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ORIGINAL CONTRIBUTION

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Specific low-shear viscosity of a liquid dispersion of solid particles from variational theory for the Fuchs stability ratio

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Abstract The contribution of a solid phase to the low-shear viscosity of a solid–liquid dispersion, i.e., the specific viscosity, η_{SP}, is investigated theoretically by applying a variational procedure. The Fuchs stability ratio has been interpreted as a general steady-state equilibrium constant for aggregation and has been extended to a functional form which describes the motion of two Brownian units in a dispersion. Application of the Euler–Lagrange equation under the validity of an adiabatic-like approximation for the Hamiltonian (approximately Brownian kinetic energy and inertial potential field) yields a constraint that involves specific viscosity, solid volume fraction, ϕ, interparticle energy and correlation functions of the dispersed phase. The Einstein formula is found as the limit of the Saito equation when an infinitely dilute hard-sphere suspension is considered, while a general closed form expression, $\eta_{SP} = \eta_{SP}(\phi)$, is proposed for a concentrated suspension. It depends on the particle coordination number and affinity, returns the low density expansion predicted by effective-medium-type theories for the viscosity, and can be represented as the sum of two dominant contributions, associated respectively with the first peak of the radial distribution function and the second peak of the total correlation function. Application to experimental data, concerning latex particles in *cis*-decalin and interacting silica–water systems, is presented and discussed.

Key words Specific low-shear viscosity · Functional stability ratio · Solid–liquid dispersion · Pair and total correlation functions · Solid volume fraction

Introduction

Since the beginning of the twentieth century, viscoelastic properties of dispersed systems have been thorougly investigated both experimentally and theoretically and represent, up to now, a challenging field in fundamentals of physics and physical chemistry and in many technological and industrial applications [1, 2]. The influence of basic quantities (such as solid volume fraction, topology and microstructure, microscopic/mesoscopic interparticle fields, etc.) on the suspension viscosity is usually considered with the aim of predicting the behaviour in both dynamical [3, 4] and quasistatic [5, 6] regimes.

As a short historical outline, we first recall the pioneering work by Einstein [7, 8] on the hydrodynamics of a suspension of hard spheres, which was then improved by other early studies [9–15] and several investigations [16]. In the 50–80 years, effective-medium-like theories (EM) for the viscosity were formulated [17–31] and subsequently provided with effects due to Brownian motion [see, for instance, the generalized Bruggeman theory (BMX) and its asymmetrical case (ABMX)] [32]. By taking advantage of the understanding of hard-sphere systems, the rheology of concentrated colloidal dispersions was dealt with by other researchers, who examined theoretically and numerically the hydrodynamical and Brownian contributions to the viscous stress, both in equilibrium and nonequilibrium states [33–47]. In general, although several equations were suggested [1] to describe viscosity as a function of the suspended solid volume fraction (ϕ), finding a physical law that is applicable to concentrated systems of both aggregates and/or nonaggregates in the whole experimental ϕ range (i.e., a closed-form expression) is not an easy task [48]. For instance, in a quite recent analysis [49], a discussion of the discrepancy between some data sets is reported and the authors proposed a universal master curve that is not well described by usual equations employed in the current literature.

On the other hand, the coupling between aggregation of particles and rheological features of a suspension has already been pointed out in different studies [6, 50–52]. The mechanical properties of a suspension are strongly related to the state of the dispersed phase [53], where particle aggregation can be affected by various factors (i.e., kinetics, number of interparticle bonds, etc.) and characterized by the so-called stability ratio [54].

The stability ratio is employed for studying rapid and slow flocculation, i.e., the individual solid particle concentration as a function of time, respectively, without and with deflocculating agents (i.e., resistance term to aggregation) [55]. In its simplest formulation, the suspended solid phase is modelled as a uniform array of spherical kinetic units, whose motion is completely ruled by Brownian-like movements within the bulk solution. The spheres are assumed to interact on contact, after which they can adhere and disappear in the form of new solid doublets. Under these assumptions, the rate of formation of a new doublet coincides with the solid particle diffusion rate across a stationary surface of radius equal to the particle diameter (Fig. 1). So, as the number of kinetic units decreases near any flocculation site, a particle concentration gradient can be introduced and is regarded as the driving force for the diffusion process. Application of Fick's first law allows the aggregation kinetics to be related to macroscopical quantities (namely, temperature, liquid medium viscosity, diffusion coefficient, etc.) and to the interparticle potential field. Accordingly, the basic relationship between rapid and slow flocculations in the absence of hydrodynamic perturbations was originally quantified by Fuchs as [56]

$$\frac{k_\mathrm{R}}{k_\mathrm{S}} \equiv w = \langle d \rangle \int_{\langle d \rangle}^{\infty} \frac{\mathrm{e}^u}{\langle d \rangle} \mathrm{d}r > 0, \tag{1}$$

where w is the stability ratio, $k_{\mathrm{R,S}}$ are the rate constants (R represents rapid, S represents slow), $\langle d \rangle$ is the average particle diameter and $u = u(r)$ is the energy barrier (in $k_\mathrm{B}T$ unit, i.e., the Boltzmann constant times the absolute temperature) as a function of the radial position $r \geq \langle d \rangle$ within the bulk phase. Equation (1) specifies that the stability ratio is the reduction factor for the rate constant of rapid flocculation due to some energy barrier. Accounting for w in concentrated suspensions requires the correction of the probability per unit time and per unit volume that two solid particles form a doublet by considering the overall mass distribution at rest, namely, the radial distribution function in local equilibrium [57].

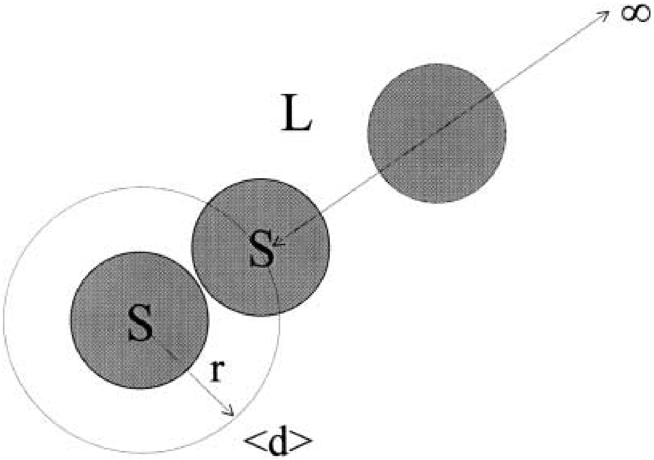

Fig. 1 Scheme of the mechanism of doublet formation associated with the equation for the Fuchs stability ratio, w (S = solid particle, L = liquid medium). A Brownian particle diffuses across a surface of radius equal to the particle diameter, $\langle d \rangle$, and interacts on contact with another solid unit

This article presents a theoretical investigation of the specific low-shear viscosity, $\eta_{\mathrm{SP}} = \frac{\eta}{\eta_0} - 1$, which in a dispersed system describes the contribution to the actual viscosity, η, associated with the volume fraction of solid particles, ϕ, suspended in a liquid having intrinsic viscosity, η_0. The relation between low-shear viscosity and aggregation is focussed here through a generalization of Eq. (1), which will be regarded as a steady-state equilibrium constant, extended to a functional form, defined over a dynamical space and investigated therein by application of a related stability condition. Annulment of the first-order functional derivative will allow a relationship to be obtained for η_{SP} and other implied physical quantities.

