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## Correlation between the high-frequency elastic modulus and the interparticle interaction potential in zirconium oxide colloidal suspensions

Received: 22 November 2004  
Accepted: 1 June 2005  
Published online: 16 July 2005  
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**Abstract** In this work, we study the high-frequency elastic modulus of aqueous suspensions made with two kinds of zirconium oxide particles, one commercially available and the other synthesized as monodisperse spheres. The effect of volume fraction of solid, ionic strength (sodium chloride as indifferent electrolyte) and particle geometry is taken into account in the study on this viscoelastic property of the suspensions. Frequency sweeps were performed at a fixed value of the applied shear-stress in order to obtain the frequency-limiting value of the elastic modulus by rheometrical methods. On the other hand, the high-frequency modulus is theoretically calculated independently by means of

the models proposed by Buscall and co-workers, Wagner and Bergenholtz and co-workers, which correlate the interaction potential between particles with this rheological parameter. The approach to the interparticle potential is the extended DLVO theory, which considers the electrical repulsion between charged colloidal particles, the van der Waals attraction and the acid–base interaction that can be attractive or repulsive depending on the thermodynamic nature of the solid–liquid interface.

**Keywords** Zirconia suspensions · Viscoelasticity · High-frequency modulus · DLVO theory

### Introduction

It is well known that high-strength ceramics require the use of particles with sizes in the colloidal domain (0.1–1  $\mu\text{m}$ ), so as to reduce the density and defects and to perform sintering at lower temperatures. Furthermore, the particles should have a narrow size distribution, with equiaxed shape, and be well dispersed (Carlström 1994). However, the high surface-to-volume ratios characteristic of such systems will lead to primordial role of interfacial forces (electrical double layer repulsion, van der Waals attraction, hydrophobic/hydrophilic interactions) in the overall behavior of the ceramic slurry (Bergström 1994).

In addition, the high concentration of the suspensions used in the ceramic technology imparts them a highly

non-Newtonian rheological behavior, with viscoelastic properties due to strong interactions between the particles (Buscall et al. 1982; Tadros 1996). The viscoelasticity of the suspensions is hence controlled by such quantities as the particle size and shape, the interparticle interactions, and of course, the volume fraction,  $\phi$ , of solids.

In the present work, such a study will be performed on suspensions of spherical and quite monodisperse particles of zirconium oxide ( $\text{ZrO}_2$ ), although, for comparison, results will also be shown on commercial zirconia of high chemical purity but with noncontrolled geometry. In addition, we will consider all the interactions that, according to the so-called extended DLVO theory (Israelachvili 1992; van Oss 1994), may exist between two colloidal particles in suspension, namely: van der Waals attraction, electrical double layer repulsion

and hydrophobic (hydrophilic) attraction (repulsion). This model was used with some success in explaining the yield stress of zirconia suspensions in a previous work (Megias-Alguacil et al. 2000).

The potential energy of interaction between the particles can be related to experimentally accessible quantities by means of the extended DLVO theory, which considers three contributions to the interaction between particles: electrostatic (EL), Lifshitz-van der Waals (LW) and acid-base (AB) interaction. In this paper we will follow the treatment developed by van Oss et al. (1988; Good 1993) for the estimation of the latter type of interaction and the Hamaker constant.

For spherical particles and low-surface potentials the electrical interaction reads,

$$V^{\text{EL}} = 2\pi\epsilon_r\epsilon_0a\zeta^2 \ln[1 + \exp(-\kappa H)] \quad (1)$$

where  $\epsilon_r\epsilon_0$  is the permittivity of the dispersed medium,  $a$  is the radius of the particles,  $\zeta$  the electrokinetic or zeta potential,  $H$  is the surface-to-surface distance between particles and  $\kappa$  is the reciprocal Debye length, calculated by:

$$\kappa = \left( \frac{\sum_{i=1}^n e^2 z_i^2 n_i}{\epsilon_r\epsilon_0 k_B T} \right)^{1/2} \quad (2)$$

where  $n_i$  is the concentration of type  $i$  ions (charge  $ez_i$ ),  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature.

The LW attraction can be written as (Gregory 1981):

$$V^{\text{LW}} = -\frac{A}{6} \left[ \frac{2a^2}{H(4a+H)} + \frac{2a^2}{(2a+H)^2} + \ln \frac{H(4a+H)}{(2a+H)^2} \right] \quad (3)$$

where  $A$  is the Hamaker constant, which depends on the characteristics of both medium. It has been demonstrated (Visser 1972; van Oss et al. 1988) experimentally that LW interactions are responsible of attractive interaction energy between colloidal particles. For spheres, the Hamaker constant is,

$$A = 24 \pi H_0^2 \gamma_{12}^{\text{LW}} \quad (4)$$

where  $H_0$  is the so-called equilibrium separation distance between interfaces, whose best estimation yields  $H_0 = (1.58 \pm 0.08) \text{ \AA}$  (van Oss et al. 1988), and  $\gamma_{12}^{\text{LW}}$  is the LW contribution to the interfacial tension of the oxide (material 1)/solution (material 2) system, that can be written in terms of the LW contribution of the individual materials to the surface free-energy (Fowkes 1963):

$$\gamma_{12}^{\text{LW}} = \left( \sqrt{\gamma_1^{\text{LW}}} - \sqrt{\gamma_2^{\text{LW}}} \right)^2 \quad (5)$$

