn} \right) \delta_{ij} + 2\mu^p \varepsilon_{ij}, \;\; \sigma_{ij} = k^m \left(\sum_{n=1}^{3} \varepsilon_{nn} \right) \delta_{ij} + 2\mu^m \varepsilon_{ij},$$

where k^p, μ^p, k^m, and μ^m are elastic coefficients of the particles and the matrix, respectively. The same law gives the relation between stress, σ, and deformation, ε, averaged over the volume:

$$\langle \sigma_{ij} \rangle = k^{eff} \left(\sum_{n=1}^{3} \langle \varepsilon_{nn} \rangle \right) \delta_{ij} + 2\mu^{eff} \langle \varepsilon_{ij} \rangle. \tag{18}$$

The Young's modulus, E, and the Poisson's ratio, v, are usually used instead of the coefficients κ and μ:

$$E = \frac{9k\mu}{3k+\mu}, \;\; v = \frac{3k-2\mu}{2(3k+\mu)}. \tag{19}$$

If the volume fraction of inclusions is small, $\delta\gamma \ll 1$,then coefficients k^{eff} and μ^{eff} have been obtained using the cell method in Christensen [3]:

$$\begin{aligned} \mu^{eff} &= \mu^m + A^\mu(\mu^m, k^m, \mu^p, k^p)\delta\gamma, \\ k^{eff} &= k^m + A^m(\mu^m, k^m, \mu^p, k^p)\delta\gamma, \end{aligned} \tag{20}$$

where

$$\begin{aligned} A^\mu(\mu^m, k^m, \mu^p, k^p) &= \frac{15(1-v^m)\left(\frac{\mu^p}{\mu^m} - 1\right)\mu^m}{7 - 5v^m + 2(4-5v^m)\frac{\mu^p}{\mu^m}}, \\ A^k(\mu^m, k^m, \mu^p, k^p) &= \frac{\left(\frac{k^p}{k^m} - 1\right)k^m}{\frac{k^p - k^m}{k^m + \frac{4}{3}\mu^m} + 1}, \end{aligned} \tag{21}$$

where

$$\nu^m = \frac{3k^m - 2\mu^m}{2(3k^m + \mu^m)}.$$

The system of Equations (14) in the case under consideration using Equations (20) and (21) results in the following system of differential equations:

$$\frac{d\mu^{eff}}{d\gamma} = \frac{15(1-\nu^{eff})\left(\dfrac{\mu^B}{\mu^{eff}}-1\right)\mu^{eff}}{\left(7-5\nu^{eff}+2(4-5\nu^{eff})\dfrac{\mu^B}{\mu^{eff}}\right)(1-\gamma)},$$

$$\frac{dk^{eff}}{d\gamma} = \frac{\left(\dfrac{k^B}{k^{eff}}-1\right)k^{eff}}{\left(\dfrac{k^B-k^{eff}}{k^{eff}+\frac{4}{3}\mu^{eff}}+1\right)(1-\gamma)}, \tag{22}$$

where $\nu^{eff} = \dfrac{3k^{eff}-2\mu^{eff}}{2(3k^{eff}+\mu^{eff})}$. The system of Equations (22) should be subjected the following obvious boundary conditions:

$$\mu^{eff}\big|_{\gamma=0} = \mu^m,\ k^{eff}\big|_{\gamma=0} = k^m. \tag{23}$$

Solution of the system of differential Equations (22) with the boundary conditions in Equation (23) 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 (22) was presented in Christensen [3] without a proper derivation. The derivation given above allows generalization in the case of composite materials with inclusions of several different types (according to Equations (14)).

In Figures 6 and 7 the comparison of the available experimental measurements from Simeonov and Ahmad [12] with the calculations according to Equations [19] and [22] (curves 1) and according to the Mori-Tanaka theory [13] (curves 2) is presented for the dependency of the Young's modulus of the composite materials on the volume fraction of inclusions.

The sum of squares deviations is taken for an estimation of the deviation from the experimental data:

$$\chi = \sum_{i=1}^{N}\left[E^{eff}_{i,\mathrm{exp}} - E^{eff}_{i,\mathrm{calc}}\right]^2, \tag{24}$$