Basic concepts

Equation (1) points out the relation between two systems characterized by $u \neq 0$ and $u = 0$ or, equivalently, the effect of the energy barrier $u = u(r)$ on the rate constant for flocculation in a single dispersion. Consider instead a flocculation process where any aggregation mechanism, i.e., with any kind of aggregation barrier, can take place in all generality and can be described as a pseudochemical reaction [54]. If (n, R) and (n, S) denote respectively rapidly and slowly coagulating particles at the nth aggregation step, the reaction scheme

$$(n-1,\mathrm{R})+(n-1,\mathrm{R})\rightarrow(n,\mathrm{R})$$
$$\rightarrow(n,\mathrm{S})\leftarrow(n-1,\mathrm{S})+(n-1,\mathrm{S}) \tag{2}$$

identifies, at the steady-state, the apparent equilibrium constant given by

$$\lim_{n\to\infty}\frac{[(n,\mathrm{R})]^2}{[(n,\mathrm{S})]^2}\equiv w\;. \tag{3}$$

A functional formulation of w is therefore expected to be stable with respect to arbitrary small changes in generalized coordinates [58] and to relate solid particle aggregation and viscous work through the Euler–Lagrange equation. In this framework, w increases with increasing system stability up to a maximum value corresponding to the minimum apparent free energy associated with Eq. (3) (i.e., $G \propto -\ln w + \mathrm{const}$). More precisely, a functional related to the time of formation of a new solid doublet (see Ω_1 in Eq. 6) will be stated in the next section by weighting the actual time with an extended writing of w ($W_{\rho,1}$ in Eq. 5).

Nevertheless, before generalizing Eq. (1), some observations are needed. First, as all particles are subject to Brownian movement, the scheme in Fig. 1 must be improved. To this end, consider the mechanism sketched in Fig. 2a, where two solid units describe a Brownian-like movement across the dispersed phase of a suspension and displace from the centre of gravity of the motion an increasing volume with increasing time. The modified stability ratio associated with Fig. 2a can be introduced according to the equivalent scheme in Fig. 2b, where

1. The potential field has been replaced with the Hamiltonian function.
2. Two energy contributions have been separated. The first is related to particle dynamics and the second to the dominant solid mass distribution at rest, which is surface-interacting within the scattered volume.

Points 1 and 2 are equivalent to stating an adiabatic-like approximation, where kinetic and potential contributions are separated, i.e., associated with moving (or Brownian) and interacting (or inertial) solid particles, respectively, (analogously, see the quantum Born–Oppenheimer approximation of the Schrödinger equation, where kinetic and Coulombic terms are separately identified with electronic and nuclear contributions to the wave function [59]).

Second, once an extended writing of w is formulated and put in correspondence to any step n (Fig. 2 , Eq. 1), the limit of very large motion (or elapsed time) can be focussed within a dynamical space, where the Lagrange functional constraint for the mechanical minimum of the particle action is expected to take place [58, 60]. This also agrees with the definition of the stability ratio, which involves the integration limit $r=\langle d\rangle\rightarrow\infty$.

As a short outline of this work, the functional formulation for the Fuchs stability ratio will basically take into consideration four steps:

1. A three-dimensional extension of integration variables.
2. The position $U\rightarrow -H$.
3. A generalized coordinate space.
4. A proper stability condition therein.

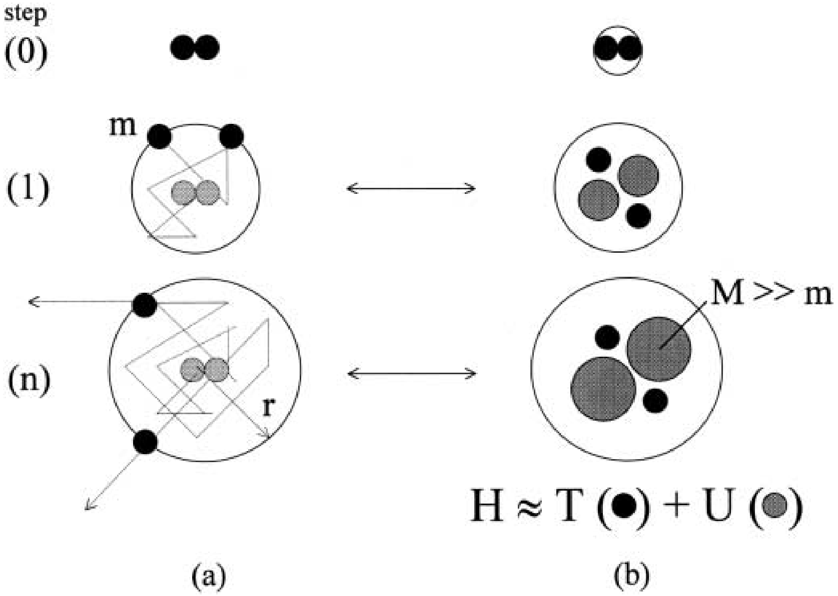

Fig. 2 Scheme of *a* the mechanism associated with the functional generalization of the stability ratio and *b* the adiabatic approximation for the total energy, H, (m = Brownian mass, M = solid mass at rest). A Brownian particle pair is moving with kinetic energy, T, and is subject to the potential field, U, of the suspended phase. The symbol n denotes a discrete elapsed time

As a first result, the Einstein formula [7, 8] will be found when the limit of infinitely dilute suspensions is considered. The theoretical approach, which can also be useful for investigating other viscous phenomena (see macromolecular systems, electrorheological and magnetorheological fluids, etc.), will subsequently be extended to describe concentrated particle systems. Analysis of effects related to the electrolyte concentration of the liquid phase and, more generally, to details of the interaction potential [61, 62] will not be dealt with in this article.

Basic formalism

In this section, we present the mathematical formalism which will be applied to study the stationary condition associated with an extended formulation for the stability ratio. Starting from the following ρ-dependent spatial writing of Eq. (1),

$$w_{\rho,1} = -\langle d\rangle \int_{\langle d\rangle}^{\rho} \mathrm{e}^{u(r)} \mathrm{d}\left(\frac{1}{r}\right) \quad , \tag{4}$$

the aforesaid three-dimensional extension can be adopted as follows

$$w_{\rho,1} \Rightarrow W_{\rho,1} = -v_{d,\rho} \int_{v_{d,\rho}}^{v_\rho} \mathrm{e}^{-H(r,\dot{r};t)} \mathrm{d}q_\mathrm{r} \quad , \tag{5}$$

t being time (so $\dot{r} \equiv \frac{\mathrm{d}r}{\mathrm{d}t}$) and the particle Hamiltonian, H, being expressed in $k_\mathrm{B}T$ unit. The notation v_r indicates the volume displaced by the solid particle pair from the primary minimum of the potential curve [63] ($\cong\langle d\rangle$) to the radial position r, the symbol $v_\mathrm{d,r}$ denotes the solid volume that is present inside v_r and $q_\mathrm{r} \equiv \frac{1}{v_\mathrm{r}}$.

Assuming $\rho \sim v_\rho^{\frac{1}{3}}$, a simple extension of Eq. (4) to a time functional, Ω_1, can be made according to

$$\Omega_1 = \int_{t'}^{t''} W_{\rho,1}(\rho, \dot{\rho}; t) \mathrm{d}t \quad , \tag{6}$$

which involves implicitly the dynamical evolution $\dot{\rho} = \dot{\rho}(t)$ and obeys the Euler–Lagrange equation, if the first-order derivative,

$$\widetilde{\Omega_1} \equiv \left(\frac{\partial W_{\rho,1}}{\partial \rho}\right) - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial W_{\rho,1}}{\partial \dot{\rho}}\right) \quad , \tag{7}$$

is zero within the time interval (t', t'') [60]. Following the limit of large ρ values in Eq. (1), the final condition reads

$$\lim_{\rho\to\infty} \widetilde{\Omega_1}(\rho, \dot{\rho}; t) = 0 \ . \tag{8}$$

Equation (8) is based on the original definition of the stability ratio and refers to a couple of solid units interacting on contact. More generally, dealing with a N-particle system requires the collective effect due to the other suspended units to be taken into account. To this end, we consider in Eqs. (6–9)

1. A slower kinetics of doublet formation [54, 55].
2. An effective contribution coming from the fluctuating Brownian forces experienced by the particle pair [11–13].