Finally, the expression for the AB term is:

$$V^{\text{AB}} = -2\pi a \lambda \gamma_{12}^{\text{AB}} \exp\left(\frac{H_0 - H}{\lambda}\right) \quad (6)$$

where  $\lambda \approx 1 \text{ nm}$  is the so-called correlation distance between water molecules (Israelachvili 1992). The parameter  $\gamma_{12}^{\text{AB}}$ , according to the formalism by van Oss et al. (1988), can be related to the polar (or Lewis AB) component of the interfacial tension between materials 1 and 2:

$$\gamma_{12}^{\text{AB}} = 2\sqrt{\gamma_1^+ \gamma_1^-} + 2\sqrt{\gamma_2^+ \gamma_2^-} - 2\sqrt{\gamma_1^+ \gamma_2^-} - 2\sqrt{\gamma_1^- \gamma_2^+} \quad (7)$$

where  $\gamma_i^+$  and  $\gamma_i^-$  are, respectively, the electron-acceptor and electron-donor components of the surface free-energy of material  $i$ .

Turning back to the rheological properties of a colloidal suspension, the dynamic or oscillatory tests are one of the most important tools in the characterization of the rheological properties of such systems due to the capability in determining the elastic and viscous components without a total destruction of the system structure. A useful viscoelastic characterization is provided by the mechanical spectrum of the system, that is, the behavior of both the elastic ( $G'$ ) and viscous ( $G''$ ) moduli respect to the frequency at which the applied shear-stress oscillates.

In many systems, it is found that when the oscillating frequency becomes high enough the system cannot respond to the oscillation and the elastic modulus shows a plateau in its value. The average value of this plateau is known as the high-frequency elastic modulus, defined as (Brady 1993):

$$G'_\infty \equiv \lim_{\omega \rightarrow \infty} G'(\omega) \quad (8)$$

This elastic modulus at high frequency,  $G'_\infty$ , can be related to the interaction potential between particles considering that if a small force is exerted on the system, the deformation of the existing structure will also be small (Tadros 1990, 1996). Variations in the position of the particles will change as well the potential energy of the system, and according to the treatment developed by Zwanzig and Mountain, the high-frequency elastic modulus expresses as (Zwanzig and Mountain 1965; Mountain and Zwanzig 1966):

$$G'_\infty = \rho kT + \frac{2\pi}{15} \rho^2 \int_0^\infty g(r) \frac{d}{dr} \left( r^2 \frac{dV}{dr} \right) dr \quad (9)$$

where  $\rho$  is the particle density number,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $g(r)$  is the radial distribution function in the radial distance,  $r$ , and  $V$  is the potential. This expression was first derived for monoatomic fluids.

Buscall et al. (1982), approximated the Zwanzig–Mountain expression considering a crystalline structure of the suspension. Under this assumption, the high-frequency elastic modulus depends on the potential of interaction between the particles as follows:

$$G'_{\infty} = \frac{3N\phi_{\max}}{32R} \left( \frac{\partial^2 V}{\partial R^2} \right) \quad (10)$$

where  $N$  is the coordination number which counts the number of neighbors particle respect to a fixed one, considered to be equal to 12 (Buscall et al. 1982; Tadros 1990); and  $\phi_{\max} = 0.64$  is the maximum packing fraction of the particles for a random closing packing (Mewis and D'Haene 1993; Quemada et al. 2002).  $R$  is the center-to-center distance between particles ( $R = 2a + H$ ) related to the volume fraction of solid dispersed in the continuous phase by (Buscall et al. 1982; Tadros 1996; Raynaud et al. 1996):

$$R = 2a \left( \frac{\phi_{\max}}{\phi} \right)^{1/3} \quad (11)$$

Special attention must be paid to the calculus of the interparticle distance,  $R$ , at each volume fraction of solids by means of Eq. 11. This expression is obtained by geometrical considerations with hard spheres, but in our case, it is necessary to take into account that there are surface properties which must modify this expression. In fact, the surface charge of the colloidal particles induces the apparition of the described ionic double layer, and this makes us consider as the particle size not the geometrical but the hydrodynamic radius. Thus, the size of the particle will depend on the Debye thickness of the double layer,  $\kappa^{-1}$ , resulting in a new effective volume fraction of solids in the suspension,  $\phi_{\text{eff}}$  (Tadros 1996; Weiss et al. 1999; Quemada et al. 2002; Sethumadhavan et al. 2002):

$$\phi_{\text{eff}} = \phi \left[ 1 + \frac{1}{\kappa a} \right]^3 \quad (12)$$

This expression takes into account an effective particle radius,  $a_{\text{eff}} = a + 1/\kappa$ . It is also possible to obtain this particle effective size using a Barker–Henderson approach (Barker and Henderson 1967):

$$a_{\text{eff}} = \frac{1}{2} \int_0^{\infty} \left( 1 - e^{-V(R)/kT} \right) dR \quad (13)$$

Some other attempts were made to obtain models involving a relationship between the high-frequency modulus and the interparticle energy. Evans and Lips (1990) proposed the following expression:

$$G'_{\infty} = nk_B T + \frac{N\phi_{\max}}{5} \left( \frac{4}{R} \frac{\partial V}{\partial R} + \frac{\partial^2 V}{\partial R^2} \right) \quad (14)$$

where  $n = 3\phi/4\pi a^3$  is the particle density number. This equation was proposed initially for microgel dispersions and then was used for suspensions of polymerically stabilized particles at high concentrations (Costello et al. 1992; Berli et al. 2000).

