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Soft Matter

Disclaimer

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Abstract

Molecular dynamics simulations of a charged colloidal suspension in the salt-free regime show that the system exhibits an electrical conductivity maximum as a function of colloid charge. We attribute this behavior to two main competing effects: colloid effective charge saturation due to counterion 'condensation' and diffusion slowdown due to the relaxation effect. In agreement with previous observations, we also find that the effective transported charge is larger than the one determined by the Stern layer and suggest that it corresponds to the boundary fluid layer at the surface of the colloidal particles.

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Charged colloidal suspensions exhibit a wide range of interesting equilibrium as well as electrokinetic behaviors. On the equilibrium side these include charge renormalization due to strong counterion screening [1–3], large Coulombic effects in sedimentation profiles [4], highly tunable phase transitions [6, 7], *et caetera*. The dynamic behavior may be even richer [8–11] due to the coupling of hydrodynamic and electrostatic interactions, even in the absence of net colloidal charges [12]. The motion of charged, mesoscopically-sized particles such as colloids or polyelectrolytes in applied electric fields, generally referred to as electrophoresis, is relevant to numerous applications, from the detection of elementary charges [13] to molecular biology [14] and nanofluidics [15]. As a result, the interest in elucidating fundamental aspects of this phenomenon remains high, with computer simulations playing a significant role [16–18]. Although the focus of such studies is often the electrophoretic mobility [17], other transport properties such as the self-diffusion coefficient and electrical conductivity are also important for fully characterizing these systems, and their behavior has considerable practical consequences [19, 20]. Colloidal suspensions in the high ionic strength regime have generally received more attention than the low salt ones [21], but the latter have recently began to be studied more systematically, with results now available for both structural [22] and electrokinetic properties [23]. In this letter we present molecular dynamics (MD) simulation results for the self-diffusion coefficients and electrical conductivity of a model charged colloidal suspension under no-salt conditions.

The system considered here contains solvent particles, colloidal particles with charge $-Ze$ and counterions of opposite unit charge, i.e. it is a salt-less suspension. The inter-particle potentials consist of short range and long range (Coulomb) contributions. The short range interactions are based on the inverse-12, 'soft-sphere' potential,

$$u(r) = \epsilon \left(\frac{d_0}{r} \right)^{12} \tag{1}$$

, which we truncate and shift at $r/d_0 = 2$. (We also define $u(r) = \infty$ for $r < 0$.) They are:

$$u_{CC}(r) = u(r - 2R_C) \tag{2a}$$

$$u_{Cc}(r) = u_{Cs}(r) = u(r - R_C) \tag{2b}$$

$$u_{cc}(r) = u_{ss}(r) = u_{cs}(r) = u(r) \tag{2c}$$

, where C stands for the colloidal particles, while c and s denote the counterions and solvent particles, respectively; R_C is an impenetrable colloidal particle core radius. Such potentials have been employed before to model neutral suspensions [24–26]. For temperatures $k_BT \simeq \epsilon$ the effective diameters corresponding to these interactions are well approximated by $d_c = d_s = d_{cs} = d_0$, $d_C = 2R_C + d_0$, and $d_{Cs} = d_{Cc} = R_C + d_0$, and satisfy additivity, $d_{Cc} = (d_C + d_c)/2$, $d_{Cs} = (d_C + d_s)/2$. The Coulomb interactions are given by

$$v_{\alpha\beta}(r) = \frac{1}{4\pi\epsilon_0\epsilon_r}\frac{q_\alpha q_\beta}{r} \tag{3}$$

where $\alpha, \beta = c, C$. Thus, while the solvent size granularity is explicitly accounted for at the microscopic level by the short range interactions, the (relative) dielectric constant ϵ_r, as is usually the case [21, 27], is not. It would be difficult to perform large scale simulations with solvent particles carrying explicit dipoles, and we do not expect that they would change the results presented here.

We focused on fairly dilute suspensions, with colloid 'volume fraction' $\phi_C = \pi n_C {d_C}^3/6 = 0.1$, solvent plus counterions 'volume fraction' $\phi_0 = \pi(n_c + n_s)d_0^3/6 = 0.35$, and with a colloid-solvent 'diameter' ratio $d_C/d_0 = 10$; n_C, n_c and n_s are the number densities of the colloidal particles, counterions and solvent particles, respectively. The first two of them satisfy $n_c = Zn_C$ due to charge conservation. We performed MD simulations of this system in the microcanonical (NVE) ensemble for 8 different values of the colloidal charge $Z : 0, 10, 20, 30, 40, 50, 70, 100$. The average temperature was set to $k_BT = \epsilon$. If we introduce the Bjerrum length $\lambda_B = e^2/4\pi\epsilon_0\epsilon_r k_BT$ and Debye screening distance associated with counterions only, $\lambda_D = 1/\kappa_D = (4\pi\lambda_B n_c)^{-\frac{1}{2}}$, the simulations correspond to $\lambda_B/d_0 = 2.32$, while λ_D/d_0 varied between 4.23 for the $Z = 10$ simulations and 1.34 for the $Z = 100$ ones. The particle masses were chosen to be $m_s = m_c = m_0$ and $m_C/m_0 = 1000$. All simulations were carried out with $N_C = 50$ and $N_s + N_c = 175000$ in a box with periodic boundaries. The Coulomb interactions were handled using the Ewald summation technique with conducting boundary conditions. The time unit is $t_0 = d_0(m_0/\epsilon)^{\frac{1}{2}}$, and the electrical conductivity unit $\sigma_0 = 10^{-4} \times e^2 t_0/m_0 d_0^3$.