To express point 1 mathematically, we can make the zero convergence of the stability ratio slower by decreasing the infinitesimal order of $w_{\rho,1}(\rho)$ when the particle diameter is approached, say, $\lim_{\rho\to\langle d\rangle} w_{\rho,1} \sim (\rho - \langle d\rangle)^{\frac{1}{v_N}} = 0$, v_N being an integer number. This is formally equivalent to applying in Eq. (4) the position $r \Rightarrow r^{v_N}$, with $v_N = N \geq 1$. To represent point 2, we can extend the problem formulation to a continuous domain, where the density of states coincides with an equivalent interparticle correlation state. Contacting and noncontacting particles will be described in the usual context of pair and total correlation functions of the dispersed phase, respectively [35, 64, 65].

Accordingly, after introducing in Eq. (5) a power-law like $v_\mathrm{r} \Rightarrow v_r^N$

$$W_{\rho,1} \Rightarrow W_{\rho,N} = -v_{d,\rho}^N \int_{v_{d,\rho}^N}^{v_\rho^N} \mathrm{e}^{-H} \mathrm{d}q_\mathrm{r}^N \quad , \tag{9}$$

one first obtains

$$\Omega_N = \int_{t'}^{t''} W_{\rho,N}(\rho, \dot{\rho}; t) \, \mathrm{d}t \tag{10}$$

and

$$\widetilde{\Omega_N} \equiv \left(\frac{\partial W_{\rho,N}}{\partial \rho}\right) - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial W_{\rho,N}}{\partial \dot{\rho}}\right) \ . \tag{11}$$

Taking a linear N superposition generated by a set of real coefficients $\{\omega_k\}$ gives us a more general stability condition,

$$\lim_{\rho\to\infty} \sum_n \omega_N \widetilde{\Omega_N}(\rho, \dot{\rho}; t) = 0 \tag{12}$$

provided the convergence to zero is uniform. Equation (12) admits extension to the continuous spatial domain, $N \Rightarrow N(\underline{\rho})$, $\omega_N \Rightarrow \omega(\underline{\rho})$ and $\widetilde{\Omega_N} \Rightarrow \widetilde{\Omega_{\underline{\rho}}}$, with $\underline{\rho} \in \mathrm{R}^3$:

$$\lim_{\rho\to\infty} \int \widetilde{\Omega_{\underline{\rho}}}(\rho, \dot{\rho}; t) \, \mathrm{d}N(\underline{\rho}) = 0 \tag{13}$$

once the state density $\omega(\underline{\rho}) = \frac{\mathrm{d}N}{\mathrm{d}\underline{\rho}}$ is introduced for evaluating $\mathrm{d}N(\underline{\rho}) = \omega(\underline{\rho})\mathrm{d}\underline{\rho}$. The last equation (Eq. 13) is developed in the next section , keeping in mind the single state $N = 1$ should imply Eq. (8) (contacting particles only).

Formal developments

Infinitely dilute and noninteracting systems ($N = 1$)

With regard to the definition of $\widetilde{\Omega_1}$ (see Eq. 7), the first member on the right side yields

$$\frac{\partial W_{\rho,1}}{\partial\rho} = \left(\frac{\partial W_{\rho,1}}{\partial v_\rho}\right)\left(\frac{\partial v_\rho}{\partial\rho}\right) = \frac{v_{d,\rho}}{v_\rho}\left(\frac{\partial \ln v_{d,\rho}}{\partial v_\rho}\right)\mathrm{e}^{-H_\rho} + \left(\frac{\partial v_{d,\rho}}{\partial\rho}\right)\left(\int_{v_{d,\rho}}^{v_\rho}\mathrm{e}^{-H}\mathrm{d}q_\mathrm{r} - \frac{\mathrm{e}^{-H_{\langle d\rangle}}}{v_{d,\rho}}\right) \ , \tag{14}$$

where the notation $H_y \equiv H(y,\dot{r};t)$ has been used. Evaluating the second contribution on the right side of Eq. (7) is equivalent to developing the term which is given by

$$-\frac{\mathrm{d}}{\mathrm{d}t}\left\{v_{d,\rho}\int_{v_{d,\rho}}^{v_\rho}\left(\frac{\partial\mathrm{e}^{-H}}{\partial\dot{\rho}}\right)\mathrm{d}q_\mathrm{r}\right\} \ . \tag{15}$$

Therefore, Eq. (7) becomes

$$\frac{\mathrm{d}v_{d,\rho}}{\mathrm{d}t} = \left(\frac{\partial H}{\partial\dot{\rho}}\right)\int_{v_{d,\rho}}^{v_\rho}\mathrm{e}^{-H}\mathrm{d}q_\mathrm{r} + v_{d,\rho}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathrm{H}}{\partial\dot{\rho}}\int_{v_{d,\rho}}^{v_\rho}\mathrm{e}^{-H}\mathrm{d}q_\mathrm{r} + v_{d,\rho}\left(\frac{\partial H}{\partial\dot{\rho}}\right)\frac{\mathrm{d}}{\mathrm{d}t}\int_{v_{d,\rho}}^{v_\rho}\mathrm{e}^{-H}\mathrm{d}q_\mathrm{r} \tag{16}$$

or, equivalently,

$$\left(\frac{\partial H}{\partial\dot{\rho}}\right)\left(W_{\rho,1}\frac{\mathrm{d}}{\mathrm{d}t}\left\{\ln\left[v_{d,\rho}\left(\frac{\partial H}{\partial\dot{\rho}}\right)\right]\right\} + v_{d,\rho}\frac{\mathrm{d}}{\mathrm{d}t}\left\{\frac{W_{\rho,1}}{v_{d,\rho}}\right\}\right) \ . \tag{17}$$

To identify the Hamiltonian function, remember $H \equiv T + U = \mu\dot{\rho}^2 - L$, where the kinetic energy is of the form $T = \frac{1}{2}\mu\dot{\rho}^2$, U is the solid-phase contribution to the potential energy and L is the Lagrangean, which obeys [60]

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial\dot{\rho}}\right) - \left(\frac{\partial L}{\partial\rho}\right) = f_\eta \ , \tag{18}$$

where f_η represents the nonconservative viscous term acting on the Brownian particle.

To proceed further, we observe the work exerted by electrostatic forces is expected to increase both the viscosity and the yield stress if the interaction character is mainly attractive, and vice versa [6, 50–52]. This suggests the correspondence $U \Rightarrow -V$, where $V = V(r)$ stands for the total potential field and is the sum of repulsive and attractive contributions. The reduced mass, $\mu \equiv \frac{m}{2}$ (see Fig. 2, and the motion equation in compact form of a two-particle system), must then hold [60]. So, taking into account Eq. (18) and using the relation between H and L, some algebraical passages transform the sum (Eq. 15) into

$$\frac{m\dot{\rho}}{2}\left(\frac{\mathrm{d}v_{d,\rho}}{\mathrm{d}t}\right)\left(W_{\rho,1} - \frac{\mathrm{e}^{-H_{\langle d\rangle}}}{v_{d,\rho}}\right) + \frac{v_{d,\rho}}{v_\rho^2}\left(\frac{\partial v_\rho}{\partial\rho}\right)\frac{m\dot{\rho}^2}{2}\mathrm{e}^{-H_\rho} + v_{d,\rho}W_{\rho,1}\left(m\frac{\partial\dot{\rho}}{\partial t} - f_\eta\right) \ , \tag{19}$$

where each term represents the inverse of a length (i.e., a force per unit $k_\mathrm{B}T$) and $W_{\rho,1} = W_{\rho,1}(V)$. By adding Eqs. (13) and (18), Eq. (7) becomes

