Spherical Cell Approach for the Effective Viscosity of Suspensions

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In the present paper, the spherical cell approach is employed for addressing the effective viscosity of suspensions of spherical particles. The proposed derivation is based on the only assumption which constitutes the essence of the spherical cell approach: a representative part of the suspension is a spherical cell which contains a particle surrounded by the continuous phase. In contrast with the previous studies on this topic, no additional assumptions are used in the present analysis. The general method of derivation and the final result, which represents the effective viscosity as a function of the solid-phase volume fraction, are compared with earlier studies where the spherical cell approach was applied for describing the effective viscosity.

1. Introduction

The spherical cell (SC) approach is an approximate method of addressing macroscopically uniform and isotropic media in terms of the parameters describing their microscopic structure. The method is based on the assumption that, at the microscopic level, a representative volume for the medium is a sphere (SC) which, in its center, contains one of the constituting kinetic units (atom, molecule, dispersed particle, etc.). While obtaining macroscopic parameters (dielectric permittivity, conductivity, hydrodynamic permeability, etc.) of a medium, such an assumption enables one to take into account complex multiparticle interactions between the species composing the medium. Despite its heuristic and approximate nature, the SC approach became a classical method for different fields of physics: macroscopic electrodynamics,[1−5] solid-state physics,[6,7] fluid mechanics,[8−11] etc.

During the past several decades, the SC approach has been extensively employed for describing thermodynamic equilibriums,[12−15] dielectric dispersion,[16−18] and electrokinetic phenomena[18−33] in colloid and disperse systems. In the above references, reasonable predictions have been made for very complex systems which can be unlikely addressed using rigorous methods of statistical mechanics.

There are many reasons to expect that the SC approach can also be a good method for studying the role of interfacial forces in rheological behavior of colloid systems. Recently, in two pioneering papers, Ruiz-Reina et al.[34] and Rubio-Hernandez et al.[35] adopted the SC approach for describing the influence of the interfacial electrical forces on the effective viscosity of a concentrated suspension of spherical solid particles. A necessary step in their analysis was to address the hydrodynamic field within the SC at zero interfacial potential, i.e., in the absence of the electrical forces. While considering the respective hydrodynamic problem, the authors faced a dilemma of choosing the correct SC model from two earlier published models (see the work of Simha[8,36] and Happel[9,10]) which led to noticeably different predictions. This dilemma and its solution will be the focus of the present paper.

Prior to discussing the essence the Simha[8,36] and Happel[9,10] models and how Ruiz-Reina et al.[34] and Rubio-Hernandez et al.[35] resolved the dilemma, recall that, for low concentrated suspensions of solid spherical particles, the effective suspension viscosity, η, is described by an expression derived by Einstein nearly a century ago.[37,38]

$$\eta_r = 1 + \frac{5}{2}\phi \tag{1}$$

where the quantity $\eta_r = \eta/\eta_0$ is referred to as the relative viscosity, η_0 is the viscosity of the continuous fluid, and ϕ is the volume fraction of the dispersed hard spherical particles. For suspensions with $\phi < 0.05$, the Einstein prediction has been confirmed in numerous experimental observations summarized and analyzed in different review papers.[36,39−42] For more concentrated suspensions, experiments show a substantially more rapid increase in $\eta(\phi)$ with greater increasing ϕ than that predicted by Einstein.[36,39−42]

During the past century, a tremendous number of theoretical studies have sought to obtain the function $\eta(\phi)$ while accounting for the hydrodynamic interparticle forces ignored in Einstein's theory. These theories were developed using statistical mechanics,[43−60] some phenomenological quasicontinuous methods,[61−67] and the SC approach.[8−10,36]

Using the SC approach, both Simha[8,36] and Happel[9,10] obtained the effective viscosity, η, by equating the relative viscosity, $\eta_r = \eta/\eta_0$, and the ratio of the dissipation rates that are produced within the suspension and within the pure continuous phase (i.e., in the absence of particles). The dissipation rates are determined by integrating the local rates over the representative SC whose radius is set as

$$b = a/\lambda \tag{2}$$

where a is the particle radius and $\lambda = \lambda(\phi)$ is a function of the

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volume fraction, ϕ. To compute the local dissipation rates, it is necessary to determine the hydrodynamic field inside the cell by solving the Stokes and continuity equations subject to boundary conditions at the particle surface and the cell outer boundary. The boundary conditions at the particle surface are common for both the theories: the local velocity $\vec{u}$ is set to be equal to the rotational component of the shear flow velocity, $\vec{u}^{(0)}$, existing in the absence of the particles.

Two major differences between the Simha and Happel theories are noted as follows. First, Happel and Simha use different functions $\lambda(\phi)$ represented in (2).

$$\lambda(\phi) = \frac{(\phi/\phi_{\max})^{1/3}}{2 - (\phi/\phi_{\max})^{1/3}} \quad \text{Simha's model} \tag{3}$$

$$\lambda(\phi) = \phi^{1/3} \quad \text{Happel's model} \tag{4}$$

where, in Simha's equation (eq 3), $\phi_{\max}$ is an adjustable parameter interpreted as the volume fraction corresponding to the close packing, i.e., $0.52 \le \phi_{\max} \le 0.74$.

Happel's definition of b given by eqs 2 and 4 directly follows from the basic assumption that the SC containing one particle is the representative part of the suspension. Clearly, Simha's definition, eqs 2 and 3, is inconsistent with such an assumption. The outer boundary of Simha's SC is drawn to be tangent to the surfaces of the nearest neighbors of a given particle (Figure 1). Consequently, the Simha SC radius $b = R - a$, where $R = 2a_{\max}$ is the distance between the centers of the nearest neighbors; $a_{\max}$ is the particle radius corresponding to the close packing. Realizing that $\lambda = a/b = a/(2a_{\max} - a)$ and assuming that $a/a_{\max} = (\phi/\phi_{\max})^{1/3}$, one obtains eq 3.

The second difference between the Simha and Happel models is that they set different conditions at the SC outer boundary having radius b:

$$\vec{u} = \vec{u}^{(0)} \quad \text{Simha's model} \tag{5}$$

and

$$(\vec{u} - \vec{u}^{(0)})\cdot\vec{n} = 0$$
$$\vec{n} \times (\bar{\bar{\sigma}} - \bar{\bar{\sigma}}^{(0)})\cdot\vec{n} = 0 \quad \text{Happel's model} \tag{6}$$

In eq 6, $\vec{n}$ is the outward normal vector; the stress tensors $\bar{\bar{\sigma}}$ and $\bar{\bar{\sigma}}^{(0)}$ are expressed using the following set of equalities

$$\bar{\bar{\sigma}} = -p\bar{\bar{I}} + \eta_0\bar{\bar{\Delta}} \quad \text{(a)}; \qquad \bar{\bar{\sigma}}^{(0)} = \eta_0\bar{\bar{\Delta}}^{(0)} \quad \text{(b)}$$
$$\bar{\bar{\Delta}} = \vec{\nabla}\vec{u} + (\vec{\nabla}\vec{u})^* \quad \text{(c)}; \qquad \bar{\bar{\Delta}}^{(0)} = \vec{\nabla}\vec{u}^{(0)} + (\vec{\nabla}\vec{u}^{(0)})^* \quad \text{(d)} \tag{7}$$

where p is the local pressure and $\bar{\bar{I}}$ is the unit tensor; the * symbol signifies a transposed tensor, and the superscript 0 denotes a property of the system in the absence of particles.