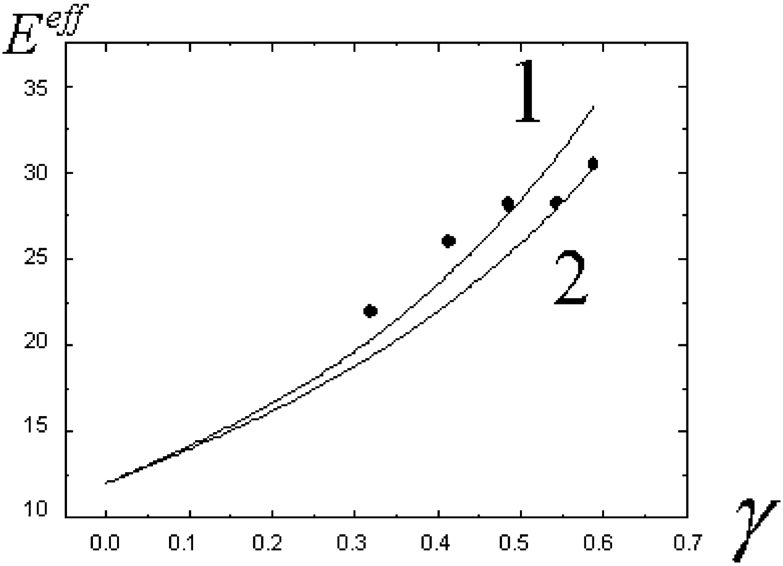


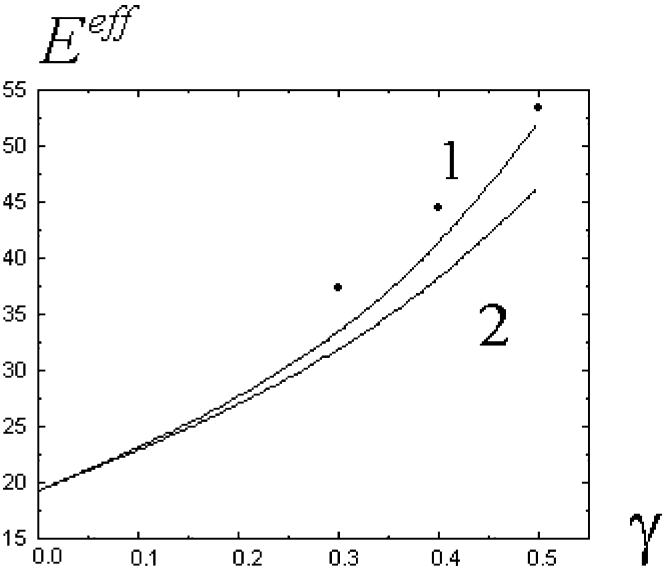
FIGURE 6 The Young modulus, E^{eff}, of cement. Experimental data from Simeonov and Ahmad [12]: 1, according to Equations (22) and (19), $\chi = 23.948$; 2, according to the Mori-Tanaka theory [13], $\chi = 27.724$. Matrix: cement past $E^m = 12$ GPa, $v^m = 0.22$. Particles: sand $E^p = 80$ GPa, $v^p = 0.21$.

where N is the number of data points (N = 5 in Figure 6 and N = 3 in Figure 7) and $E^{eff}_{i,\exp}$ $(i = 1,\ldots,N)$ are the experimental values of Young's modulus [12]. Figures 6 and 7 show that the calculations according to Equations (19) and (22) result in better agreement with the experimental data, than do calculations based on the Mori-Tanaka theory.

In Table 1 comparison of the experimental data on the elastic properties of the concrete with two types of inclusions from Simeonov and Ahmad [12] are compared with our predictions calculated according to Equations (14) and (19). Comparison shows that the predictions according to our theory in all cases overestimate the experimental values. Calculations according to Mori-Tanaka theory in all cases underestimate the same experimental data.

6 VISCOSITY OF CONCENTRATED SUSPENSIONS: INFLUENCE OF CLUSTER FORMATION

In Starov *et al.* [4], cluster formation in concentrated suspensions has been taken into account, and based on this consideration a new



FIGRUE 7 The Young modulus, E^{eff}, of cement. Experimental data from Simeonov and Ahmad [12]: 1, according to Equations (22) and (19), $\chi = 32.577$; 2, according to Mori-Tanaka theory [13], $\chi = 131.782$. Matrix: cement $E^m = 12$ GPa, $v^m = 0.22$. Particles: steel $E^p = 207$ GPa, $v^p = 0.3$.

equation of the dependency of the effective viscosity on the volume fraction of particles, γ, has been deduced:

$$\frac{d\eta}{d\gamma} = 2.5\eta\left[\frac{d\left(\overline{A}\frac{\gamma}{\overline{\gamma}_{\max}}\right)}{d\gamma} + \frac{\overline{A}\frac{\gamma}{\overline{\gamma}_{\max}}}{1-\frac{\gamma}{\overline{\gamma}_{\max}}}\frac{d\left(\frac{\gamma}{\overline{\gamma}_{\max}}\right)}{d\gamma}\right], \tag{25}$$

where $\overline{A} = \frac{\sum_{i=1}^{\infty} A_i\gamma_i}{\sum_{i=1}^{\infty}\gamma_i}$, $\overline{\gamma}_{\max} = \frac{\sum_{i=1}^{\infty}\gamma_{i,\max}\gamma_i}{\sum_{i=1}^{\infty}\gamma_i}$; γ_i and $\gamma_{i,\max}$ $(i = 1, 2, 3, \ldots)$ are volume fraction of clusters and averaged packing densities of single particles inside clusters, respectively; $\gamma_{1,\max} = 1$; and A_i $(i = 1, 2, 3, \ldots)$ are deviations of the friction coefficient of clusters with $i (i = 1, 2, 3, \ldots)$ particles from the corresponding value for solid particles $(A_1 = 1)$.