$$\widetilde{\Omega_1} = \left(W_{\rho,1} - \frac{\mathrm{e}^{-H_{\langle d\rangle}}}{v_{d,\rho}}\right)\left[\frac{m\dot{\rho}}{2}\left(\frac{\mathrm{d}v_{d,\rho}}{\mathrm{d}t}\right) + \left(\frac{\partial v_{d,\rho}}{\partial\rho}\right)\right] + \frac{v_{d,\rho}}{v_\rho^2}\frac{\partial v_\rho}{\partial\rho}\left(1 + \frac{m\dot{\rho}^2}{2}\right)\mathrm{e}^{-H_{\langle d\rangle}} - v_{d,\rho}W_{\rho,1}F_\eta \ , \tag{20}$$

with $F_\eta \equiv f_\eta - m\frac{\partial\dot{\rho}}{\partial t}$ denoting the difference between viscous and inertial forces and being a functional in the generalized motion coordinates. By expanding the temporal derivative, $\frac{d}{dt} = \frac{\partial}{\partial t} + \dot{\rho}\frac{\partial}{\partial\rho}$, and employing the adiabatic-like property exemplified in Fig. 2, namely

$$W_{\rho,1} \simeq \mathrm{e}^{-T}W_1(V) \ , \tag{21}$$

Eq. (20) can be rearranged as

$$\widetilde{\Omega_1} = \left(1 - \frac{g^*}{W_1}\right)\left[\left(1 + \frac{m\dot{\rho}^2}{2}\right)\frac{\partial}{\partial\rho} + \frac{m\dot{\rho}}{2}\frac{\partial}{\partial t}\right]\ln v_{d,\rho} + \left(1 + \frac{m\dot{\rho}^2}{2}\right)\frac{\mathrm{e}^{V(\rho)}}{W_1}\frac{v_{d,\rho}}{\rho v_\rho} - F_\eta \ , \tag{22}$$

where W_1 contains the potential field associated with the mass distribution at rest (Fig. 2b),

$$W_1 = -v_{d,\rho}\int_{v_{d,\rho}}^{v_\rho}\mathrm{e}^{V(r)}\mathrm{d}q_\mathrm{r}, \tag{23}$$

and $g* \sim \mathrm{e}^{-V(\langle d\rangle)}$, the minimum of the interparticle potential curve.

To develop Eq. (22) in the limit of large ρ and/or t values, we can first consider the implied kinetic quantities. Use of the energy equipartition theorem, $\frac{m\dot{\rho}^2}{2} = \frac{3}{2}$, and of the limit solution of the Brownian movement in liquid media, $\rho^2 = 12Dt$ $(2 \times 6Dt)$ [66], transforms Eq. (22) into

$$\widetilde{\Omega_1} = \left(1 - \frac{g*}{W_1}\right)\left(\frac{5}{2}\frac{\partial}{\partial\rho} + \frac{9D}{\langle v\rangle}\frac{\partial}{\partial\rho^2}\right)\ln v_{d,\rho} + \frac{5}{2}\frac{\mathrm{e}^{V(\rho)}}{W_1}\frac{v_{d,\rho}}{\rho v_\rho} - F_\eta \ , \tag{24}$$

D being the particle diffusion coefficient and $\langle v\rangle = \left(\frac{3k_\mathrm{B}T}{m}\right)^{\frac{1}{2}}$ the average velocity. Multiplication of both sides of Eq. (24) by ρ and application of Eq. (8), i.e., $\lim_{\rho\to\infty}\widetilde{\Omega_1} = 0$, allow the expression of the (nondimensional) work, $Q_\eta \equiv \lim_{\rho\to\infty}F_\eta$, which is done on the Brownian particle by the force F_η:

$$Q_\eta = \frac{5}{2}\lim_{\rho\to\infty}\left[\left(\frac{\partial \ln v_{d,\rho}}{\partial \ln \rho}\right)\left(1-\frac{g^*}{W_1}\right)+\frac{v_{d,\rho}}{v_\rho}\frac{\mathrm{e}^{V(\rho)}}{W_1}\right] , \qquad (25)$$

where the second derivative on the right side of Eq. (24) has been neglected upon $\rho\to\infty$, $\frac{9D}{\langle v\rangle}\frac{\partial}{\partial\rho^2}\frac{5}{2}\frac{\partial}{\partial\rho} = \frac{9D}{5\langle v\rangle\rho} \simeq 0$. Equation (25) consists of the sum of surface and bulk contributions, and its structure resembles the equation for the viscoelastic response of concentrated hard-sphere suspensions, where $\frac{g^*}{W_1}$ and $\frac{v_{d,\rho}}{v_\rho}\frac{\mathrm{e}^{V(\rho)}}{W_1}$ take the place of nondimensional effective hydrodynamic interactions [35]. We will focus the contribution coming from the bulk phase by neglecting $\left(\frac{\partial \ln v_{d,\rho}}{\partial \ln \rho}\right)$ at the boundary liquid surface.

Under the validity of a Langevin equation, and if no additional forces are applied, the particle dynamics is governed by viscous terms and stochastic processes with vanishing average value, $F(t)$, and one has $F_\eta = \langle F\rangle \equiv 0$ when the motion equation for the Brownian movement is considered in the functional F_η [60, 66]. In our case, this implies ρF_η is only related to the contribution of the phase dispersed in the liquid. Taking advantage of the so-called hard-sphere limit, i.e., assuming an infinitely viscous solid phase [24, 32], we set $Q_\eta = A\eta_{\mathrm{SP}}^{\alpha}$. It is not difficult to verify that A and α must equal unity. Let $\phi \in [0,1]$ be the solid volume fraction, then the limit at large ρ values returns

$$e^{V(\rho)} \to 1 \; ; \; \frac{v_{d,\rho}}{v_\rho} \to \phi \qquad (26)$$

or, equivalently,

$$\eta_{\mathrm{SP}} = \frac{5}{2}\frac{\phi}{W_{\infty,1}} , \qquad (27)$$

provided $Q_\eta = \eta_{\mathrm{SP}}$ and with $W_{\infty,1} \equiv \lim_{\rho\to\infty} W_1$. When $V \equiv 0$, since

$$W_{\infty,1} = \lim_{\rho\to\infty}\left[v_{d,\rho}\left(\frac{1}{v_{d,\rho}}-\frac{1}{v_\rho}\right)\right] = 1-\phi , \qquad (28)$$

one obtains

$$\eta_{\mathrm{SP}} = \frac{5}{2}\frac{\phi}{1-\phi} . \qquad (29)$$

For all values of ϕ, Eq. (29) coincides with the Saito expression, found in the framework of effective-medium theories for the viscosity. Then, in the limit of infinitely dilute hard-sphere dispersions, Eq. (29) returns the Einstein equation $\eta_{\mathrm{SP}} \simeq \frac{5}{2}\phi + O(\phi^2)$ [7, 8]. More correctly, the Einstein formula follows from the direct evaluation of Eq. (27) when $\phi \to 0^+$. In fact, for any choice of $V = V(r)$, one has $W_{\infty,1} \cong 1 + O(\phi)$ (see Eq. 27).