In their original publications, Simha[8,36] and Happel[9,10] present only qualitative reasons for choosing the proposed boundary conditions. According to Simha, due to the "shielding" effect, which is produced by rigid particles surrounding a given one, the distortion, $\vec{u} - \vec{u}^{(0)}$, of the initial uniform shear flow, $\vec{u}^{(0)}$, does not penetrate through the external boundary (the "cage") formed by the surfaces of the nearest neighbors.[8,36] Such a shielding leads to eq 5. Arguments given by Happel are that boundary conditions 6 reflect the "independency" of the representative cells. Consequently, the first and second of conditions 6 impose zero rates for, respectively, the mass exchange and the friction between the cells.

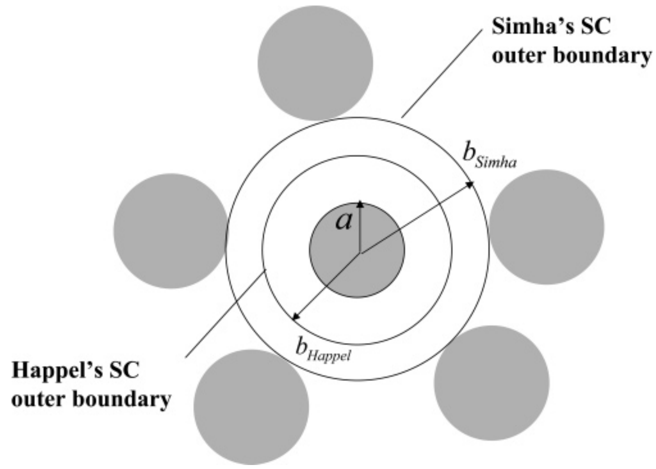

Figure 1. Simha and Happel's spherical cells.

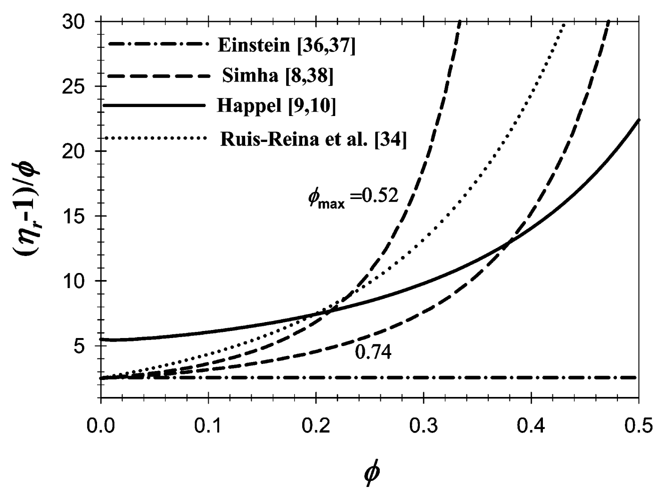

Figure 2. Normalized viscosity increment as function of volume fraction for the Simha, Happel, and hybrid models.

Due to the above-discussed differences, the Simha and Happel theories lead to different expressions for the relative viscosity:

$$\eta_r(\phi,\lambda) = 1 + \phi\frac{10(1 - \lambda^7)}{4(1 + \lambda^{10}) - 25\lambda^3(1 + \lambda^4) + 42\lambda^5} \quad \text{Simha's theory} \tag{8}$$

where the function $\lambda(\phi)$ is given by (3) and

$$\eta_r(\phi) = 1 + \phi\frac{22\phi^{7/3} + 55 - 42\phi^{2/3}}{10(1 - \phi^{10/3}) - 25\phi(1 - \phi^{4/3})} \quad \text{Happel's theory} \tag{9}$$

In Figure 2, the curves, which were plotted according to eqs 1 (Einstein), 3 and 8 (Simha), and 9 (Happel), display the behavior of the normalized viscosity increment, $(\eta_r - 1)/\phi$, as a function of volume fraction. It becomes clear that predictions from different models substantially differ. For low volume fractions, the Simha theory gives a smaller value of the increment, $(\eta_r - 1)/\phi$, than the Happel theory. Remarkably, when $\phi \to 0$, the Simha result approaches the Einstein limit given by eq 1, $(\eta_r - 1)/\phi = 5/2$, whereas the limiting form of Happel's expression, $(\eta_r - 1)/\phi = 11/2$, contradicts the Einstein result. At sufficiently high volume fractions, Simha's result substantially exceeds the prediction from the Happel model.

Ruiz-Reina et al.[34] and Rubio-Hernandez et al.[35] resolved the dilemma of choosing a proper model by proposing a third, hybrid model. The authors used Simha boundary conditions 5 but set them at the outer boundary of the Happel cell whose radius is given by eqs 2 and 4. Consequently, they derived an expression for the relative viscosity, which can be obtained by substituting Happel's equation (eq 4) into Simha's expression (eq 8).

$$\eta_r = 1 + \phi\frac{10(1-\phi^{7/3})}{4(1+\phi^{10/3}) - 25\phi(1+\phi^{4/3}) + 42\phi^{5/3}} \quad (10)$$

Equation 10 gives a third dependency of the relative effective viscosity on volume fraction. The curve plotted in Figure 2 demonstrates that the third concept leads to a prediction which differs from that from both the first and second ones.

In summary, each of the different approaches is based on two assumptions:

(i) A representative part of the suspension is a spherical cell containing a particle surrounded by continuous phase.

(ii) The outer boundary conditions for the hydrodynamic boundary problem, which should be solved inside the SC, are given by either eq 5 (the cage model) or eq 6 (the free surface model).

The first of the above assumptions constitutes the essence of the SC approach and, thus, is unavoidable while using such a method. As for the second assumption, any of two conditions, eqs 5 or 6, are not based on strict arguments. At the same time, the difference in the outer boundary conditions results in a noticeable difference in the predictions of the effective viscosity.

The objective of the present paper is to derive an expression for the effective viscosity by using the first of the above assumptions, only. We will show that no additional assumptions are required to propose a correct form of the outer boundary condition. Using the new derived version of the outer boundary condition, we will obtain expression for the effective viscosity and compare the obtained result with the predictions from the Simha,[8,36] Happel,[9,10] and Ruiz-Reina et al.[34] models.