It is important to notice that $\overline{A}$ and $\overline{\gamma}_{\max}$ are functions of both the volume fraction, γ, and the applied shear stress, τ. The latter means that it is not necessary to deduce a separate equation for dependency of viscosity on the applied shear stress/rate: it is enough to develop a

TABLE 1 Elastic Properties of Concretes: Two Types of Inclusions

Cement phase (matrix) $E^m = 12\,GPa$ $v^m = 0.22\,GPa$ volume fraction, $1 - \gamma_1 - \gamma_2$	Sand (phase 1) $E^m = 800\,GPa$ $v^m = 0.21\ GPa$ volume fraction, γ_1	Gravel (phase 2) $E^m = 69\,GPa$ $v^m = 0.23\,GPa$ volume fraction, γ_2	Concrete E (GPa), calculated using Mori-Tanaka method [13]	Concrete E (GPa), calculated according to Equations (14)	Concrete E (GPa), experimental data from Simeonov and Ahmad [12]
0.374	0.446	0.18	32.14	34.96	34.90
0.342	0.408	0.25	33.92	37.00	34.20
0.328	0.392	0.28	34.73	37.93	35.40
0.319	0.381	0.30	35.29	38.55	36.20
0.297	0.353	0.35	36.74	40.09	36.60
0.274	0.326	0.40	38.28	41.78	39.60

model that gives dependency of both $\overline{A}$ and $\overline{\gamma}_{\max}$ on the applied shear stress/rate.

Let us assume that $\overline{A}$ is independent of the volume fraction, γ. In this case the latter equation takes the following form:

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

or

$$\frac{d\eta}{d\gamma} = \frac{2.5\eta\overline{A}}{1-\frac{\gamma}{\overline{\gamma}_{\max}}}\frac{d\left(\frac{\gamma}{\overline{\gamma}_{\max}}\right)}{d\gamma}, \tag{26}$$

with the boundary condition

$$\eta(0) = \eta^{m}. \tag{27}$$

It is important to emphasise that $\overline{\gamma}_{\max}$ is not supposed to retain a constant value, independent of the volume fraction, γ.

The solution of Equation (26) with the boundary condition in Equation (27) is

$$\frac{\eta(\gamma)}{\eta_0} = \frac{1}{\left(1-\frac{\gamma}{\overline{\gamma}_{\max}}\right)^{2.5\overline{A}}}. \tag{28}$$

Equation (28) almost coincides with the Dougherty-Krieger equation [14, 15]:

$$\frac{\eta(\gamma)}{\eta_0} = \frac{1}{\left(1-\frac{\gamma}{\overline{\gamma}_{\max}}\right)^{[\eta]\gamma_{\max}}}, \tag{29}$$

where $[\eta]$ is an intrinsic viscosity.

It is necessary to emphasise that in spite of a striking similarity between Equations (28) and (29) there are two very substantial differences between these equations:

1. The physical meaning of parameters included in Equation (28) is quite different from those used in Equation (29). According to the theory developed above, viscosity dependence on concentration is

related to cluster formation and this physical phenomenon is incorporated in Equation (28).

2. Equation (28) describes both dependency on particle volume fraction and on the applied shear stress/rate. This dependency is hidden in the dependency of both $\overline{A}$ and $\overline{\gamma}_{\max}$ on the applied shear stress/rate.

If particles do not form clusters, that is, $\gamma_1 = \gamma;\ \gamma_i = 0,\ i = 2, 3, 4, \ldots$, and hence $\overline{\gamma}_{\max} = \overline{A} = 1$ should be used in Equation (28), which gives in this particular case

$$\frac{\eta(\gamma)}{\eta_0} = \frac{1}{(1-\gamma)^{2.5}}. \tag{30}$$

The latter equation coincides with the earlier obtained expressions for the dependence of the effective viscosity of suspensions that do not form clusters [16, 17].

A comprehensive review of experimental data on viscosity of concentrated suspensions is presented in Thomas [18]. In Starov and Zhdanov [6], the comparison of experimental data with predictions according to Equations (30) and (28) has been presented. The comparison showed that the whole array of experimental data can be described using Equation (28) at difference but reasonable parameters $\overline{\gamma}_{\max}$ and $\overline{A}$. It has been shown in Starov and Zhdanov [6] that prediction according to Equation (30)—no cluster formation, particles evenly distributed in space—underestimates experimental data.

Let us make the next simplification and assume that both $\overline{A}$ and $\overline{\gamma}_{\max}$ are independent of the particle volume fraction, γ; that is, both depend only on the applied shear stress, τ.

Experimental data on the rheology of a synthetic latex (shear stress dependence in a wide range of concentration) presented in Maron and Fok [19] are used below.

Two experimental values of the effective viscosity of suspensions at particle volume fractions $\gamma = 0.299$ and $\gamma = 0.6017$ (the lowest and the highest available, respectively) at each shear stress, τ from Table 2 are used to calculate two unknown values, $\overline{A}$ and $\overline{\gamma}_{\max}$, for each value of the shear stress, τ. This procedure results in the system of two equations with two unknown values, $\overline{\gamma}_{\max}(\tau)$ and $\overline{A}(\tau)$. In this way, at each shear stress, τ, these two values were determined. Determined dependences $\overline{A}(\tau)$ and $\overline{\gamma}_{\max}(\tau)$ are presented in Figures 8 and 9, respectively. Figure 9 shows that the average packing density inside clusters, $\overline{\gamma}_{\max}(\tau)$, increases with applied shear stress, that is, clusters become denser.