The general case ($N \geq 1$)

To apply the previous method to a concentrated and interacting dispersion, we will consider in Eqs. (14) and (15) the position $W_{\rho,1} \Rightarrow W_{\rho,N}$. Note that the energy equipartition theorem is not valid anymore and that the second limit (Eq. 26) is bounded by the maximum packing fraction ϕ_{M} ($\geq\phi$), above which the scheme in Fig. 2 ceases to be valid and the viscosity is expected to diverge [48]. By combining this information and following the same procedure as in the previous subsection, the contribution to the sum (Eq. 12) coming from the condition $\lim_{\rho\to\infty}\Omega_N = 0$ reads

$$\eta_{\mathrm{SP}}^{(N)} = [\eta]\frac{\phi^N}{W_{\infty,N}} \simeq \mathrm{e}^{-\langle V\rangle}[\eta]\frac{\phi^N}{1-\phi^N} , \qquad (30)$$

where $[\eta]$ is the intrinsic viscosity, $\bar{\phi} = \frac{\phi}{\phi_{\mathrm{M}}}$ is the ratio between actual and maximum solid volume fractions, and where the mean-value theorem for integrals [67] has been applied to

$$W_{\infty,N} \equiv \lim_{\rho\to\infty} W_N = -\lim_{\rho\to\infty} v_{d,\rho}^N \int_{v_{d,\rho}^N}^{v_\rho^N} \mathrm{e}^V \mathrm{d}q_{\mathrm{r}}^N . \qquad (31)$$

The macroscopic term $\langle V\rangle$ in Eq. (30) is independent of N and should be regarded as a macroscopic, global contribution. Qualitatively, it implies that the viscosity tends coherently to increase if the average interparticle potential is negative (cohesive, attractive forces) and, vice versa, to decrease when repulsive fields are involved. To work out Eq. (13) and to extend Eq. (30) to the continuous domain, we need to identify the state density $\omega(\underline{\rho})$, i.e., to sum over the states representative of both contacting (Fig. 1) and noncontacting (the collective effect produced by surrounding units) solid particles. The simplest way is by introducing the particle correlation states in $r \in [\langle d\rangle,\infty]$ described by the autocorrelation function [63]

$$S(r) = \bar{\rho}\delta(r) + \bar{\rho}^2 h(r) , \qquad (32)$$

for density fluctuations around the average density value $\bar{\rho}$. In this way, the singlet particle correlation and the affinity between solid units, represented, respectively, by the Dirac distribution and the total correlation function, $h(r)$, will be dealt with as contacting and noncontacting states. Then, since ω has the dimension of the inverse of a volume, we adopt a van Hove function for density fluctuation [68] and set $\omega(\rho) \equiv \frac{S}{\bar{\rho}}$, where $\rho \equiv \frac{r}{\langle\lambda\rangle}$ and $\langle\lambda\rangle$ is the correlation length. By employing Eq. (32), for $|\underline{\rho}| \geq 1$ we can write

$$\omega(\underline{\rho}) \equiv \delta(\underline{\rho}-1) + \bar{\rho}h(\underline{\rho}) , \qquad (33)$$

where the delta distribution refers to correlation between particles interacting on contact and the correlation function refers to collective contributions coming from the other solid units. Accordingly, substituting Eqs. (30) and (33) into Eq. (13) gives (with this set of choices $\overline{\rho}$ is adimensional)

$$\eta_{\mathrm{SP}} = \mathrm{e}^{-\langle V\rangle}[\eta]\left(\bar{\rho}\int h\left(\underline{\rho}\right)\frac{\phi^\rho}{1-\bar{\phi}^\rho}\mathrm{d}\underline{\rho} + \frac{\phi}{1-\bar{\phi}}\right) , \qquad (34)$$

which, as $h(\rho \geq 1, \phi \to 0^+) = 0$ [63, 69] and $\langle V \rangle$ $(\phi \to 0^+) = 0$, reduces to the Einstein formula for an infinitely dilute suspension with $[\eta] = \frac{5}{2}$.

The exact calculation of the integral Eq. (37) is an interesting but tough issue, which is left for future work. It is convenient, instead, to work in units of $\langle \lambda \rangle$ and to set $\bar{\rho} = 1$. To this end, we represent the peaks of $h(\rho)$, corresponding to each particle $k = 1, ..., N$ and located at $\rho_k \simeq k$, as Dirac distributions [70] and consider the following development in polar coordinates:

$$h\left(\underline{\rho}\right) \sim \frac{1}{\rho^2 \sin\theta} \sum_{k=1}^{N} h_k \delta[\theta - \theta_k(t)] \\ \times \delta[\varphi - \varphi_k(t)] \delta(\rho - \rho_k) \ , \tag{35}$$

where $\theta_k(t)$ and $\varphi_k(t)$ are the angular positions occupied by the Brownian particle at time t and when $\rho = \rho_k \simeq k$. Using Eqs. (30) and (35) we can integrate Eq. (34) over $\mathrm{d}\underline{\rho} = \rho^2 \sin\theta \, \mathrm{d}\rho \, \mathrm{d}\theta \, \mathrm{d}\varphi$ and define

$$\eta_N \equiv \mathrm{e}^{-\langle V \rangle} [\eta] \left(\sum\nolimits_{k=1}^{n} h_k \int_{\Re^3} \frac{\phi^\rho}{1 - \bar{\phi}^\rho} \delta[\theta - \theta_k(t)] \\ \times \delta(\rho - k) \, \mathrm{d}\rho \, \mathrm{d}\theta \, \mathrm{d}\varphi + \frac{\phi}{1 - \bar{\phi}} \right) \ , \tag{36}$$

and so

$$\eta_{\mathrm{SP}} \equiv \lim_{N \to \infty} \eta_N = \mathrm{e}^{-\langle V \rangle} [\eta] \left(\frac{\phi}{1 - \bar{\phi}} + \sum_{k=1}^{\infty} h_k \frac{\phi^k}{1 - \bar{\phi}^k} \right) \ , \tag{37}$$

or, equivalently,

$$\eta_{\mathrm{SP}} = \mathrm{e}^{-\langle V \rangle} [\eta] \\ \times \left(g_1 \frac{\phi}{1 - \bar{\phi}} + h_2 \frac{\phi^2}{1 - \bar{\phi}^2} + \cdots + h_N \frac{\phi^N}{1 - \bar{\phi}^N} \right) \\ + O\left(\phi^{N+1}\right) \ , \tag{38}$$

where $g_1 = h_1 + 1$ denotes the contribution coming from the first peak of the pair correlation function, $g(\rho)$ [63, 68, 69]. Equation (38), whose physical meaning has been sketched in Fig. 3, will be applied and discussed in the next section. Basically, we regard the set of coefficients $\{h_{\mathrm{k}}\}$ introduced in Eq. (35) as average terms, provided with the condition $h_{\mathrm{k}} < 1$. To reduce the number of best-fit parameters, the state equation for the equilibrium radial distribution function at contact will be employed according to the Carnahan–Starling and results. The other quantities, $\langle V \rangle$, $[\eta]$ and ϕ_{M}, will be dealt with according to the experimental properties of the system under examination.

Application to experimental data and discussion

Equation (38) can be first regarded as an improvement of Eq. (29). To derive the expansion in the concentration when $\phi \to 0^+$ we can develop, at first order in zero, the state equation for the equilibrium radial distribution function at contact, $g_1 = g_1(\phi)$ [71]. If one adopts $[\eta] = \frac{5}{2}$ and keeps in mind the set of functions $h_k(\phi)$ are infinitesimal in $\phi = 0$, substituting in Eq. (38) the Carnahan–Starling result [35, 72], $g_{\mathrm{CS}}(\phi) = \frac{1 - \phi/2}{(1-\phi)^3} = 1 + \frac{5}{2}\phi + O\left(\phi^2\right)$, returns in the limit of $\bar{\phi} \ll \phi$ the well-known low-density expansion found in the context of effective-medium-type theories (see the hard-sphere limit of the so-called Bruggeman formula, and Refs. [22–25, 28–32]):

$$\eta_{\mathrm{SP}} = \frac{5}{2}\phi + \left(\frac{5}{2}\phi\right)^2 + O\left(\phi^3\right) \\ \simeq 2.5\phi + 6.25\phi^2 \ ; \ \ \phi \to 0^+ \ , \tag{39}$$

whereas Eq. (29) implied $\eta_{\mathrm{SP}} = \frac{5}{2} \sum \phi^i \simeq 2.5\phi + 2.5\phi^2 + O\left(\phi^3\right)$. Note that the employment of the Percus–Yevick state equation [57, 73], $g_{\mathrm{PY}}(\phi) = \frac{1 + \phi/2}{(1-\phi)^2} = 1 + \frac{5}{2} + O\left(\phi^2\right)$, does not change the second-order approximation for η_{SP}. Equation (39) has been applied and discussed by several workers (see, for instance, Refs. [16, 25, 28, 32, 74]) and is in reasonable agreement with the outcome of experimental data, $\eta_{\mathrm{SP}} = (2.6 \pm 0.2)\phi + (6 \pm 5)\phi^2 + O(\phi^3)$ [25, 49, 75], and of theoretical analysis, which predict a second-order term equal to $5.9\phi^2$ [30, 49, 76]. From third order on, we find a general contribution N of the form $\frac{5}{2}\left[\frac{1}{(N-1)!}\left(\frac{\partial^{N-1} g_1}{\partial \phi^{N-1}}\right)_0 + \sum_{r+s=N} \frac{1}{k!}\left(\frac{\partial^r h_s}{\partial \phi^r}\right)_0\right]$, which cannot be evaluated with simple analytic expressions [57, 68].