2. Definition of the Suspension Viscosity

In the present section, we will interrelate the suspension effective viscosity with distributions of the local velocity and pressure inside the representative SC. To this end, we will consider a plane-parallel viscometer and a suspension between the viscometer walls, ABCD and KLMN, separated by the distance h_1 (Figure 3). The distance h_1 is assumed to be much smaller than the linear dimensions of the walls, h_2 and h_3. Simultaneously, h_1 should be much bigger than a length scale parameter characterizing the internal structure of the suspension. For the present case, such a parameter is the SC radius b. Consequently, the following inequalities should be satisfied

$$b \ll h_1 \ll h_{2,3} \quad (11)$$

Let us introduce the Cartesian coordinate system $x_1x_2x_3$, as shown in Figure 3, and consider movement of one viscometer wall (KLMN) with reference to the other (ABCD) with a constant speed $\vec{U} = U\vec{\imath}_2$. Such a movement occurs due to applied external forces, $\vec{F}_{KLMN} = F\vec{\imath}_2 = -\vec{F}_{ABCD}$ to the walls ABCD and KLMN. For any Newtonian fluid confined between the

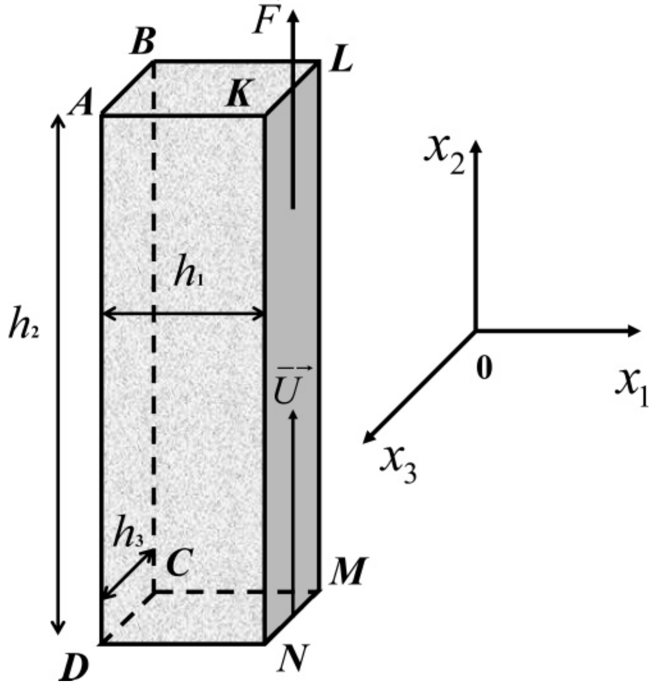

Figure 3. Sketch of a suspension in a plane-parallel viscometer.

walls, under conditions 11, the fluid viscosity is determined by using the measured values of F and U, as

$$\eta = \frac{F/h_2h_3}{U/h_1} \quad (12)$$

where h_3h_2 is the common area of the viscometer walls (Figure 3). Equation 12 will be a starting point for our analysis.

Prior to transforming eq 12 into a convenient form, we will present two useful identities. The first of the identities can be derived by taking into account that, for any point inside the suspension (including the particle bulks)

$$\vec{\nabla}\cdot\bar{\bar{\sigma}} = 0 \quad (13)$$

To understand why eq 13 is valid inside the particle, one can imagine the particle as a fluid with very high viscosity. Using (13), one can prove that, inside the suspension, the following equality is valid for any volume, V, enveloped by a closed surface, S_V.

$$\int_V \sigma_{21}\,dV = \oint_{S_V} x_1\sigma_{2k}\vec{\imath}_k\cdot\overrightarrow{dS} \quad (14)$$

Equation 14 gives the first of the above-mentioned identities. Note that (14) does not contain the particle viscosity and, thus, is valid for the case of solid particles, i.e., when the local inner viscosity takes an infinitely high value.

Making use of definition 7c and realizing that, everywhere inside the suspension, the local velocity, $\vec{u}(\vec{r})$, is a continuous function of the radius vector $\vec{r}$, one obtains

$$\int_V \Delta_{12}\,dV = \vec{\imath}_1\cdot\oint_{S_V}\overrightarrow{dS}\vec{u}\cdot\vec{\imath}_2 + \vec{\imath}_2\cdot\oint_{S_V}\overrightarrow{dS}\vec{u}\cdot\vec{\imath}_1 \quad (15)$$

Thus, eq 15 gives the second of the identities. Detailed derivations of the identities given by eqs 14 and 15 are presented in the Appendix.

While transforming eq 12, identities 14 and 15 will be used twice. First, we will identify V as the whole volume of the suspension ($V = V_{susp}$) confined between the viscometer walls

(Figure 3). Consequently, the enveloping surface, S_V, includes the interfaces between the suspension and the viscometer walls (ABCD and KLMN), and the side surface of the suspension.

Contributions of the integrals over the side surface are of order of $O(h_1/h_3)$ (Figure 3) and thus, for a sufficiently small ratio h_1/h_3, can be ignored. Consequently, realizing that, for the wall-suspension interfaces ABCD and KLMN, $d\vec{S}_{KLMN} = \vec{i}_1\, dS_{KLMN}$ and $d\vec{S}_{ABCD} = -\vec{i}_1\, dS_{ABCD}$, eqs 14 and 15 are specified as

$$\int_{V_{susp}} \sigma_{21}\, dV = h_1 \oint_{S_{KLMN}} \sigma_{21}\, dS \tag{16}$$

$$\int_{V_{susp}} \Delta_{21}\, dV = h_2 h_3 U \tag{17}$$

The condition of zero total force exerted on the wall KLMN (Figure 3) takes the form

$$\oint_{S_{KLMN}} \sigma_{21}\, dS = F \tag{18}$$

Combining (12) and (16)−(18), we arrive at the expected relationship

$$\eta = \frac{\langle \sigma_{21} \rangle_{susp}}{\langle \Delta_{21} \rangle_{susp}} \tag{19}$$

where

$$\langle ... \rangle_{susp} = \frac{1}{h_1 h_2 h_3} \int_{V_{susp}} ...\, dV \tag{20}$$

signifies averaging over the suspension volume. It should be noted that eq 19 is valid for arbitrary suspensions provided that the viscometer geometry satisfies inequality 11.