TABLE 2 Experimental Dependence of the Effective Viscosity of Butadiene-styrene Latex Suspensions

	$\gamma = 0.299$	$\gamma = 0.397$	$\gamma = 0.4398$	$\gamma = 0.4876$	$\gamma = 0.5390$	$\gamma = 0.5603$	$\gamma = 0.5866$	$\gamma = 0.6017$
$\tau = 50$	3.293	6.424	9.879	17.18	52.20	107.07	404.10	1089.3
$\tau = 100$	3.218	6.081	8.993	15.17	40.02	71.18	208.78	464.0
$\tau = 200$	3.157	5.802	8.363	13.44	31.55	52.20	122.21	241.8
$\tau = 300$	3.132	5.689	8.082	12.70	27.96	45.39	96.58	176.9
$\tau = 500$	3.110	5.607	7.790	12.03	24.51	39.15	79.28	131.2
$\tau = 800$	—	—	7.597	11.66	21.98	34.80	68.01	105.3

Average particle diameter was 1390Å [19]. η^{eff}/η^{m} as a function of the shear stress, τ, (dynes/cm^2) at different values of volume fraction of particles, γ.

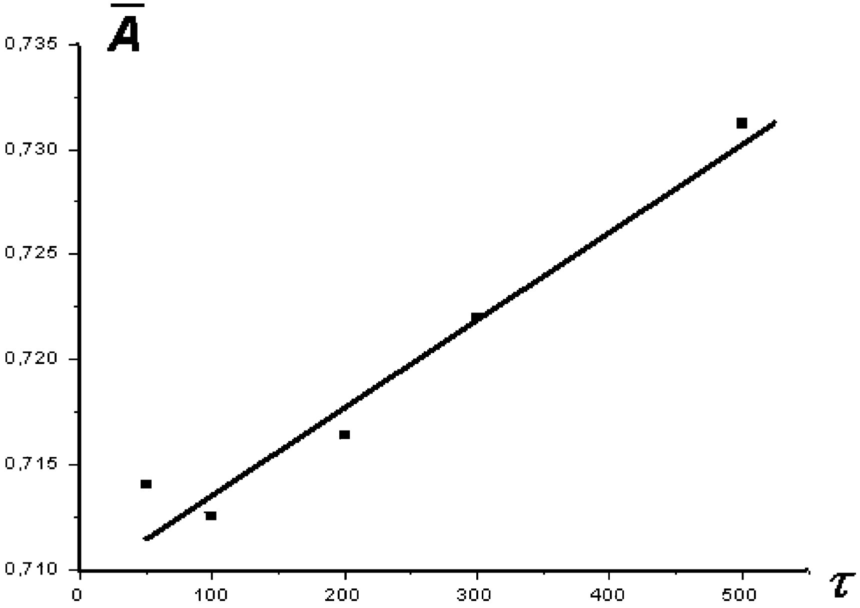


FIGURE 8 Dependence of average parameter, $\bar{A}$, on applied shear stress, τ.

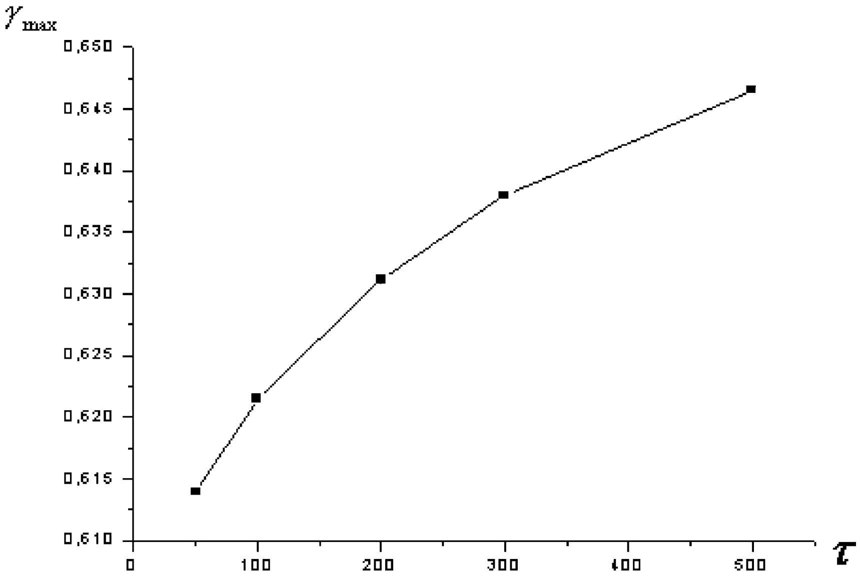


FIGURE 9 Dependence of average packing density inside clusters, $\bar{\gamma}_{\max}$, on applied shear stress, τ.

In this situation the average friction coefficient, $\overline{A}$, should increase, which is in agreement with Figure 8.

Equation (28) can be rewritten as

$$\frac{\eta(\gamma,\tau)}{\eta_0}=\frac{1}{\left(1-\dfrac{\gamma}{\overline{\gamma}_{\max}(\tau)}\right)^{2.5\overline{A}(\tau)}}. \tag{31}$$

The above determined $\overline{\gamma}_{\max}(\tau)$ and $\overline{A}(\tau)$ dependences are used for calculation of $\eta(\gamma,\tau)$ at all shear stress, τ, all volume fractions, γ. Calculated dependencies of effective viscosity on the volume fraction according to Equation (31) are compared with the corresponding experimental values of effective viscosity at different volume fractions, γ, taken from the set of values {0.397, 0.4398, 0.4876, 0.5390, 0.5603, 0.5866} (Table 2). Comparison is presented in Figure 10, which shows that the assumed independently of $\overline{\gamma}_{\max}(\tau)$ and $\overline{A}(\tau)$ from the volume fraction of particles is reasonably fulfilled.