A similar expression was obtained by Wagner (1993), which neglects the kinetic term—first term on the right hand side of Eq. 14—arising from the thermal motion of the particles:

$$G'_{\infty} = \frac{N\phi_{\max}}{5} \left( \frac{4}{R} \frac{\partial V}{\partial R} + \frac{\partial^2 V}{\partial R^2} \right) \quad (15)$$

This expression was also obtained by van der Vorst et al. (1995).

Bergenholtz et al. (1998a, b; Horn et al. 2000) proposed a simplified perturbation model for calculating the high-frequency modulus from the Zwanzig–Mountain model, Eq. 9, in which was assumed that only interactions with the nearest neighbor particles in a disordered noncrystalline dispersion contribute to the elasticity:

$$G'_{\infty} \frac{a^3}{kT} = \frac{3\phi}{4\pi} + \frac{3\phi^2}{40\pi} (2a_{\text{eff}})^4 g(\phi_{\text{eff}}) \left( -\frac{\partial V(R)/kT}{\partial R} \right) \Big|_{2a_{\text{eff}}} \quad (16)$$

where  $a_{\text{eff}}$  is the effective particle radius, and  $g(\phi)$  is the Carnahan–Starling (1969) expression for the radial distribution function for  $\phi < 0.5$ :

$$g(\phi) = \frac{1 - \phi/2}{(1 - \phi)^3} \quad (17)$$

## Materials and methods

Two kinds of  $\text{ZrO}_2$  have been used in this work: one was commercially obtained (Aldrich) and the other was synthesized in our laboratory as monodisperse spheres, both of high purity.

The zirconia spherical particles were prepared following the homogeneous precipitation method described by Aiken et al. (1990). The chemical products used in the synthesis were:  $\text{Zr}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$  (Alfa), polyvinylpyrrolidone PVP-40 (Sigma Chem.), urea and nitric acid (both supplied by Panreac). The deionized water employed in the preparation of the suspensions was produced in a Milli-Q academic device.

TEM microphotographs showed that the synthesized particles are spherical and considerably monodisperse, with an average diameter of  $(540 \pm 20)$  nm. The commercial particles had an average diameter of  $(300 \pm 50)$  nm and no regular shape.

Rheological measurements of the suspensions were performed as a function of ionic strength, ranging in the interval  $10^{-5}$ – $10^{-1}$  M in sodium chloride (Fluka), and volume fraction, up to approximately 20%, for both kinds of particles in a controlled-stress rheometer Bohlin CS-10 (England). The chosen measuring geometry to carry our determinations out was a coaxial cylinders Bohlin SSC25 device, whose inner and outer radii are, respectively,  $(20.50 \pm 0.05)$  mm and  $(20.60 \pm 0.05)$  mm. To avoid loss of material through evaporation, a cover was coupled to the external jacket of the CS-10. Before measuring, the samples were subjected to a preshear process in order to establish the same initial conditions for all the systems. The temperature at which all the experiments were performed was thermostatically controlled at  $(25.0 \pm 0.1)^\circ\text{C}$ .

Due to the difficulties involved in synthesizing large amounts of zirconia spherical particles, their rheology was studied for different volume fractions of solids but only at one single electrolyte concentration ( $10^{-3}$  M NaCl).

For electrokinetic and interfacial characterization of the particles, the electrophoretic mobility,  $\mu_e$ , was measured on dilute suspensions ( $\phi \approx 10^{-4}$ ) in a Zetasizer 2000 (Malvern Instrum., England) at a constant temperature of  $(25.0 \pm 0.1)^\circ\text{C}$ . The effect of NaCl concentration on  $\mu_e$  was analyzed, and the corresponding zeta potential was obtained from those data using the theory of O'Brien and White (1978). The contact angle technique was employed for obtaining the surface free energy of the solids. To that aim, glass microscope slides were uniformly covered with suspensions of  $\text{ZrO}_2$  particles ( $\phi \approx 0.1$ ) in the presence of the corresponding electrolyte, and left dry overnight at room temperature in a dessicator, thus providing a smoothly uniform surface of our solid. Microdrops of three probe liquids (water, formamide and diiodomethane) were placed on the dry solid layer to measure the corresponding contact angles,  $\theta$ , with a (Ramé-Hart 100-07-00, USA) goniometer.

The free-energy parameters of the solid were obtained solving the Young equation (Adamson 1982; van Oss 1994) for three liquids of well-known parameters:

$$2\sqrt{\gamma_1^{\text{LW}}\gamma_2^{\text{LW}}} + 2\sqrt{\gamma_1^+ \gamma_2^-} + 2\sqrt{\gamma_1^- \gamma_2^+} = \gamma_2(1 + \cos \theta) \quad (18)$$

where  $\gamma^{\text{LW}}$ ,  $\gamma^+$  and  $\gamma^-$  are, respectively, the LW, electron-acceptor and electron-donor components. The subscript  $l$  corresponds to the solid phase and 2 to the liquid phase.