According to assumption i presented at the end of the Introduction, we will consider the SC having radius b as a representative part of the suspension (Figure 4). This enables us to equate the averages over the suspension and spherical cell volumes

$$\langle \sigma_{21} \rangle_{susp} = \langle \sigma_{21} \rangle_{cell} = \frac{3}{4\pi b^3} \int_{V_{cell}} \sigma_{21}\, dV$$
$$\langle \Delta_{21} \rangle_{susp} = \langle \Delta_{21} \rangle_{cell} = \frac{3}{4\pi b^3} \int_{V_{cell}} \Delta_{21}\, dV \tag{21}$$

To transform the above integrals into surface integrals, we will use identities 14 and 15, once again. However, now, the volume, V, and the enveloping surface, S_V, are identified as the spherical cell volume and its outer boundary, respectively. Consequently, combining (7), (14), (15), and (21) yields

$$\langle \sigma_{21} \rangle_{susp} = \langle \sigma_{21} \rangle_{cell} = \frac{3}{4\pi b^4} \oint_{S_{cell}} \sigma_{2k} x_1 x_k\, dS = \frac{3\eta_0}{4\pi b^4} \oint_{S_{cell}} \left[\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right) x_1^{\,2} + \left(-\frac{p}{\eta_0} + 2\frac{\partial u_2}{\partial x_2} \right) x_1 x_2 + \left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} \right) x_1 x_3 \right] dS \tag{22}$$

and

$$\langle \Delta_{21} \rangle_{susp} = \langle \Delta_{21} \rangle_{cell} = \frac{3}{4\pi b^4} \oint_{S_{cell}} (u_1 x_2 + u_2 x_1)\, dS \tag{23}$$

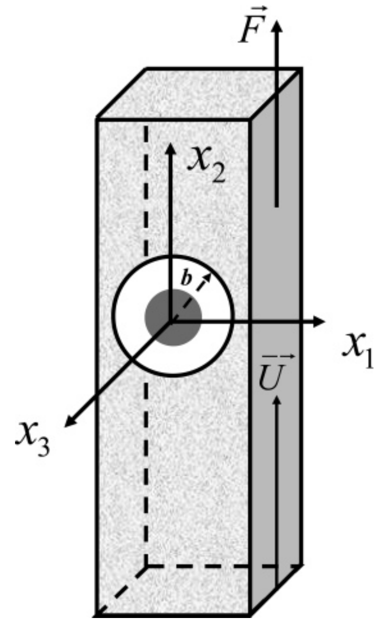

Figure 4. Representative spherical cell inside a plane-parallel viscometer.

Thus, substituting final expressions from eqs 22 and 23 into eq 19 enables one to obtain the effective viscosity.

The above analysis is a generalization of the method used by Landau and Lifshitz[68] in their derivation of Einstein's equation (eq 1). In contrast with the Landau and Lifshitz derivation, the integrals in (22) and (23) are taken over the surface of the sphere having a finite radius, b. To evaluate these integrals, one should know the velocity and pressure distributions inside the SC. Such distributions will be considered next.

3. Hydrodynamic Field and Effective Viscosity for Uncertain Outer Boundary Conditions

To understand how the uncertainty in the outer boundary condition affects the prediction of the effective viscosity, we will obtain the hydrodynamic field inside the cell where the outer boundary condition is not specified.

It is convenient to conduct the analysis by linking the reference system to the center of the particle inside the representative cell (Figure 4). In such a reference system, the particle rotates but does not participate in the translation motion. Due to symmetry reasons, the angular velocity $\vec{\Omega}$ of the particle rotation inside the representative cell can be written in the form

$$\vec{\Omega} = \Omega \vec{i}_3 \tag{24}$$

Thus, inside the cell, the velocity and pressure distributions should satisfy equation set

$$\eta_0 \nabla^2 \vec{u} = \vec{\nabla} p; \quad \vec{\nabla} \cdot \vec{u} = 0 \tag{25}$$

subject to the boundary condition

$$\vec{u} = \vec{\Omega} \times \vec{r} \quad \text{at the particle surface} \tag{26}$$

Solution of equation set 25 can be written using the Lamb expansion in terms of the spherical functions.[69] By assuming an isotropic (spherical) representative cell around a particle, we imply that the presence of the neighboring particles does not change the angular dependency of the velocity and pressure as compared with another isotropic geometry considered by Einstein[37]—a single spherical particle in the shear flow. Therefore, in the Lamb expansion, we retain the spherical functions having the same angular dependency as those employed in Einstein's expression for a single particle.[37] Finally, making use of boundary condition 26, the pressure and velocity can be represented as

$$\vec{u} = B\left[5Y(r/a,A)\frac{x_1x_2}{a^2}\vec{r} + Z(r/a,A)\vec{\nabla}(x_1x_2)\right] + \Omega\vec{\imath}_3 \times \vec{r}$$

$$p = 2B\frac{x_1x_2}{a^2}H(r/a,A) \tag{27}$$

where A, B, and Ω are unknown constants and $Y(r/a,A)$, $Z(r/a,A)$, and $H(r/a,A)$ are the spherically symmetrical functions depending on one of the constants, A.

$$Y(r/a,A) = 4A + \left(\frac{a}{r}\right)^5 - (1 + 4A)\left(\frac{a}{r}\right)^7$$

$$Z(r/a,A) = 21A - 1 - 25A\left(\frac{r}{a}\right)^2 + (1 + 4A)\left(\frac{a}{r}\right)^5$$

$$H(r/a,A) = 5\left[\left(\frac{a}{r}\right)^5 - 21A\right] \tag{28}$$

Thus, eqs 27 and 28 give the velocity and pressure distributions inside the cell for uncertain boundary conditions at the cell border.

It is important that, using respective outer boundary conditions, the distributions given by eqs 27 and 28 are transformed into the functions describing the hydrodynamic field in the Einstein,[37] Simha,[8] or Happel publications.[9] For example, setting at infinity $\vec{u}_{r\to\infty} = \vec{u}^{(0)} = \vec{\imath}_2\omega x_1$ (Einstein's case) gives $A = 0$ and $B = \Omega = \omega/2$. Consequently, eqs 27 and 28 are transformed into the expressions describing the hydrodynamic field around a single spherical particle in the uniform shear flow.[37] As well, after substituting $\vec{u}^{(0)} = \vec{\imath}_2\omega x_1$ into Simha boundary condition 5 and eliminating A, B, and Ω with the help of (5), eqs 27 and 28 give the hydrodynamic field obtained in the paper of Simha.[8] The same substitution ($\vec{u}^{(0)} = \vec{\imath}_2\omega x_1$) into Happel boundary conditions 6 enables one to determine two constants A and B. By setting $\Omega = \omega/2$, eqs 27 and 28 become equivalent to the expression given by Happel.[9]