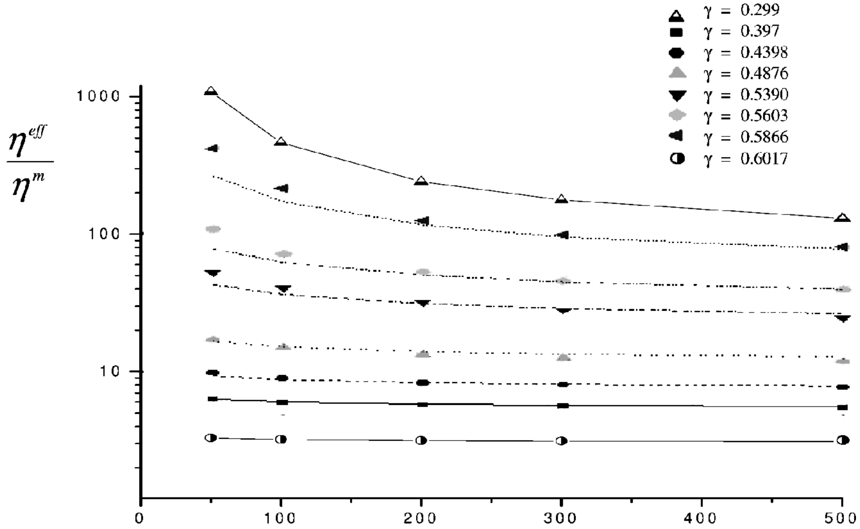


FIGURE 10 Dependency of the effective viscosity of suspensions on shear stress calculated according to Equation (31) at different particle volume fractions. Experimental data from Manon and Fok [19]. $\bar{A}(\tau)$ and $\bar{\gamma}_{\max}(\tau)$ dependencies from Figures 8 and 9, both assumed independent of the volume fraction of particles.

APPENDIX A1: CALCULATION OF THE EFFECTIVE DIFFUSION COEFFICIENT USING THE CELL METHOD

Let us consider a porous medium built up by the spherical impermeable particles (Figure 2) with a liquid or a gas in between. 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 3. 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^{eff}. The radius of the cell, R, is given using the following condition $\gamma = \frac{4\pi}{3}a^3/\frac{4\pi}{3}R^3 = \left(\frac{a}{R}\right)^3, R = a/\gamma^{1/3}$, where $\varphi = 1 - \gamma$ is the porosity and γ is the volume fraction of the particles.

Molecular diffusion of some admixture take 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 the condition in Equation (A1.7)). 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 us zero (impermeability condition). The concentration outside and inside of the cell obeys the Laplace equation:

$$\Delta C^{eff} = 0, \quad r > R, \tag{A1.1}$$

$$\Delta C^{m} = 0, \quad r > R. \tag{A1.2}$$

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

$$\vec{n}. \nabla C^m \bigg|_{r=a} = 0. \tag{A1.3}$$

The boundary conditions on the boundary of the cell of radius R are

$$C^m \bigg|_{r=R} = C^{eff} \bigg|_{r=R} \tag{A1.4}$$

and

$$D^m \nabla C^m \bigg|_{r=R} = D^{eff} \nabla C^{eff} \bigg|_{r=R}, \tag{A1.5}$$

where D^m is the diffusion coefficient in the dispersion medium-and D^{eff} is the effective diffusion coefficient to be determined.

The solution of Equation (A1.1) can be presented in the following form:

$$C^{eff} = g(r)\cos\theta, r > R. \tag{A1.6}$$

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

$$C^{eff} = C^{\infty} r \cos\theta, \tag{A1.7}$$

where C^{∞} is the constant describing the concentration field far from the cell. The cell under consideration is a part of the porous medium and hence does not disturb the concentration field outside the cell. The latter remark and comparison of Equation (A1.6) and (A1.7) shows that $g(r) = C^{\infty}$.

The solution of Equation (A1.2) can be presented in the same form as Equation (A1.6):

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

Substitution of the latter expression in Equation (A1.2) gives

$$C^{m} = \left(Gr + \frac{Q}{2}\right) cos\,\theta. \tag{A1.8}$$

where G and Q are integration constants. The unknown effective diffusion coefficient, D^{eff}, can be calculated using the three boundary conditions in Equations (A1.3)–(A1.5). Indeed, the concentration profiles outside and inside the cell, Equations (A1.8) and (A1.7), include two integration constants, G and Q as well as the unknown effective diffusion coefficient, D^{eff}. That is, we have system of three equations with three unknowns. This system has the following solution:

$$Q = \frac{C^{\infty} a^{3}}{2 + \gamma}, \tag{A1.9}$$

$$G = \frac{2C^{\infty}}{2 + \gamma}, \tag{A1.10}$$

$$D^{eff} = \left(1 \frac{3\gamma}{\gamma + 2}\right) D^{m}. \tag{A1.11}$$

Equation (A1.11) has been deduced by Maxwell [9] in a different way.