The probe liquids used in this work were formamide ( $\gamma^{\text{LW}} = 39.9 \text{ mJ/m}^2$ ;  $\gamma^+ = 2.28 \text{ mJ/m}^2$ ;  $\gamma^- = 39.6 \text{ mJ/m}^2$ ), diiodomethane ( $\gamma^{\text{LW}} = 50.8 \text{ mJ/m}^2$ ;  $\gamma^+ = \gamma^- = 0 \text{ mJ/m}^2$ ) and water ( $\gamma^{\text{LW}} = 21.8 \text{ mJ/m}^2$ ;  $\gamma^+ = \gamma^- = 25.5 \text{ mJ/m}^2$ ). The expressed values were taken from van Oss (1994).

## Results and discussion

In order to determine the potential of interaction between particles using the extended DLVO theory, it is necessary to determine experimentally the electrophoretic mobility,  $\mu_e$ , and the contact angles of the probe liquids on surfaces created with the  $\text{ZrO}_2$  particles at the ionic strengths studied in this work. From these quantities, measured as described in the Materials and methods section, the total potential of interaction between the particles was calculated by means of Eqs. 1, 2, 3, 4, 5, 6, 7.

Table 1 displays the values of the measured  $\mu_e$  and the corresponding data of zeta-potential,  $\zeta$ , calculated using the O'Brien and White theory (1978). Note that the general behavior of the electrokinetic potential is as expected for an indifferent electrolyte:  $\zeta$  decreases with the concentration of NaCl due to the double layer compression (increased screening of the surface charge due to the raising number of ions in the diffuse atmosphere). Its value is positive, in agreement with the fact that the isoelectric point (pH of zero zeta-potential) for zirconia is located between pH = 5.6 and pH = 6.1 (Aiken et al. 1990; Prica et al. 1996; Megias-Alguacil et al. 2000), and we worked at the natural pH (without further adjustments) of the suspensions whose value, pH  $\approx 4.6$ , belongs to the positive branch.

In Table 2 are shown the surface free-energy components of  $\text{ZrO}_2$ , calculated with Eq. 18, after pretreatment with the NaCl concentrations studied in this work. The LW component is constant to within the experi-

**Table 1** Electrophoretic mobility,  $\mu_e$ , and  $\zeta$ -potential of both synthetic and commercial  $\text{ZrO}_2$  particles for the different ionic strengths

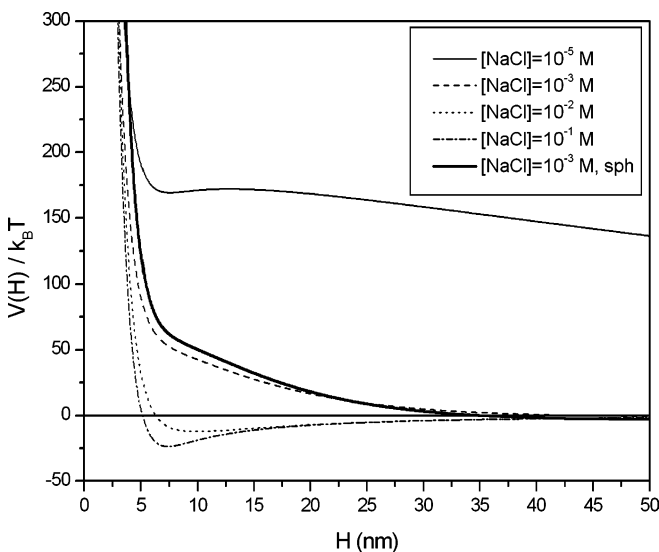
[NaCl] (M)	Spheres		Commercial powder	
	$\mu_e$ ( $\mu\text{m s}^{-1}/\text{V m}^{-1}$ )	$\zeta$ (mV)	$\mu_e$ ( $\mu\text{m s}^{-1}/\text{V m}^{-1}$ )	$\zeta$ (mV)
$10^{-5}$	$0.51 \pm 0.04$	29.8	$1.10 \pm 0.03$	43.1
$10^{-3}$	$2.25 \pm 0.02$	32.1	$4.45 \pm 0.02$	35.7
$10^{-2}$	$1.97 \pm 0.03$	24.8	$3.7 \pm 0.1$	33.4
$10^{-1}$	$1.94 \pm 0.05$	6.5	$2.0 \pm 0.1$	11.8

**Table 2** Surface free-energy and AB components of zirconia for the different NaCl concentrations

[NaCl] (M)	$\gamma_1^+$ (mJ/m <sup>2</sup> )	$\gamma_1^-$ (mJ/m <sup>2</sup> )	$\gamma_1^{\text{LW}}$ (mJ/m <sup>2</sup> )	$\gamma_1^{\text{AB}}$ (mJ/m <sup>2</sup> )
$10^{-5}$	$0.26 \pm 0.01$	$50.6 \pm 0.6$	$49.2 \pm 0.2$	$-18.7 \pm 0.3$
$10^{-3}$	$0.26 \pm 0.02$	$51.7 \pm 0.3$	$49.1 \pm 0.2$	$-19.4 \pm 0.3$
$10^{-2}$	$0.15 \pm 0.04$	$55.2 \pm 0.2$	$49.0 \pm 0.2$	$-22.2 \pm 0.4$
$10^{-1}$	$0.09 \pm 0.01$	$57.3 \pm 0.3$	$49.1 \pm 0.2$	$-23.9 \pm 0.4$