To represent the behaviour of $\eta_{\mathrm{SP}} = \eta_{\mathrm{SP}}(\phi)$ in the whole volume fraction range, Eq. (38) can be truncated to some order $N \geq 2$, $\eta_{SP} = \eta_N + O(\phi^{N+1})$, where g_1 and h_k are dealt with as average coefficients or to the first-order approximation $h_{\mathrm{SP}} = h_1^* \equiv \gamma \mathrm{e}^{-\langle V \rangle} [\eta] \phi g_1 (\phi)/(1 - \bar{\phi}) + O(\phi^2)$, where $g_1(\phi)$ is the state equation and γ a heuristic parameter. For the sake of comparison, Fig. 4 reports Eq. (38) with some theoretical closed-form expressions currently adopted in the literature. They are the Krieger–Dougherty [77, 78] $[\eta_{\mathrm{SP}} =$

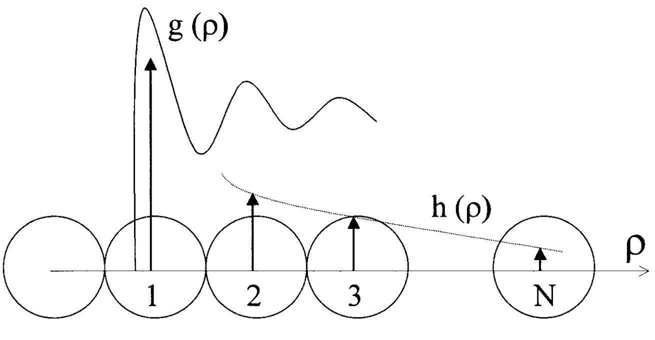

Fig. 3 Scheme of the physical meaning of the equation $\eta_{\mathrm{SP}} = \eta_N(\phi)$

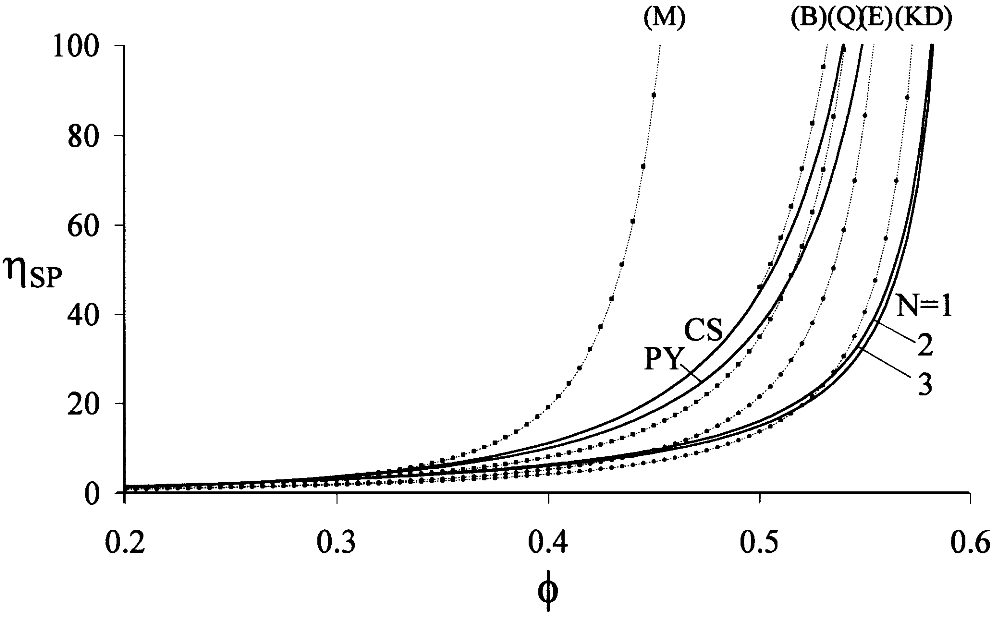

Fig. 4 Behaviour of $\eta_{SP} = \eta_N(\phi)$, and $\eta_{SP} = \eta_1^*(\phi)$, in comparison to other theoretical models (*KD* = Krieger–Dougherty, *M* = Mooney, *E* = Eilers, *Q* = Quemada, *B* = Brady). For $\eta_{SP} = \eta_N(\phi)$ we employed $g_1 = 2.0$ ($N = 1$), $h_2 = 0.5$ ($N = 2$), $h_3 = 0.2$ ($N = 3$), while for $\eta_{SP} = \eta_1^*(\phi)$ the Carnahan–Starling (*CS*) $\left(g_{CS} = \frac{1-\phi/2}{(1-\phi)^3}\right)$ and Percus–Yevick (*PY*) $\left(g_{PY} = \frac{1+\phi/2}{(1-\phi)^2}\right)$ state equations were adopted with $\gamma = 1$. In all cases, we set $[\eta] = 2.5$, $\langle V \rangle = 0$ and $\bar{\phi} = 0.6$

$(1-\bar{\phi})^{-[\eta]\bar{\phi}}-1]$, Quemada [79] $\left[=(1-\bar{\phi})^{-2}-1\right]$, Mooney [80] $\left[=\exp\left([\eta]\frac{\phi}{1-\bar{\phi}}\right)-1\right]$ and Eilers [81] $\left[=\left(1+\frac{[\eta]\phi}{2(1-\bar{\phi})}\right)^2-1\right]$ equations, and the asymptotic law found by Brady [34–36] $\left[\eta_{SP} \sim 1.3(1-\bar{\phi})^{-2}-1\right]$ for a concentrated dispersion when $\bar{\phi} \to 1^-$. Experimental coefficients have been set to $[\eta] = 2.5$, $\langle V \rangle = 0$ and $\phi_M = 0.6$ in all cases, while we employed $g_1 = 2$, $h_2 = 0.5$, $h_3 = 0.2$ for calculating $\eta_{SP} = \eta_N(\phi)$ ($N = 1$, 2, 3) and the Carnahan–Starling and Percus–Yevick state equations, $g_{CS}(\phi)$ and $g_{PY}(\phi)$ with $\gamma = 1$, to work out $\eta_{SP} = \eta_1^*(\phi)$. In any case, as emerges from Fig. 4 and usual behaviours of correlation functions [68, 69, 71], Eq. (38) are expected to converge rapidly to the limit solution, starting from the second-order term (in fact, $\frac{g_1}{h_N}\frac{\phi^{1-N}(1-\bar{\phi}^N)}{1-\bar{\phi}} \gg 1$, for $N > 2$). Equations (34) and (38) then point out that the viscous properties of a solid–liquid material can be expressed as a superposition of autocorrelation states averaged on the suspension volume according to weight factors such as $\frac{\phi^k}{1-\bar{\phi}^k}$. Specifically, it consists of a modified writing of the particle affinity ($\sim \int h \mathrm{d}\underline{\rho}$), where, as expected from other analysis [11–13, 34–46], the contribution originating from the pair distribution function at contact is involved. At first account, two contributions would be dominant: the first peak of the pair correlation function and the second peak of the total correlation function.