APPENDIX A2: CALCULATION OF THE DIFFUSION COEFFICIENT USING THE MODIFIED BRUGGERMAN'S METHOD

The volume fraction of particles is defined as

$$\gamma = \frac{V^p}{V}, \tag{A2.1}$$

where V is the total volume of the porous medium and V^p is the total volume of particles.

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

$$D^{eff} = D(D^m, \gamma), \tag{A2.2}$$

which is calculated below.

In the case $\gamma = 0$, Equation (A2.2) is reduced to

$$D^m = D(D^m, 0). \tag{A2.3}$$

If the fraction of the particles is small, $\delta\gamma \ll 1$, the Equations (A2.2) and (A2.3) result in

$$D^{eff} = D^m + A^{diffusion}(D^m)\delta\gamma, \tag{A2.4}$$

where $A^{diffusion}$ is the new function that which is determined earlier according to Equation (3).

Let us randomly mark some small number of particles, and remaining particles are left unmarked. The volume fraction of marked particles, $\delta\theta$, is

$$\delta\theta = \frac{\delta V}{V}, \tag{A2.5}$$

where δV is the volume of marked particles. The volume fraction of the nonmarked particles, $\gamma - \delta\gamma$ is

$$\gamma - \delta\gamma = \frac{V^p - \delta V}{V - \delta V}. \tag{A2.6}$$

Equations (A2.1), (A2.5), and (A2.6) result in the following relation:

$$\delta\gamma = (1-\gamma)\frac{\delta\theta}{1-\delta\theta}, \tag{A2.7}$$

or, keeping only first-order small terms,

$$\delta\theta = \frac{\delta\gamma}{1-\gamma}. \tag{A2.8}$$

The porous structure can now be considered as a mixture of marked particles surrounded by the rest of the porous structure built up by unmarked particles (Figure 1b). Thus, the effective diffusion coefficient can be expressed in two different ways: (1) using the definition in Equation (A2.2) and (2) using "marked particles" with volume fraction $\delta\theta$, surrounded by an effective medium of "unmarked particles" with volume fraction $\gamma - \delta\gamma$. The unknown diffusion coefficient in the effective medium built up by "unmarked particles" according to the definition in Equation (A2.2), is $D(D^m, \gamma - \delta\gamma)$. As the effective diffusion coefficient does not depend on how it is calculated, it yields the following equation:

$$D(D^m, \gamma) = D(D(D^m, \gamma - \delta\gamma), \delta\theta). \tag{A2.9}$$

Using Taylor's series and saving terms of the first-order proportional to $\delta\gamma$ and $\delta\theta$, the latter equation gives

$$\begin{aligned} D(D(D^m, \gamma - \delta\gamma), \delta\theta) = {} & D(D(D^m, \gamma), 0) + \left.\frac{\partial D(D(D^m, \gamma - \delta\gamma), \delta\theta)}{\partial \delta\gamma}\right|_{\substack{\delta\gamma=0 \\ \delta\theta=0}} \delta\gamma \\ & + \left.\frac{\partial D(D(D^m, \gamma - \delta\gamma), \delta\theta)}{\partial \delta\theta}\right|_{\substack{\delta\gamma=0 \\ \delta\theta=0}} \delta\theta. \end{aligned} \tag{A2.10}$$

Equation (A2.10) can be simplified using the condition in Equation (A2.3):

$$D(D(D^m, \gamma), 0) = D(D^m, \gamma). \tag{A2.11}$$

The combinations of Equations (A2.3) and (A2.2) results in

$$\begin{aligned} \left.\frac{\partial D(D(D^m, \gamma - \delta\gamma), \delta\theta)}{\partial \delta\theta}\right|_{\substack{\delta\gamma=0 \\ \delta\theta=0}} & = \left.\frac{\partial D(D(D^m, \gamma), \delta\theta)}{\partial \delta\theta}\right|_{\delta\theta=0} \\ & = \left.\frac{\partial D(D^{eff}, \gamma)}{\partial \delta\theta}\right|_{\delta\theta=0} \\ & = A^{diffusion}(D^{eff}). \end{aligned} \tag{A2.12}$$

The condition in Equation (A2.3) gives

$$\begin{aligned} & \left.\frac{\partial D(D(D^m, \gamma - \delta\gamma), \delta\theta)}{\partial \delta\gamma}\right|_{\substack{\delta\gamma=0 \\ \delta\theta=0}} = \left.\frac{\partial D(D(D^m, \gamma - \delta\gamma), 0)}{\partial \delta\gamma}\right|_{\delta\gamma=0} \\ & = \left.\frac{\partial D(D^m, \gamma - \delta\gamma)}{\partial \delta\gamma}\right|_{\delta\gamma=0} = -\frac{\partial D(D^m, \gamma)}{\partial \gamma} = -\frac{dD^{eff}}{d\gamma} \end{aligned} \tag{A2.13}$$

Substitution of Equations (A2.11)–(A2.13) into Equation (A2.10) gives

$$0 = A^{diffusion}(D^{eff})\delta\theta - \frac{dD^{eff}}{d\gamma}\delta\gamma. \tag{A2.14}$$

Substitution of Equations (A2.4) and (A2.8) into Equation (A2.14) results in the following differential equation:

$$\frac{dD^{eff}}{d\gamma} = \frac{A^{diffusion}(D^{eff})}{1-\gamma}, \tag{A2.15}$$

with the boundary condition in Equation (A2.3):

$$D^{eff}|_{\gamma=0} = D^m. \tag{A2.16}$$

APPENDIX A3: THE SYSTEM OF PARTIAL DIFFERENTIAL EQUATIONS FOR THE CALCULATION OF THE ELASTIC PROPERTIES OF THE 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 types of inclusions is deduced below using the above-described modified Bruggerman's method.