mental uncertainty; considering its average value, the Hamaker constant,  $A$ , is obtained using Eq. 4 having a value of  $(9.245 \pm 0.014) \cdot 10^{-20}$  J, which agrees with the corresponding values for diverse inorganic compounds (Prca et al. 1996). The electron-acceptor component,  $\gamma_1^+$ , is close to zero in all conditions studied, and so, zirconia is like most other inorganic materials (e.g., silica and alumina) a monopolar electron-donor solid (Chibowski 1992; Plaza et al. 1998). The treatment of the solid with NaCl provokes changes only in  $\gamma_1^-$ : this quantity increases in about  $7 \text{ mJ/m}^2$  when  $[\text{NaCl}]$  is raised between  $10^{-5}$  and  $10^{-1}$  M. This behavior has been ascribed to a particular ordering of water dipoles in the vicinity of the surfaces when ionic concentration is high enough (Chibowski et al. 1993).

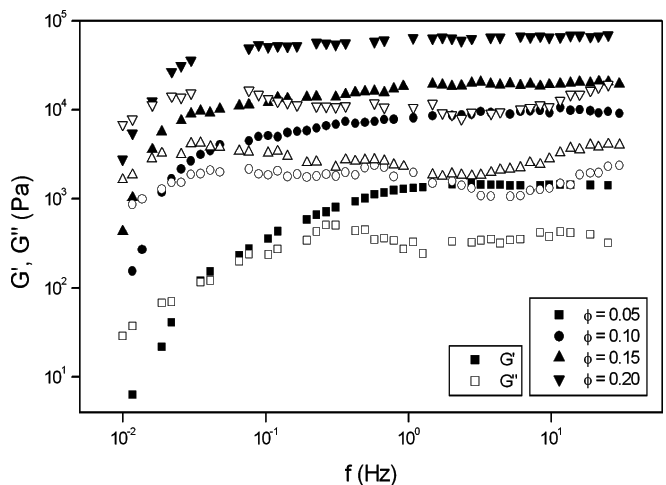
Figure 1 shows the curves of the total potential energy of interaction,  $V(H)$ , for the different ionic strengths and both kinds of particles employed in this work. It can be observed that: (1) curves corresponding to spheres and commercial powder with the same electrolyte concentration,  $10^{-3}$  M, are quite close (the separation of the curves comes from the different particle size) and follow the same trend, as expected; (2) the arrangement of the curves as a function of NaCl concentration, at a fixed distance  $H$ , shows less positive  $V$  values as the ionic strength becomes higher, as a consequence of a decreasing zeta-potential with  $[\text{NaCl}]$  (Table 1) which leads to smaller repulsive electrical components of the potentials; (3) the curve corresponding to the smallest electrolyte concentration,  $[\text{NaCl}] = 10^{-5}$  M, shows a minimum of positive value at a short distance between the surfaces of neighbor par-



**Fig. 1** DLVO potential energies of interaction (dimensionless by factor  $k_B T$ ) as a function of the surface-to-surface distance between particles,  $H$ , for both commercial and spherical particles at the ionic strengths indicated

ticles which is a consequence of the overlapping of the electrical double layers.

In order to measure the mechanical spectra of the suspensions, previous determinations of the viscoelastic linear region were carried out (Megias-Alguacil 2004). These tests let us to choose the value of shear-stress (belonging to this linear region) to apply in the oscillogram, which ensures a nondestructive measurement of the structure of the system as well as a shear-independence of the dynamical functions. Under this consideration, frequency sweeps were carried out with the suspensions considered, applying the whole range in frequency,  $f$ , available for our rheometer,  $10^{-2}$ – $10^2$  Hz. Figures 2 and 3 show the elastic,  $G'$ , and viscous,  $G''$ , moduli for zirconia suspensions (spheres and commercial powder, respectively) as a function of the solid concentration,  $\phi$ , at an electrolyte concentration  $[\text{NaCl}] = 10^{-3}$  M. In all the cases, the suspensions initially show a frequency-dependent response to the oscillating shear-stress. At low frequencies the structure of the suspension is able to relax during the oscillation period and dissipates most of the energy supplied during the cycle ( $G'' > G'$ ); but as the frequency increases, the dissipation of the energy is less and less effective, until the oscillation is so fast that the structure of the system is not able to relax because it can not react to the oscillation, consequently, most of the energy delivered by the stress is stored and the system response is predominantly elastic ( $G' > G''$ ). In terms of the dynamical function  $G'$ , this means that after a continuous increasing of its values, the elastic modulus reaches a steady frequency-independent plateau, the so-called high-frequency modulus,  $G'_\infty$ .