Now, considering the constants A, B, and Ω as unknown values, we will substitute the velocity and pressure distributions given by eq 27 into the expressions for the averages given by (22) and (23). After some straightforward transformations, one obtains

$$\langle\sigma_{21}\rangle_{\mathrm{susp}} = \langle\sigma_{21}\rangle_{\mathrm{cell}} = \eta_0 B\left[9\left(\frac{b}{a}\right)^2 Y_{r=b} + 2\frac{b^3}{a^2}\left(\frac{\mathrm{d}Y}{\mathrm{d}r}\right)_{r=b} + 2Z_{r=b} + \frac{7}{5}b\left(\frac{\mathrm{d}Z}{\mathrm{d}r}\right)_{r=b} - \frac{2}{5}\left(\frac{b}{a}\right)^2 H_{r=b}\right]$$

$$\langle\Delta_{21}\rangle_{\mathrm{susp}} = \langle\Delta_{21}\rangle_{\mathrm{cell}} = 2B\left[\left(\frac{b}{a}\right)^2 Y_{r=b} + Z_{r=b}\right] \tag{29}$$

Subsequently, combining eqs 19, 28, and 29, we arrive at a surprisingly simple result for the relative viscosity, $\eta_{\mathrm{r}} = \eta/\eta_0$

$$\eta_{\mathrm{r}} = 1 + \frac{5\lambda^3}{2[1 - \lambda^3 + 21A(\lambda^{-2} - 1)]} \tag{30}$$

where, according to (2), $\lambda = a/b$.

It is interesting to note that, according to eq 30, η_{r} depends on one of the uncertain constants (A) only, i.e., η_{r} is independent of the two other constants (B and Ω) represented in (27). Such an independency reflects the Newtonian behavior of the suspension. It can be shown that the constants B and Ω are defined by the imposed velocities of the viscometer walls and/or the forces asserted on the walls. Hence, because the Newtonian fluid viscosity is independent of a viscometer working regime, then the function $\eta_{\mathrm{r}}(\lambda)$ should be independent of B and Ω as well.

Thus, for obtaining the effective viscosity, there is no need to use all the three of Simha's (or Happel's) outer boundary condition eqs 5 (or eqs 6). For determining the single unknown constant, A, it is sufficient to set only one condition. The correct form of such a single boundary condition will be derived next.

4. Outer Boundary Condition

The derivation proposed below will be based on the equality between the power consumed by the viscometer (Figure 3) from external sources and the power being dissipated inside the suspension. Such an equality can be written in the form

$$FU = h_1h_2h_3\langle w\rangle_{\mathrm{susp}} \tag{31}$$

The left-hand side of (31) is the work produced by the external forces (Figure 3) per unit time. The right-hand side gives dissipation which is expressed through the volume mean value of the local dissipation rate, w.

$$w = \frac{\eta_0}{2}\bar{\bar{\Delta}}:\bar{\bar{\Delta}} \tag{32}$$

The latter equality is valid everywhere within the suspension including the particles (where $w \equiv 0$).

Combining eqs 16−18 and 20, the left-hand side of (31) can be rewritten as

$$FU = h_1h_2h_3\langle\sigma_{21}\rangle_{\mathrm{susp}}\langle\Delta_{21}\rangle_{\mathrm{susp}} \tag{33}$$

Hence, power balance 31 takes a simple form

$$\langle\sigma_{21}\rangle_{\mathrm{susp}}\langle\Delta_{21}\rangle_{\mathrm{susp}} = \langle w\rangle_{\mathrm{susp}} \tag{34}$$

Now, following assumption i given in the end of Introduction, we will replace the averaging over the suspension volume by the averaging over the SC volume. Consequently, using (32) and (34), one obtains

$$\langle\sigma_{21}\rangle_{\mathrm{cell}}\langle\Delta_{21}\rangle_{\mathrm{cell}} = \frac{\eta_0}{2}\langle\bar{\bar{\Delta}}:\bar{\bar{\Delta}}\rangle_{\mathrm{cell}} \tag{35}$$

Thus, eq 35 gives the general expression for the required boundary condition.

Remarkably, both the right- and left-hand sides of (35) are proportional to B^2 which is thus canceled out. Since the rotation with a constant angular velocity does not lead to additional dissipation, both sides of eq 35 do not depend on the constant Ω. Hence, eq 35 depends on one unknown constant, A, only. In the next section, we will determine A by solving the algebraic equation which follows from eq 35 and substitute A into eq 30 for obtaining the relative viscosity.

5. Final Result

Let us now substitute the solution given by eq 27 into condition 35. Note that both the multipliers on the left-hand side of (35) are already found (see eq 29). To determine the right-hand side of eq 35, we will consider the transformation of the integral over the cell volume into the cell surface integral. Such a transformation, which can be found elsewhere,[10] yields

$$\langle\bar{\bar{\Delta}}:\bar{\bar{\Delta}}\rangle_{\text{cell}} = \frac{3}{8\pi b^3}\int_{V_{\text{cell}}-V_{\text{paricle}}} \bar{\bar{\Delta}}:\bar{\bar{\Delta}}\ \mathrm{d}V = \frac{3}{8\pi b^4}\oint_{S_{\text{cell}}} (\vec{u} - \Omega\vec{\imath}_3 \times \vec{r})\cdot\sigma\cdot\vec{r}\ \mathrm{d}S \quad (36)$$

Combining (7), (27), and (36), after some straightforward transformations, one obtains

$$\langle\bar{\bar{\Delta}}:\bar{\bar{\Delta}}\rangle_{\text{cell}} = B^2\left\{30\left(\frac{b}{a}\right)^4 Y_{r=b}{}^2 + 5\frac{b^5}{a^4}\left(\frac{\mathrm{d}Y^2}{\mathrm{d}r}\right)_{r=b} + 4Z_{r=b}{}^2 + \frac{7}{5}b\left(\frac{\mathrm{d}Z^2}{\mathrm{d}r}\right)_{r=b} + 22\frac{b^2}{a^2}Y_{r=b}Z_{r=b} + 4\frac{b^3}{a^2}\left[\frac{\mathrm{d}(YZ)}{\mathrm{d}r}\right]_{r=b} - \frac{2}{5}\left(\frac{b}{a}\right)^2 H_{r=b}\left[5Y\left(\frac{b}{a}\right)^2 + 2Z\right]_{r=b}\right\} \quad (37)$$

Now, we will substitute the terms given by (29) and (37) into condition 35. Consequently, using eqs 4 and 27, after rearrangement, eq 35 becomes

$$[A\lambda^{-2}(16\lambda^7 + 19) - 4\lambda^3(1 - \lambda^2)]Y_{r=b} = 0 \quad (38)$$