The volume fraction of inclusions of type k, γ^k, is defined as follows:

$$\gamma^k = \frac{V^k}{V}, \tag{A3.1}$$

here V is the volume of the composite material and V^k is the volume of inclusions of type k ($k = 1, 2, \ldots, M$).

Let h^{eff} be the effective elastic coefficient of the composite material h^m the elastic coefficient of the matrix and h^k the elastic coefficient of the inclusions of type $k(k = 1, 2, \ldots, M)$. The coefficients h^{eff}, h^m, and h^k can be tensors, vector, or scalars (for example, both Young's modulus and Poisson's ratio) depending on the problem under consideration. It is assumed below that the following relation describes the effective elastic coefficients:

$$h_j^{eff} = h_j[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M], \quad j = 1, 2, \ldots, N. \tag{A3.2}$$

Below the index j is dropped as an abbreviation.

In the case $\gamma^1 = \gamma^2 = \cdots = \gamma^M = 0$ (no inclusion), Equation (A3.2) results in

$$h^m = h[h^m, h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0]. \tag{A3.3}$$

which is used below as the boundary condition. In the case $\gamma^i = 0$ $(i = 1, 2, \ldots, \mathrm{k}-1, \mathrm{k}+1, \ldots, \mathrm{M})$ (only inclusions of type k), Equation (A3.2) results in

$$h^{\mathrm{single},k}[h^m, h^k, \gamma^k] = h[h^m, h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0, \gamma^k, 0, \ldots, 0]. \tag{A3.4}$$

Dependence $A^{\mathrm{single},k}(k = 1, 2, \ldots, \mathrm{M})$ are defined as

$$A^{\mathrm{single},k}(h^m, h^k) = \left.\frac{\partial h^{\mathrm{single}}[h^m, h^k, \delta\gamma^k]}{\partial \delta\gamma^k}\right|_{\delta\gamma^k=0}, (k = 1, 2, \ldots, \mathrm{M}). \tag{A3.5}$$

Let us randomly mark a small number of inclusions of each type. The small volume fractions of the marked inclusions, $\delta\theta^k (k = 1, 2, \ldots, \mathrm{M})$, are equal to

$$\delta\theta^k = \frac{\delta V^k}{V}, \tag{A3.6}$$

where δV^k is the volume of marked inclusions. The volume fraction of the unmarked inclusions are

$$\gamma^k - \delta\gamma^k = \frac{V^k - \delta V^k}{V - \sum\limits_{i=1}^{M} \delta V^i}. \tag{A3.7}$$

Equations (A3.1), (A3.6) and (A3.7) result in

$$\delta\gamma^k = \frac{\left(\delta\theta^k - \gamma^k \sum\limits_{i=1}^{M} \delta\theta^i\right)}{1 - \sum\limits_{i=1}^{M} \delta\theta^i}, \tag{A3.8}$$

or, neglecting the small volume fractions of higher order,

$$\delta\gamma^k = \delta\theta^k - \gamma^k \sum_{i=1}^{M} \delta\theta^i. \tag{A3.9}$$

The composite material can be treated now as a mixture of marked inclusions surrounded by an effective medium with unmarked inclusions. Thus, the effective elastic coefficients of the composite material, h^{eff}, can be expressed in two different ways: (1) according to the definition in Equation (A3.2), and (2) using "marked" inclusions (with the volume fractions $\delta\theta^k,\ k = 1, 2, \ldots, M$) surrounded by the effective medium with "unmarked" inclusions (with the volume fractions given by Equation (A3.9)). The latter effective medium has the elastic property $h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2, \ldots, \gamma^M - \delta\gamma^M]$ according to the definition in Equation (A3.2).

The coefficients calculated in these two ways should be equal. This results in the following system of equations:

$$\begin{aligned} &h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M] \\ &\quad = h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M], \\ &\qquad h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M], \end{aligned} \tag{A3.10}$$

The system of Equations (A3.10) is transformed below using the Taylor series with small parameters $\delta\gamma$ and $\delta\theta$:

$$\begin{aligned} &h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M], \\ &\quad h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M] \\ &\quad = h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M], h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0] \\ &\qquad + \sum_{k=1}^{M} \frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M],}{\partial\delta\theta^k} \\ &\qquad \times \left. \frac{h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\theta^k} \right|_{\substack{\delta\theta=0 \\ \delta\gamma=0}} \delta\theta^k \\ &\qquad + \sum_{k=1}^{M} \frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M],}{\partial\delta\gamma^k} \\ &\qquad \times \left. \frac{h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\gamma^k} \right|_{\substack{\delta\theta=0 \\ \delta\gamma=0}} \delta\gamma^k. \end{aligned} \tag{A3.11}$$