Figure 5 shows the master curve η_{SP} versus $\bar{\phi}$, recently derived from viscosity measurements in hard-sphere suspensions of latex particles dispersed in *cis*-decalin [49]. We used a second-order best-fit curve $\eta_{SP} = \eta_2(\phi, \langle V \rangle = 0)$ and the first-order equation $\eta_{SP} = \eta_1^*(\phi, \langle V \rangle = 0)$. In good agreement with the experimental analysis conducted in Ref. [49], and in correspondence to typical orders of magnitude of correlation peaks [82–84], $g_1 = 1.8$ and $h_2 = 0.2$, we determined from the second-order best-fit curve $[\eta] = 2.6$ and $\phi_M = 0.5$. From the first-order equation, we extrapolated the same values of intrinsic viscosity and maximum packing fraction, when $\gamma \cong 0.4$, and both Carnahan–Starling and Percus–Yevick state equations are considered in $\eta_1^*(\phi)$.

The rheological behaviour of aqueous silica suspensions is presented in Fig. 6 for different pH values [85]. The interacting character of such systems has been explained in terms of the interactions between the silica particles and the size of the units formed. At pH 7 and 9, significant double-layer repulsions take place, while at pH 3, close to the isoelectric point of silica, repulsive potential fields only occur at high solid volume fractions. However, in all pH and ϕ ranges, the aggregation properties are strongly affected by van der Waals dispersion forces [61, 85]. In the second case, an analysis of the phenomenological coefficients employed in $\eta_2(\phi)$ returns the average values $[\eta] \sim 3.3$ and $\langle V \rangle \sim -0.5 \times 10^{-20}$ J, when $1.8 \le g_1 \le 3.4$, $0.2 \le h_2 \le 0.6$ and $\phi_M = 0.094$, 0.109, 0.137. Best-fit functions $\eta_1^*(\phi)$ based on the same $[\eta]$, $\langle V \rangle$ and ϕ_M values require $\gamma_{CS} \cong \gamma_{PY} \cong 2.9$, 24.6, 30.1, respectively whenthe pH is 3, 7 or 9. Note that the estimated energy belongs to the range determined experimentally for the Hamaker constant of silica molecules in water, i.e., $A \cong (0.2-1.4) \times 10^{-20}$ J

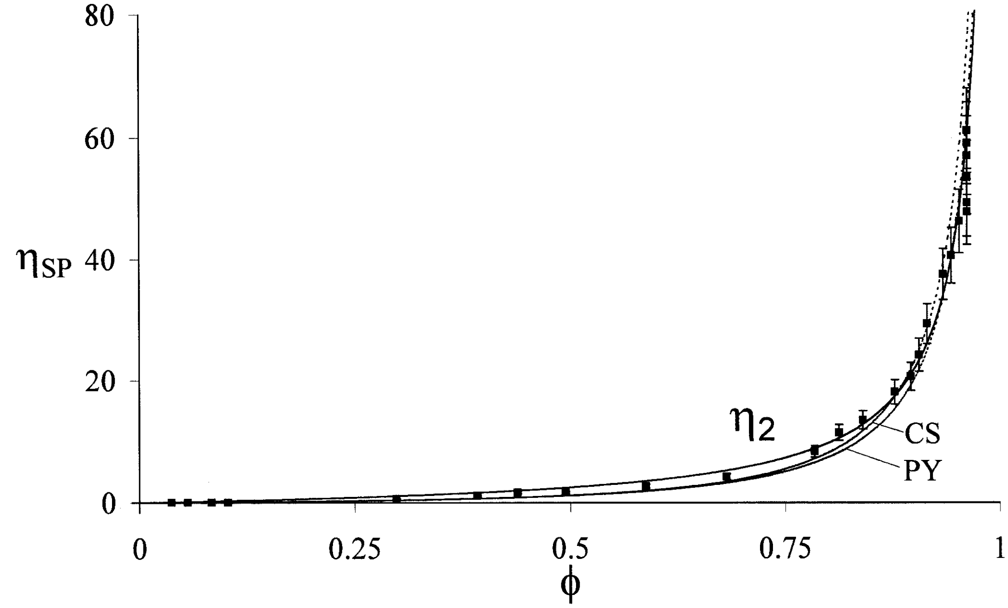

Fig. 5 Experimental measurements η_{SP} versus ϕ in latex–*cis*-decalin hard-sphere dispersions [49] described with a second-order function $\eta_{SP} = \eta_2(\phi)$ (*solid line*) and the first-order expression $\eta_{SP} = \eta_1^*(\phi)$ (*dotted line*). We used $[\eta] = 2.6$, $\langle V \rangle = 0$, $\phi_M = 0.5$ in all cases, $g_1 = 1.8$ and $h_2 = 0.2$ for the second-order function and $\gamma_{CS} \cong \gamma_{PY} \cong 0.4$ for the first-order expression

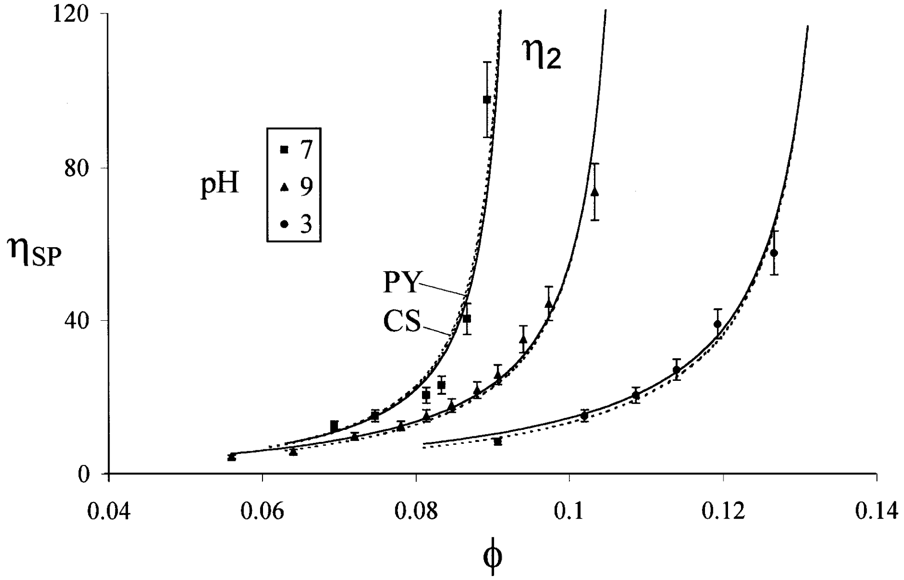

Fig. 6 Experimental measurements η_{SP} versus ϕ in silica–water suspensions [85] described with $\eta_{SP} = \eta_2(\phi)$ (*solid line*) and $\eta_{SP} = \eta_1^*(\phi)$ (*dotted line*). Best fits for $\eta_{SP} = \eta_2(\phi)$ returned the average values $[\eta] \sim 3.3$ and $\langle V \rangle \sim -0.5 \cdot 10^{-20}$ J, when $\phi_M = 0.094$, 0.109, 0.137 and $1.8 \leq g_1 \leq 3.4$, $0.2 \leq h_2 \leq 0.6$. For $\eta_{SP} = \eta_1^*(\phi)$ we derived $\gamma_{CS} \cong \gamma_{PY} \cong 2.9$, 24.6 and 30.1 when the pH was 3, 9 and 7, respectively

at room temperature [63]. The difference between the returned intrinsic viscosity and the Einstein value probably reflects geometrical and hydration effects [54]. Silica particles aggregate in chains that in aqueous solution can give rise to three-dimensional networks [86].