The multiplayer given in brackets cannot be zero. Otherwise, for sufficiently low volume fractions, $A = 4\lambda^5/19 + O(\lambda^7)$. Consequently, making use of (30), we obtain $\eta_r = 1 + 5\lambda^3[1 - 64\lambda^3/19 + O(\lambda^5)]/2 < 1 + 5\phi/2$. The latter inequality is obtained while expressing λ from either eq 3 or eq 4. Thus, assuming a zero value for the expression in brackets in (38), one obtains a decreased relative viscosity as compared with the Einstein result, eq 1. Note that, in Einstein's papers,[37,38] the relative viscosity increment, $\eta_r - 1$, is determined from the excess energy dissipation rate which is considered as a sum of independent contributions due to the shear flow distortions by individual particles. Accounting for the hydrodynamic interactions between the particles should always lead to an increasing dissipation rate (for fixed velocities of the viscometer walls) as compared with Einstein's approximation.[70] The latter is a fundamental rule which, as we see, is violated when the expression in the brackets takes a zero value. Consequently, eq 38 leads to the following condition

$$Y_{r=b} = 0 \quad (39)$$

Using (4), (28), and (39), one obtains the constant A as

$$A = -\frac{1}{4}\lambda^5\frac{1 - \lambda^2}{1 - \lambda^7} \quad (40)$$

Substituting (40) into (30), after minor rearrangement, gives

$$\eta_r(\lambda) = 1 + \lambda^3\frac{10(1 - \lambda^7)}{4(1 + \lambda^{10}) - 25\lambda^3(1 + \lambda^4) + 42\lambda^5} \quad (41)$$

Thus, eq 41 gives an expression for the relative viscously as a function of the ratio of the particle to cell radius, λ. Surprisingly, the right-hand side of (41) nearly coincides with the Simha result given by eq 8. The only difference between eqs 8 and 40 is that eq 8 contains the multiplier ϕ before the second term on the right-hand side whereas, at the same place, eq 40 contains multiplayer λ^3 which, within the framework of Simha's concept, is not equal to ϕ, eq 3.

As it was mentioned in the Introduction, Simha's relationship (eq 3) contradicts the main assumption of the SC approach that the SC is a representative part of the suspension. Such an assumption dictates the use of Happel's equation (eq 4). Consequently, substituting (4) into (41), we arrive at eq 10.

Thus, using the basic assumption of the SC approach (the SC is a representative part of a suspension) only, the derivation presented in this paper leads to the expression for effective viscosity, eq 10, which, using another method, was derived by Ruiz-Reina et al.[34] and Rubio-Hernandez et al.[35] who assumed that Simha's cage boundary conditions should be set at the external boundary of Happel's SC (Figure 1).

6. Discussion

In the previous sections, using the SC approach, we derived an expression, eq 41, which describes the relative viscosity, η_r, of a suspension of spherical solid particles as a function of the ratio of the particle to the SC radius, λ. The proposed derivation is based only on the assumption that the representative part of the suspension is a sphere containing a single particle in the center. In contrast with earlier publications of Simha,[8,36] Happel,[9,10] Ruiz-Reina et al.,[34] and Rubio-Hernandez et al.,[35] who additionally assumed a certain form of the boundary conditions at the cell outer boundary, our derivation does not deal with any additional assumptions.

Our general method of predicting the viscosity differs from that presented in the above cited works.[8−10,34,35,37] In particular, within the framework of the approach presented in this study, only one unknown constant should be obtained from the outer boundary condition, whereas, in the previous studies,[8−10,34,35,37] it was necessary to determine three constants. Consequently, our analysis deals with one outer boundary condition, only, instead of the three conditions set in the cited papers. The general form of such a single outer boundary condition, eq 35, was derived using the same assumption that the SC is a suspension representative part.

The dependency of the relative viscosity, η_r, on the volume fraction, ϕ, is determined by combining the final result, eq 41, with the expression for the function $\lambda(\phi)$ given by eq 4. Despite all the differences between the approaches, after such a substitution, the obtained function $\eta_r(\phi)$ turns out to be completely equivalent to that given by eq 10 derived earlier by Ruiz-Reina et al.[34] and Rubio-Hernandez et al.[35] who set the cage boundary condition of Simha, eq 3, at the external boundary of Happel's SC. To understand the reasons for such an agreement, let us discuss the cage model in light of the analysis conducted in the previous sections.

Revisiting the Cage Model. Inspecting Figures 3 and 4, the initial shear flow $\vec{u}^{(0)}$, which is represented in Simha's condition (eq 5), is written as $\vec{u}^{(0)} = \vec{\imath}_2\omega x_1$ where $\omega = U/h_1$. Hence, using the Cartesian coordinate system shown in Figures 3 and 4, the cage condition giving single vector eq 5 is equivalent to a set of the following three scalar boundary conditions

$$\begin{aligned} u_1 &= 0 && \text{(a)} \\ u_2 &= \omega x_1 && \text{(b)} \quad \text{at the cell boundary} \\ u_3 &= 0 && \text{(c)} \end{aligned} \quad (42)$$

Remarkably, the newly derived boundary condition, eq 35, is equivalent to the third of the cage conditions, eq 42c. The latter can be demonstrated by combining eq 39, which follows from condition 35, with the velocity distribution given by (27).

Within the framework of the method employed in the present paper, it was sufficient to set condition 42c, only. Therefore, two other cage conditions, (42a) and (42b), were not in use. The requirement to specify all the three outer boundary conditions is peculiar to the dissipation method utilized in previous theories.[8−10,34,35,37] The dissipation method is based on the relative viscosity definition through dissipation, as

$$\eta_r = \left(\frac{\langle w\rangle_{\rm susp}}{\langle w^{(0)}\rangle_{\rm susp}}\right)_{U={\rm const}} \tag{43}$$

where $w^{(0)}$ is the local dissipation rate observed in the absence of the particles. It should be stressed that the condition of constant relative velocity of the viscometer walls, U, is important for the validity of eq 43. For example, while considering the dissipation rates under the condition of the constant force, F, exerted on the walls (Figure 3), the relative viscosity is given by inversion of the fraction on the right-hand side of (43)

$$\eta_r = \left(\frac{\langle w^{(0)}\rangle_{\rm susp}}{\langle w\rangle_{\rm susp}}\right)_{F={\rm const}} \tag{44}$$

Thus, while obtaining the effective viscosity from eq 43, the hydrodynamic field inside the cell should satisfy the condition of a given relative velocity of the viscometer walls. It can be shown that the role of the two cage conditions, (42a) and (42b), is to impose a constant magnitude of the wall relative velocity, U. To demonstrate that, we will combine eqs 17, 20, 29, and 39 (or, equivalently, eq 42c)

$$(U/h_1)_{u_3} = 0 = (\langle\Delta_{21}\rangle_{\rm susp})_{u_3=0} = (\langle\Delta_{21}\rangle_{\rm cell})_{u_3=0} = 2BZ_{r=b} \tag{45}$$

Making use of 27, 39, and 45, the first and second velocity components become

$$u_1 = \left(\frac{U}{2h_1} - \Omega\right)x_2$$
$$u_2 = \left(\frac{U}{2h_1} + \Omega\right)x_1 \quad \text{at the cell boundary} \tag{46}$$