**Fig. 2** Elastic (*solid symbols*) and viscous (*open symbols*) moduli of commercial zirconia suspensions as a function of the frequency,  $f$ , of the applied shear-stress at an ionic strength of 1 mM NaCl, for the different volume fractions



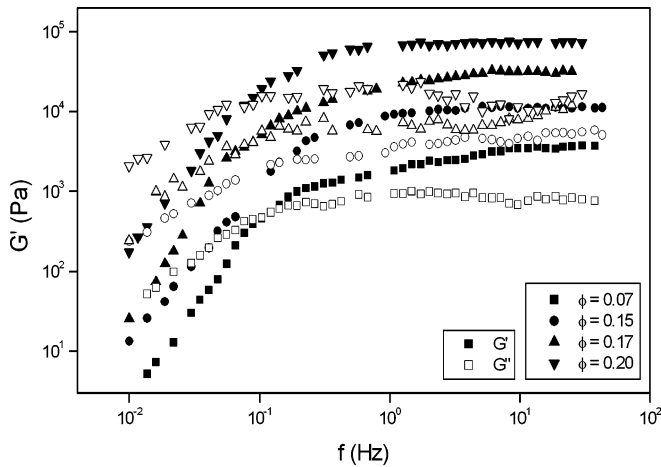


Fig. 3 Same as Fig. 2, but for synthesized spheres suspensions

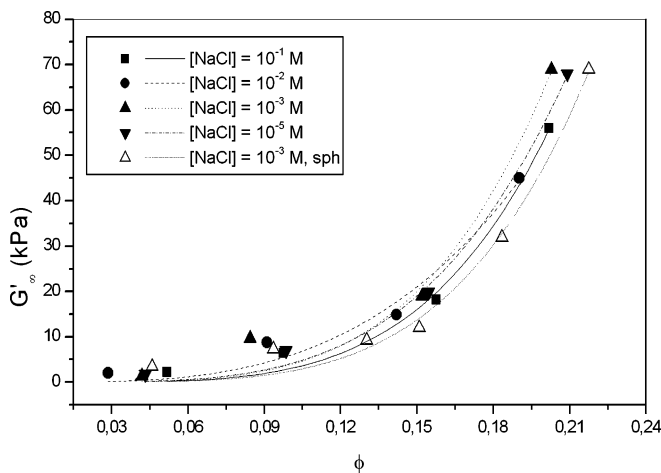


Fig. 4 High-frequency values of the elastic modulus,  $G'_s$  as a function of the volume fraction of solids and the electrolyte concentrations indicated

Figure 4 shows the experimental data of the high-frequency modulus (obtained as the averaged values of the high-frequency plateaus like those shown in Figs. 2 and 3) as a function of the volume fraction,  $\phi$ , for the different suspensions and both kinds of particles. As expected,  $G'_s$  increases rapidly with  $\phi$  displaying a high increment of the elasticity of the suspensions with the concentration of solids; the presence of more and more particles in the system leads to a closing arrangement of them, thus featuring an increasing solid-like behavior. On the other hand, not a clear impact of the electrolyte concentration can be observed on  $G'_s$  in despite of the more repulsive trend of  $V$  vs.  $H$  with the decreasing ionic strength shown in Fig. 1. Also shown in Fig. 4 is the corresponding power-law scalings of the high-frequency modulus with respect to the volume fraction, which have the form (Sonntag and Russel 1987; Patel and Russel 1989; Pons et al. 1995):

$$G' = k \phi^m \quad (19)$$

where  $k$  is a constant and exponent  $m$  can be related to flocculation processes (Liang et al. 1993). The values of parameter  $m \approx 4$  (for all the cases studied here) are in agreement with results for other inorganic colloids (Shih et al. 1990; Rueb and Zukoski 1997); this value has been related to a flocculated state of the suspension (Tadros et al. 1993; Miano and Rabaioli 1994). The rheology of the suspensions also suggests a partly flocculated state of the suspensions. As seen from the frequency sweeps, like those shown in Figs. 2 and 3, the crossover frequency for  $G' = G''$  is found to be around  $f_c \approx 0.1$  Hz, which corresponds to a characteristic time of the order of 10 s. On the other hand, the structural relaxation time  $\approx a^2/D_0$  (being  $D_0$  the Stokes-Einstein diffusion coefficient) (Bergenholtz et al. 1998a, b) for both kinds of particles, commercial and synthesized spheres, is in the order of  $10^{-2}$  s. A simple calculation indicates that a floc size of around 27 commercial particles and 11 spheres should be necessary to match both times. This could explain the high experimental values shown in Fig. 4.

After carrying out all the experimental determinations explained above, the predicted values of the high-frequency modulus can be calculated using the models (named here “theoretical”). For this purpose, the first and second derivatives of the total potential of interaction between the particles with respect to the distance were calculated.

Let us notice that originally, the models expressed above—Eqs. 10, 11, 12, 13, 14, 15—were developed considering as the potential energy of interaction only the repulsive electrical interaction, neglecting any other contribution like the van der Waals attraction. Nevertheless, we try to consider a more realistic potential in describing the interactions of colloidal particles by means of the extended DLVO theory. The theoretical values of the high-frequency modulus were calculated with Eqs. 10, 15 and 16. Since the data obtained with the model by Evans and Lips, Eq. 14, are numerically very close to those calculated with the model by Wagner, Eq. 15, we will not distinguish them in further discussions for the sake of clarity.

Figure 5 shows the results of  $G'_s$  vs  $H$  for the different ionic strengths. Notice that the values from the Bergenholtz model are also displayed as a function of  $H$  for sake of comparison with the other models and the experimental data, even when the interparticle distance does not explicitly appear in Eq. 16.

When considering the models by Buscall, Eq. 10, and Wagner, Eq. 15, it is found that quantitatively, the experimental data are 2–3 orders of magnitude higher than both sets of theoretical ones. Other authors also found discrepancies in theory-experiment of at least one order of magnitude (Costello et al. 1992; Weiss et al. 1999). In our case, the main reason for this disagreement

must be attributed to the low-volume fractions of the suspensions, which leads to very long distances between neighbor particles, and thus the magnitude of the potential is small (Fig. 1).