Conclusions

1. The Fuchs stability ratio has been regarded as a steady-state equilibrium constant of a liquid dispersion of solid particles, where any aggregation mechanism can take place in all generality.
2. A functional description for the Brownian movement of two solid particles in a dispersed system has been formulated to extend and to study variationally the stability ratio over a generalized coordinate space. The Hamiltonian function has been dealt with according to an adiabatic separation of Brownian kinetic energy and interparticle potential field. Contacting and noncontacting particle states have been described in terms of the autocorrelation function for density fluctuations around the average value.
3. The stable solution has been determined by applying the Euler–Lagrange theorem and yields the Saito equation, for a contacting particle system, which gives the Einstein formula when the functional describes an

infinitely dilute hard-sphere system, and a general closed-form expression for a concentrated suspension, when the noncontacting particle states are accounted for in the variational procedure. It relates the specific viscosity to actual and maximum solid volume fractions, average interparticle field and pair and total correlation functions of the dispersed phase. The second-order density expansion determined in the framework of effective-medium theories, is found in the limit of low concentration values.

4. It is suggested the viscosity of a solid–liquid material can be written as the modified writing of the solid particle affinity in Eq. (34), which is mainly affected by the first peak of the pair correlation function and by the second peak of the total correlation function.
5. The experimental behaviour η_{SP} versus ϕ, of hard-sphere latex dispersions in *cis*-decalin and of silica–water suspensions, has been described by using first-order and second-order equations derived from the closed-form expression obtained. The first is provided with the state equation for the equilibrium radial distribution function at contact (see, for instance, Carnahan–Starling or Percus–Yevick results), the second with average correlation coefficients. The agreement between theory and experiments turned out to be satisfactory in all cases here examined.

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References

1. Barnes HA, Hutton JF, Walters K (1989) An introduction to rheology. Elsevier, Amsterdam
2. Moldenaers P, Keunings R (1992) Theoretical and applied rheology. Elsevier, Amsterdam
3. Cates ME (1996) J Phys Condens Matter 8:9167
4. Bruinsma R (1996) Physica A 234:249
5. Chang J, Lange F, Pearson D (1994) J Am Ceram Soc 77:19
6. Mezzasalma SA (1998) Phys Rev E 57:3134
7. Einstein A (1906) Ann Phys 19:289
8. Einstein A (1911) Ann Phys 34:591
9. Taylor GI (1932) Proc R Soc Lond Ser A 138:41
10. Peterson JM, Fixman M (1963) J Chem Phys 39:2516
11. Batchelor GK, Green J (1972) J Fluid Mech 56:375
12. Batchelor GK (1976) J Fluid Mech 74:1
13. Batchelor GK (1977) J Fluid Mech 83:97
14. Felderhof BU, Jones RB(1987) Physica A 146:417
15. Felderhof BU (1987) Physica A 147:203
16. Jorquera H, Dahler JS (1994) J Chem Phys 101:1392
17. Saito N (1950) J Phys Soc Jpn 5:4
18. Saito N (1952) J Phys Soc Jpn 7:447
19. Freed KF, Edwards SF (1975) J Chem Phys 62:4032
20. Freed KF, Muthukumar M (1982) J Chem Phys 76:6195
21. Felderhof BU (1976) Physica A 82:596
22. Felderhof BU (1976) Physica A 82:611
23. Bedeaux D, Kapral R, Mazur P (1977) Physica A 88:88
24. Bedeaux D (1983) Physica A 121:345
25. Bedeaux D (1987) J Colloid Interface Sci 118:80
26. Beenakker CWJ, Mazur P (1983) Physica A 120:388
27. Beenakker CWJ, MazurP (1984) Physica A 126:349
28. Beenakker CWJ (1984) Physica A 128:48
29. Mazur P, van Saarloos W (1982) Physica A 115:21
30. Cichocki B, Felderhof BU (1989) J Chem Phys 89:3705
31. Cichocki B, Felderhof BU, Schmitz R (1989) Physica A 154:233
32. Choy TC (1995) Physica A 221:263
33. Russel WB, Gast AP (1986) J Chem Phys 84:1815
34. Brady JF (1993) J Chem Phys 98:3335
35. Brady JF (1993) J Chem Phys 99:567
36. Brady JF (1994) J Chem Phys 101:1758
37. Bossis G, Brady JF (1984) J Chem Phys 80:5141
38. Bossis G, Brady JF (1989) J Chem Phys 91:1866
39. Wagner NJ, Russel WB (1989) Physica A 155:475
40. Wagner NJ (1994) Phys Rev E 49:376
41. Rastogi SR, Wagner NJ, Lustig SR (1996) J Chem Phys 104:9234
42. Rastogi SR, Wagner NJ, Lustig SR (1996) J Chem Phys 104:9249
43. Rastogi SR, Wagner NJ (1997) J Rheol 41:893
44. Gan HH, Eu BC (1992) Phys Rev A 46:6344
45. Farhat H, Eu BC (1999) J Chem Phys 110:97
46. Ladd AJC (1990) J Chem Phys 93:3484
47. Lundgren TS (1972) J Fluid Mech 51:273
48. Collins IR (1996) J Colloid Interface Sci 178:361
49. Meeker SP, Poon WCK, Pusey PN (1997) Phys Rev E 55:5718
50. Martynov SI (1998) J Eng Phys Thermophys 71:687
51. Leong YK, Scales PJ, Healy TW, Boger DV (1993) J Chem Soc Faraday Trans 89:2473
52. Mezzasalma SA (1997) J Colloid Interface Sci 190:302
53. Krieger IM (1972) Adv Colloid Interface Sci 3:111
54. Hiemenz PC (1986) Principles of colloid and surface chemistry. Dekker, New York
55. Parfitt GD (1969) Dispersion of powders in liquids. Elsevier, London
56. Fuchs N (1934) Z Phys 89:736
57. Jun J, Blum L, Haoping W (1995) Colloid Polym Sci 273:175
58. Strieder W, Aris R (1973) Variational methods applied to problems of diffusion and reaction. Springer, Berlin Heidelberg, New York
59. McWeeny R (1973) Coulson's valence. Oxford University Press, Oxford
60. Landau LD, Lifsits EM (1982) Meccanica. Riuniti, Rome
61. Israelachvili J (1985) Intermolecular and surface forces. Academic, London
62. Borkovec M (1993) Langmuir 9:2247
63. Lyklema J (1993) Fundamentals of interface and colloid science. Academic, London
64. Bird RB, Armstrong RC, Hassager O (1987) Dynamics of polymeric liquids. Wiley Interscience, New York
65. Ottinger HC (1985) J Chem Phys 83:6535

66. Reif F (1965) Fundamentals of statistical and thermal physics. McGraw-Hill, New York
67. Apostol TM (1974) Mathematical analysis. Addison-Wesley, Reading, Mass
68. Hansen J-P, McDonald IR (1986) Theory of simple liquids. Academic, London
69. Hill TL (1956) Statistical mechanics. McGraw-Hill, New York
70. Mazur S (1992) J Chem Phys 97:9276
71. Balescu R (1975) Equilibrium and nonequilibrium statistical mechanics. Wiley, New York
72. Carnahan NF, Starling KE (1969) J Chem Phys 51:635
73. ThieleE (1963) J Chem Phys 39:474
74. Smeets G, Koper GJM, van der Ploeg JPM, Bedeaux D (1994) Langmuir 10:1387
75. de Kruif CG, van Iersel EMF, Vrij A, Russel WB (1985) J Chem Phys 83:4717
76. Brady JF, Vicic M (1995) J Rheol 39:545
77. Krieger IM, Dougherty TJ (1972) Trans Soc Rheol 3:137
78. Krieger IM, Dougherty TJ (1972) Adv Colloid Interface Sci 3:111
79. Quemada D (1994) Europhys Lett 25:149
80. Mooney M (1951) J Colloid Interface Sci 6:162
81. Eilers H (1943) Kolloid Z. 102:154
82. Watzlawek M, Nagele G (1997) Physica A 235:56
83. Bergenholtz J, Wagner NJ (1997) Physica A 235:34
84. Lohle B, Klein R (1997) Physica A 235:224
85. Tadros TF (1992) In: Galassi C (ed) Chimica dei Colloidi e Reologia Applicata ai Ceramici. CNR-IRTEC, Imola, p 31
86. Iler KR (1979) The chemistry of silica. Wiley, New York