Under condition $h_1/h_2 \ll 1$ (Figure 3), using the Stokes theorem leads to the following equality

$$\oint_{S_{\rm cell}} {\rm d}S\ \vec{\imath}_3\cdot\vec{\nabla}\times\vec{u} = Uh_2 \tag{47}$$

Integrating both sides of (47) over the coordinate x_3 within the suspension volume yields

$$\vec{\imath}_3\cdot\langle\vec{\nabla}\times\vec{u}\rangle_{\rm susp} = U/h_1 \tag{48}$$

where, while deriving eq 48, we used eq 20. Utilizing the basic assumptions of the SC approach, we will equate the averages over the suspension and cell volumes. Consequently, after substituting the velocity distribution given by (27) into (48), one obtains

$$\vec{\imath}_3\cdot\langle\vec{\nabla}\times\vec{u}\rangle_{\rm susp} = \vec{\imath}_3\cdot\langle\vec{\nabla}\times\vec{u}\rangle_{\rm cell} = 2\Omega \tag{49}$$

Introducing the notation $\omega = U/h_1$ and comparing (48) and (49) give

$$\Omega = U/2h_1 = \omega/2 \tag{50}$$

Finally, combining eqs 46 and 50 and taking into account that $\vec{u}^{(0)} = \vec{\imath}_2\omega x_1$, one obtains the cage boundary conditions 42a and 42b.

Thus, we arrive at a new understanding of the cage model. The boundary conditions set by eqs 42a, 42b, and 42c or, equivalently, by eq 5 do not require us to interpret the cell boundary as a rigid wall of a cage.[8,10,38] The origin of the conditions is the *basic* property of the SC as a representative part of the suspension. Accordingly, boundary condition 42c provides the equality between the average dissipation rates over the suspension and representative cell volumes. Boundary conditions 42a and 42b are set to impose the specific regime of viscosity measurements: an unchanged velocity of the viscometer walls, in the case.

Considering another regime of viscosity measurements (for example, an unchanged force exerted on the viscometer walls, F = constant), boundary condition 42c remains the same, whereas, instead of (42a) and (42b), one should set two other conditions (for example, conditions of zero changes in the applied force). For the above-mentioned case of the unchanged force, the final expression for the viscosity, which is obtained from eq 44 (instead of eq 43), takes the same form given by eq 10.

Thus, any analysis, which is consistently based on the assumption that the SC is a representative part of the suspension, should lead to eq 10. The deviations of the Simha and Happel results from eq 10 originate from inconsistencies with such an assumption. In the case of Simha's theory, the inconsistency amounts to using eq 3 which clearly contradicts the assumption. Note that using the consistent relationship between λ and ϕ (eq 4, instead of eq 3) also leads to eq 10. As for Happel's free surface model, the inconsistencies are associated with boundary conditions 6.

Critics of the "Free Surface" Model. Clearly, while using boundary conditions 6, the obtained hydrodynamic field does not satisfy boundary condition 42c and, hence, the equivalents of eq 42c given by eqs 35 or 39. Thus, Happel's boundary conditions lead to a violation of the dissipation balance which is expressed by eq 35. It is interesting to note that one of the reasons presented by Happel to argue the validity of boundary conditions 6 was that the consumed power should be dissipated by equal portions within each of the SC's constituting the suspensions.[9] As shown in section 3, it is eq 35 that gives mathematical formulation for such a principle, not Happel's conditions (eq 6).

As mentioned in the Introduction, at low volume fractions, the asymptotic behavior of the function $\eta_r(\phi)$ given by Happel's equation (eq 9), $\eta_r(\phi) = 1 + 11\phi/2 + O(\phi^2)$, disagrees with Einstein's equation (eq 1). It can be shown that the non-Einsteinian asymptotic behavior of Happel's function $\eta_r(\phi)$ is caused by the violation of the dissipation balance (eq 35). To demonstrate this, we will consider the comments which are presented in the Happel and Brenner book[10] regarding the disagreement.

According to Happel and Brenner,[10] for the limiting case of $\phi \to 0$, the hydrodynamic field obtained by Happel[9,10] exactly coincides with that obtained by Einstein, but for the same limiting case, the corresponding dissipation rates predicted by the two theories differ. In terms of the unknown constant A represented in eqs 27 and 28, the latter means that, in Einstein's theory, it is a priori assumed that $A = 0$ whereas, in Happel's theory, A takes a nonzero value which, however, approaches zero when $\phi \to 0$. The terms, which are proportional to A, are missing in the expression for Einstein's hydrodynamic field and, obviously, do not contribute to the dissipation rates. In the expression for Happel's hydrodynamic field, the terms proportional to A are presented and bring nonzero contributions into the dissipation rate. Paradoxically, at $\phi \rightarrow 0$, such a contribution takes a nonzero (positive) value although $A \rightarrow 0$. The latter manifests itself in the increased (as compared with the Einstein result) relative viscosity given by Happel's equation (eq 9).

Having discussed the above described paradoxical behavior, Happel and Brenner[10] expressed a point of view that there are no rational reasons to prefer Einstein's choice for A ($A = 0$) over A obtained by using boundary conditions 6. The analysis conducted in the present paper gives such a reason. Using boundary condition 35, which establishes a balance between the consumed and dissipated powers, we confirmed the validity of eq 10 whose asymptotic behavior at low volume fractions agrees with the Einstein result (Figure 2). At the same time, Happel's hydrodynamic field does not satisfy the dissipation balance given by eq 35 and, at low volume fractions, the dissipation rate attributed to Happel's field is higher than the consumed power. Such an overprediction of the dissipation leads to an overprediction of the effective viscosity as $\phi \rightarrow 0$ (Figure 2).

At sufficiently high volume fractions, the dissipation rate obtained from Happel's hydrodynamic field becomes lower than the consumed power. Therefore, for higher volume fractions, Happel's theory underpredicts the effective viscosity (Figure 2).

One should also mention an additional inconsistency associated with the Happel model. Obtaining viscosity on the basis of eq 43 (employed in Happel's theory) requires us to set conditions 42a and 42c which, as shown above, set the regime of a constant relative velocity of the viscometer walls. Happel's conditions (eq 6) contradict (42a) and (42c) and, thus, do not satisfy the necessary requirements for using eq 43 as the viscosity definition.

Comparison with Experiment. During the past century, results of measuring the effective viscosity of suspensions as a function of the solid-phase volume fraction have been reported in a very large number of publications. There is a substantial spread in the data presented by different authors. In some review papers, the authors conducted statistical analysis of the available date to present "average" results. It should be noted that such average dependencies $\eta_r(\phi)$ reported in different review papers noticeably differ, as well.