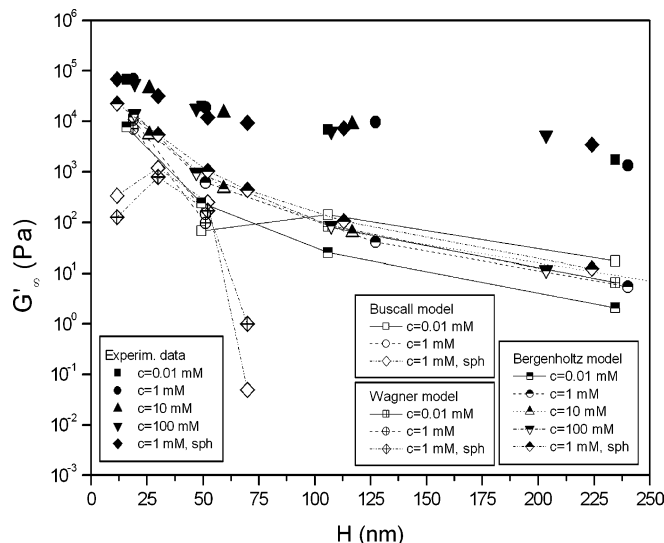
As a general feature, we find that the values calculated with the model of Wagner are sensibly smaller than the ones obtained with the model of Buscall and co-workers. It is clear that this diminution in the numerical values comes from the fact that the first derivative of the potential of interaction between particles is negative for all the experimental conditions considered in this work. When considering the extended DLVO theory we find that, for suspensions of spheres, the high-frequency modulus values calculated with the models by Buscall and Wagner do not follow a uniform decreasing trend with respect to  $H$  as expected. This effect comes from the fact that at the long distances between the particles considered, the contribution of the LW component to the potential is significant with respect to the repulsive contributions, thus lowering the potentials.

Analogous behavior is found for the suspensions of commercial zirconia particles for the case of electrolyte concentrations  $10^{-5}$  M and  $10^{-3}$  M, although a better agreement between the theoretical and experimental data is found especially for the more concentrated suspensions at 1 mM in NaCl, in which the values differs just one order or magnitude.

For the other two ionic strengths,  $10^{-2}$  M and  $10^{-1}$  M in sodium chloride, the values of  $G'_\infty$  from the models by Buscall and Wagner are always negative (not plotted in the graph) since, in these cases, the potential is decreasing faster with the distance between particles because the smaller electrical repulsion and compression of the double layer thickness (first derivative negative) and convex (second derivative negative) after the minimum induced by the LW component shown in Fig. 1.

This is not the case of the data calculated with the model of Bergenholtz, which is able to offer a good qualitative agreement with respect to the experimental data (monotonic trend for the whole range of volume fraction considered), and also quantitative for the most concentrated suspensions, being these theoretical values of the same order of magnitude than the experimental data. The good description of the experiments with this model may rely in the fact that for this model it is not necessary to calculate an interparticle distance according to a certain structure of the suspensions, but to the solid concentration which is less susceptible to a particular lattice selection. Unfortunately, a full matching between Bergenholtz model values and experimental ones is not observed due to possible flocculated states of the systems which increase the rheometrical measurements.

Regarding the geometry of the particles, the Bergenholtz model is able to capture the more repulsive potential,  $V(H)$ , (Fig. 1) experienced by the spheres with respect to the commercial particles at the same



**Fig. 5** High-frequency modulus as a function of the surface-to-surface distance between particles at the different [NaCl]. *Solid symbols* rheological data; *open symbols* Buscall and co-workers model; *cross symbols* Wagner model; *half-solid symbols* Bergenholtz and co-workers model

electrolyte concentration (1 mM); indeed, the values calculated from this model for the spheres (half-filled diamonds in Fig. 5) are higher than those for the irregular commercial powder (half-filled circles).

The attractive component of the interparticle potential induces a poor agreement between the experimental and theoretical data of  $G'_\infty$ , and even more, makes impossible to calculate them via the models of Buscall and Wagner for the ionic strengths  $10^{-2}$  M and  $10^{-1}$  M (which potentials are more influenced by this component). These results support the idea that the elastic behavior of the suspensions is mainly governed by repulsive forces between the particles. Consequently, we reconsider our first approach of using the total interparticle potential, and so, we restrict it to the repulsive components of the potential  $V(H)$ , taking into account the electrical repulsion and the AB component which is also repulsive for our  $ZrO_2$  (see Table 2), and neglecting the van der Waals attractive component.

When recalculating the values with the models of Buscall and Wagner in such a case, no negative values for the theoretical  $G'_\infty$  are found in any conditions, as well as a monotonic decreasing respect to the distance between particles of solid for all the ionic strengths. The values obtained with the models of Buscall and Wagner are practically the same for  $[NaCl] \leq 10^{-3}$  M. Figure 6 displays the data from the model of Buscall when considering just the repulsive components of the potential together with the experimental ones, for comparison.