In the latter equation, and below, the following abbreviation, ${}^{\delta\theta=0}_{\delta\gamma=0}$, stands for

$$\begin{aligned} \delta\theta^1 = \cdots = \delta\theta^M = 0 \\ \delta\gamma^1 = \cdots = \delta\gamma^M = 0 \end{aligned}.$$

Equation (A3.11) can be simplified using the relations in Equations (A3.3) and (A3.2):

$$\begin{aligned} &h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M], h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0] \\ &\quad = h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M] = h^{eff}. \end{aligned} \tag{A3.12}$$

The combination of Equations (A3.3)–(A3.5) results in

$$\frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M],}{\partial\delta\gamma^k}$$

$$\times \frac{h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\theta^k}\Bigg|_{\substack{\delta\theta=0\\ \delta\gamma=0}}$$

$$= \frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M], h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\theta^k}\Bigg|_{\delta\theta=0}$$

$$= \frac{\partial h^{single}[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M], h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\theta^k}\Bigg|_{\delta\theta^k=0}$$

$$= A^{single,k}(h^{eff}, h^k). \tag{A3.13}$$

Equations (A3.4) and (A3.2) give

$$\frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M],}{\partial\delta\gamma^k}$$

$$\times \frac{h^1, h^2, \ldots, h^M, \delta\theta^1, \delta\theta^2, \ldots, \delta\theta^M]}{\partial\delta\gamma^k}\Bigg|_{\substack{\delta\theta=0\\ \delta\gamma=0}}$$

$$= \frac{\partial h[h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M],}{\partial\delta\gamma^k}$$

$$\times \frac{h^1, h^2, \ldots, h^M, 0, 0, \ldots, 0]}{\partial\delta\gamma^k}\Bigg|_{\delta r=0}$$

$$= \frac{\partial h[h^m, h^1, h^2, \ldots, h^M, \gamma^1 - \delta\gamma^1, \gamma^2 - \delta\gamma^2, \ldots, \gamma^M - \delta\gamma^M]}{\partial\delta\gamma^k}\Bigg|_{\delta r=0}$$

$$= \frac{\partial h[h^m, h^1, h^2, \ldots, h^M, \gamma^1, \gamma^2, \ldots, \gamma^M]}{\partial\delta\gamma^k} = \frac{\partial h^{eff}}{\partial\gamma^k}. \tag{A3.14}$$

Now Equation (A3.11) can be simplified using Equations (A3.12)–(A3.14) as follows:

$$0 = \sum_{k=1}^{M} A^{\mathrm{single},k}(h^{eff}, h^k)\delta\theta^k - \sum_{k=1}^{M} \frac{\partial h^{eff}}{\partial\gamma^k}\delta\gamma^k \tag{A3.15}$$

The "marked" inclusions are selected randomly, therefore the small volume fractions, $\delta\theta^i (i = 1, 2, \ldots, \mathrm{M})$, are independent. Therefore, Equation (A3.9) after substitution in Equation (A3.15) and collecting terms proportional to $\delta\theta^k$ results in

$$0 = A^{\text{single},k}(h^{eff}, h^k) - \frac{\partial h^{eff}}{\partial \gamma^k} + \sum_{i=1}^{M} \frac{\partial h^{eff}}{\partial \gamma^i}\gamma^i, \; k = 1, 2, \ldots, \mathrm{M}. \tag{A3.16}$$

Multiplying Equations (A3.16) by γ^k and summation over k yields

$$\sum_{i=1}^{M} \frac{\partial h^{eff}}{\partial \gamma^i}\gamma^i = \frac{\sum_{i=1}^{M} A^{\text{single},i}(h^{eff}, h^i)\gamma^i}{1 - \sum_{i=1}^{M}\gamma^i}. \tag{A3.17}$$

Substitution of Equation (A3.17) into Equation (A3.16) results in the following system of differential equations:

$$\frac{\partial h^{eff}}{\partial \gamma^k} = A^{\text{single},k}(h^{eff}, h^k) + \frac{\sum_{i=1}^{M} A^{\text{single},i}(h^{eff}, h^i)\gamma^i}{1 - \sum_{i=1}^{M}\gamma^i}, \; k = 1, 2, \ldots, M. \tag{A3.18}$$

The effective elastic coefficients of the composite material, h^{eff}, can be calculated as solutions of the system of nonlinear partial differential Equations (A3.18) with the boundary conditions deduced from the condition in Equation (A3.3)

$$h^{eff}\Big|_{\gamma^1=\gamma^2=\cdots=\gamma^M=0} = h^m. \tag{A3.19}$$

NOMENCLATURE

a	radius of particles (droplets)
C	concentration
D	diffusion coefficient
E	Young's modulus
h	elastic moduli of composite material
Q, G	integrating constants
R	radius of cell
u	displacement
V	volume

Greek Symbols

ε	dielectric permeability or deformation
η	viscosity
γ	volume fraction of particles/droplets
ϕ	porosity
μ	elastic shear modulus of composite material
ν	determined in Equation (19)

χ	squares deviation
θ	fraction

Superscripts

eff	effective
diffusion	diffusion
single	characteristics of a material with only one type of inclusion
m	matrix (medium)
p	particles (droplets)

Subscripts

max	packing density inside clusters
exp	experimental
calc	calculated

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