To compare the prediction given by eq 10 with the experiment, we present the resulting points of Rutgers[40] and Thomas[41] who statistically analyzed large arrays of experimental data (Figure 5). More recent experimental results collected by Liu and Masliyah[42] are mostly spread within the plot area bound by the Rutgers and Thomas data points.

Due to the nature of the SC approach, one can expect reasonable predictions when the volume fraction is sufficiently lower than that corresponding to close packing. Accordingly, in Figure 5, we presented the data for $\phi \leq 0.6$. At higher volume fractions, eq 10 substantially underpredicts the relative viscosity, η_r.

The plots in Figure 5 shows that eqs 10 or 41 give good predictions when $\phi \leq 0.1$. For $0.1 \leq \phi \leq 0.55$, the observed deviations from the Rutgers and Thomas data are confined within 30% and 100%, respectively. Note that the plots in Figure 5 are given for the normalized viscosity increment $(\eta_r - 1)/\phi$. With respect to the relative viscosity η_r, the maximum deviations are reduced to 10% and 40%, respectively.

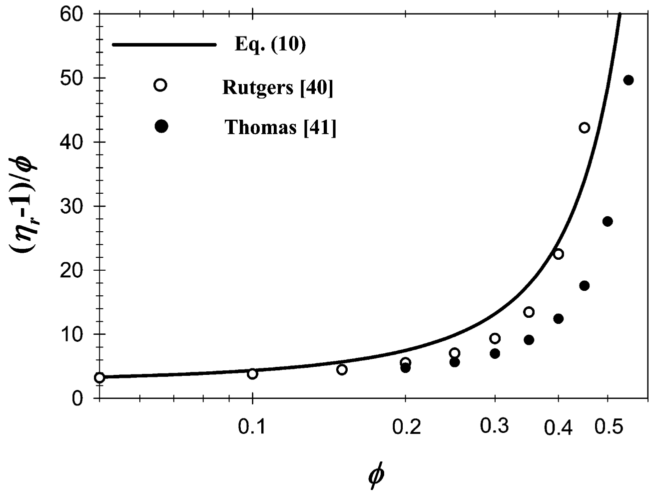

Figure 5. Normalized viscosity increment as function of volume fraction—comparison with experimental data.

7. Conclusions

(1) The analysis given in the present paper shows that, using the spherical cell approach, the effective viscosity of a suspension of spherical particles is determined on the basis of only one assumption: a representative part of the suspension is a spherical cell containing a particle surrounded by the continuous phase. Additional assumptions that were used in previous theories[8−10,34,35,37] about the outer boundary conditions are unnecessary.

(2) Within the framework of the proposed derivation, for obtaining the expression for the effective viscosity as a function of the solid phase volume fraction, it is sufficient to set only one condition at the cell external boundary. The form of such a single condition, eq 35, is not assumed a priori but derived by equating the dissipation rate inside the suspension and the power consumed by the viscometer from an external source.

(3) The derived expression for the effective viscosity differs from those of Simha[8] and Happel[9] and is equivalent to the result obtained by Ruiz-Reina et al. [34] and Rubio-Hernandez et al.[35] who set Simha's cage conditions (eq 5) at the outer boundary of Happel's cell.

(4) The concept of the cage boundary conditions was elucidated. One of the cage conditions, eq 42c, is equivalent to the dissipation balance condition, eq 35, derived in the present paper. The two other cage conditions, eqs 42a and 42b, set the relative velocity of the viscometer walls to be constant. The latter is a necessary condition for the validity of eq 43 which is employed in the publications of Simha,[8] Happel,[9] Ruiz-Reina et al.,[34] and Rubio-Hernandez et al.[35]

(5) It was shown that, at low volume fractions, Happel's outer boundary conditions lead to overestimation of the dissipation rate as compared with the consumed power. For high dilutions, such an overestimation results in an overprediction of the viscosity and thus in deviation of Happel's result from Einstein's asymptotic expression. Using the dissipation balance given by (35) as the outer boundary conditions, one obtains expression 10 whose asymptotic behavior agrees with the Einstein result.

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the 100th anniversary of the classical paper of A. Einstein: Eine neue Bestimmung der Molek üldimensionen. *Ann. Phys*. **1906,** *19*, 289.

Appendix. Derivation of Identities Given by Equations 14 and 15

Derivation of Equation 14. Let us consider a chain of identities

$$\vec{\nabla}\cdot(\vec{\imath}_k\sigma_{2k}x_1) = \vec{\imath}_n\cdot\vec{\imath}_k\frac{\partial}{\partial x_n}(\sigma_{2k}x_1) = \frac{\partial}{\partial x_k}(\sigma_{2k}x_1) = x_1\frac{\partial\sigma_{2k}}{\partial x_k} + \sigma_{21} = \sigma_{21} \quad \text{(A1)}$$

While obtaining the latter equality in (A1), we took into account eq 13 which yields

$$\partial\sigma_{2k}/\partial x_k = 0 \quad \text{(A2)}$$

Consequently, using (A1)

$$\int_V\sigma_{21}\,\mathrm{d}V = \int_V\vec{\nabla}\cdot(\vec{\imath}_k\sigma_{2k}x_1)\,\mathrm{d}V \quad \text{(A3)}$$

Using the Gauss theorem for the integral on the right side of (A3), we arrive at eq 14.

Derivation of Equation 15. Straightforward transformations give

$$\vec{\imath}_1\cdot\nabla\vec{u}\cdot\vec{\imath}_2 = \vec{\imath}_1\cdot\vec{\imath}_k\vec{\imath}_n\cdot\vec{\imath}_2\frac{\partial u_n}{\partial x_k} = \frac{\partial u_2}{\partial x_1}$$
$$\vec{\imath}_2\cdot\nabla\vec{u}\cdot\vec{\imath}_1 = \vec{\imath}_2\cdot\vec{\imath}_k\vec{\imath}_n\cdot\vec{\imath}_1\frac{\partial u_n}{\partial x_k} = \frac{\partial u_1}{\partial x_2} \quad \text{(A4)}$$

Using (A4), one obtains

$$\int_V\left(\frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_2}\right)\mathrm{d}V = \vec{\imath}_1\cdot\int_{V_{\text{cell}}}\nabla\vec{u}\,\mathrm{d}V\cdot\vec{\imath}_2 + \vec{\imath}_2\cdot\int_{V_{\text{cell}}}\nabla\vec{u}\,\mathrm{d}V\cdot\vec{\imath}_1 \quad \text{(A5)}$$

Since, inside the suspension, the local velocity is a continuous function of the coordinates, one can use the gradient theorem which yields

$$\int_V\nabla\vec{u}\,\mathrm{d}V = \oint_{S_V}\mathrm{d}\vec{S}\vec{u} \quad \text{(A6)}$$

Combining (A5) and (A6), we arrive at eq 15.

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