The values from those models show now a better agreement with the experimental data for the suspensions of spheres and commercial powder at  $10^{-5}$  and

$10^{-3}$  M in NaCl. In addition, the models are able to give positive values of  $G'_{\infty}$  for the highest ionic strengths (0.1 and 0.01 M), although with a considerable underestimation of these data with respect to the experimental ones for the less concentrated suspensions whose values tend very fast to zero (not plotted in Fig. 6) when the distance between particles increases. In such cases, the explanation of this numerical disagreement comes from the fact that the repulsive components of the interparticle potential decays very fast with the distance between particles—due to the negative exponential in Eqs. 1 and 6—and so, when the concentration of solids is low this repulsive potential is practically negligible, being this effect more pronounced when the ionic strength increases, due to the smaller values of the zeta potential (Table 1). In addition, it must be mentioned that the theoretical models from Buscall and Wagner were developed for the case of high concentration of sterically stabilized particles. In our case, the systems are not very concentrated and thus the distance between the particles is essentially high; moreover, the interactions between our particles are mainly governed by electric interactions in nature and some flocculation processes can occur during the experimental time, producing an increase of the values of the elastic modulus.

The model of Bergenholtz is less sensitive to reducing the interparticle potential to the repulsive component because the first derivative of the potential was already evaluated at short distances, where the repulsive component predominates. Nevertheless, the qualitative agreement with the experimental values is also improved ( $\sim 10$ – $12\%$ ) in this case. The comparison with the values obtained with the three models, Fig. 6, indicates that the

Bergenholtz one approaches much more to the experimental data than the other two (Buscall and Wagner), specially in the case of less-concentrated suspensions, in which the later models show considerable disagreements with respect to the experiments.

## Conclusions

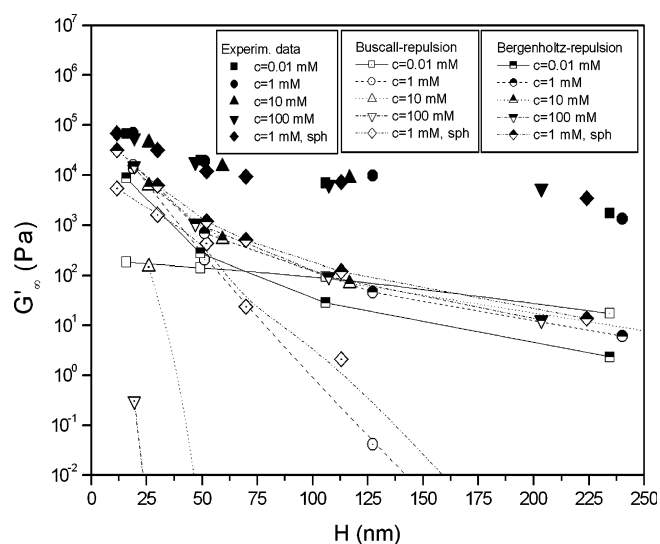
The high-frequency modulus of colloidal aqueous suspensions of  $ZrO_2$  is experimentally measured as a function of electrolyte concentration and volume of fraction of particles. These data are compared to those calculated using the models of Buscall and co-workers, Wagner, and Bergenholtz and co-workers.

For the theoretical calculations, the extended DLVO theory is considered for calculating the total potential of interaction between particles in an attempt at applying the most complete description on colloidal interactions. In order to build the curves of potential, a full characterization of the particles, both electrokinetic and surface thermodynamics, is carried out, finding out that the solid surface is positively charged and that the oxide is a monopolar electron-donor material.

When using the extended DLVO in the theoretical calculations, it is found that the model of Wagner gives values smaller than the model of Buscall in all the cases. Quantitatively, these theoretical values are 2–3 orders of magnitude lower than the experimental ones, and in addition, the inclusion of the attractive term of  $V(H)$  in the calculations induces negative values of  $G'_{\infty}$  for the highest electrolyte concentrations. On the other hand, the model by Bergenholtz offers qualitatively acceptable results in the whole range of volume fractions considered, and the quantitative agreement is found to be very good for the most concentrated suspensions.

Restricting the interparticle potential to the repulsive components, the new theoretical values calculated with the models of Buscall and Wagner, improve the qualitative and quantitative agreement with respect to the experimental data at the lowest ionic strength; but in the cases of higher electrolyte concentrations, the divergence with respect to the experimental data is still very pronounced.

The main reason for such a quantitative disagreement is the low solid concentrations involved, which leads to high interparticle distances, and thus to small values of the potential of interaction between them, and also to partly flocculated states of the suspensions which increases the experimental values and make their microstructure to be different from that assumed by the models: ordered (Wagner and Buscall and co-workers models) and fluid ordering (Bergenholtz and co-workers model). Hence, we expect good correlations theory-experiment in case of concentrated suspensions with



**Fig. 6**  $G'_{\infty}$  vs  $H$  considering only the repulsive component of the potential in the models calculations. *Solid symbols* experimental data; *open symbols* Buscall and co-workers model; *half-solid symbols* Bergenholtz and co-workers model



strong repulsive interactions (low ionic strengths or steric repulsions in colloids coated with polymers). When neglecting the attractive van der Waals component, the Bergenholtz and co-workers model slightly improves its agreement with the experiments, also indicating that the main factor responsible of the elasticity

of the systems is the repulsive component of the potential of interaction between the particles.

**Acknowledgements** This work was carried out in the Department of Applied Physics of the University of Granada (Spain). The author wishes to express his gratitude to Prof. Angel Delgado for his support during the stage in his group.

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