After equilibration the simulations were run for $4 - 5 \times 10^5$ time steps, accumulating structural as well as dynamic information necessary for the calculation of self-diffusion and electrical conductivity coefficients. The self-diffusion coefficients D_δ, $\delta = C, c, s$ were determined using the velocity autocorrelation relation:

$$D_\delta = \lim_{t\to\infty} \frac{1}{3} \int_0^t \langle \mathbf{v}_\delta(0) \cdot \mathbf{v}_\delta(\tau) \rangle d\tau \tag{4}$$

with no tail corrections. The conductivity calculation was done by integrating the charge current autocorrelation,

$$\mathbf{j}^q(t) = \sum_i^N q_i \mathbf{v}_i(t) \tag{5a}$$

$$\sigma = \lim_{t\to\infty} \frac{1}{V k_B T} \int_0^t \langle \mathbf{j}^q(0) \cdot \mathbf{j}^q(\tau) \rangle d\tau \tag{5b}$$

The current autocorrelation integrated up to time t is denoted by $\sigma(t)$.

The colloid-counterion pair correlation functions - Fig. 1 - show strong counterion stratification at the surface of the colloidal particles and the formation of what is typically designated as the Stern layer [21], with a thickness of roughly one atomic diameter. This surface 'condensation' effect and the associated chemical equilibrium between 'condensed' and 'free' counterions is expected to lead to colloid-colloid interactions corresponding to a renormalized or effective colloid charge Z_{eff}, which saturates at large Z [1, 2]. The present simulations permit the assessment of this scenario at the microscopic level. To this end we proceed to define Z_{eff} in what appears to be the natural way, as the charge contained on the average in a sphere centered on a colloidal particle and extending up to the first minimum of $g_{Cc}(r)$, i.e. inside the outer boundary of the Stern layer. The result is plotted in Fig. 1 (inset) and shows that Z_{eff} so defined exhibits the predicted saturation behavior in the range of 'bare' charges Z covered in these simulations.

The self-diffusion coefficients of the colloidal particles and counterions - Fig. 2, are both decreasing functions of Z (the self-diffusion coefficient of the solvent particles is essentially independent of Z). Their behavior can likely be understood by extending to charged colloidal systems arguments usually employed in the study of the self-diffusion coefficients of electrolyte solutions. The classic analysis due to Onsager [28] singles out the most important contribution to self-diffusion to be the relaxation effect, i.e. the drag exercised on a moving ion by its lagging, distorted charge atmosphere. This direct, phenomenological treatment is particularly suitable for the colloidal particles, which are primarily screened by the small counterions. In this case the ionic atmosphere subject to relaxation should reasonably be expected to consist only of the counterions beyond the tightly bound Stern layer, so an analysis in terms of the effective charge Z_{eff} is likely appropriate; we outline it briefly below following the ideas in [28]. The screening atmosphere of a charged colloidal particle moving with velocity v will lag behind a distance ζ equal with the one traveled by the particle in the time τ

needed by the atmosphere (a charge shell of typical size λ_D) to equilibrate through diffusive redistribution of the screening counterions: $\zeta = v\tau$, where $\tau \propto \lambda_D^2/D_c$ and $D_c = k_BT/\mu$ (Einstein relation for counterions), with mobility $\mu \propto \eta d_c$ (Stokes relation with viscosity η). This lag or distortion will result in a retarding force between the charged particle and its screening atmosphere, $F_r \propto \zeta Z_{eff}^2 e^2/\lambda_D^3\epsilon_r$. Now the Stokes drag on the colloidal particle is $F_s \propto \eta d_C v$, so the total drag force will be $F_{total} = F_s + F_r \propto \eta d_C v[1 + f\lambda_B(d_c/d_C)Z_{eff}^2/\lambda_D]$, where f is a numerical factor. This corresponds to an effective mobility $\mu\prime \propto \eta d_C[1+f(d_c/d_C)Z_{eff}^2\lambda_B/\lambda_D]$ which yields, according to the Einstein relation, the self-diffusion coefficient of the charged colloidal particles:

$$D_C = \frac{D_0}{1 + f\frac{d_c}{d_C}\frac{\lambda_B}{\lambda_D}Z_{eff}^2} \tag{6}$$

The original Onsager analysis of electrolytes with equally sized anions and cations also determines the factor f, e.g. $f \simeq 0.1$ for the charge symmetric case [28]. For the present highly asymmetric charged colloidal system we test the above relaxation effect prediction by simply assuming f to be a free parameter. The comparison with the MD results, shown in Fig. 2 (inset) with $f \simeq 0.022$, indicates that the concept of renormalized charge is suitable for describing the self-diffusive motion of charged colloids in conjunction with the relaxation effect. This may provide a convenient avenue for estimating the self-diffusion coefficients of such colloids over a wide range of charged states.

Electrical conductivity (σ) measurements are an important means for characterizing the properties of charged suspensions [4, 20, 30]. Our MD simulation results reveal that, surprisingly, σ exhibits a maximum as a function of the 'bare' charge Z - see Fig. 3. The decrease of conductivity at high Z is well established in the simulations, as further highlighted by the time dependent conductivity $\sigma(t)$ - Fig. 3 (inset). (Interestingly, the transient behavior of $\sigma(t)$ on short time scales also suggests strong frequency effects at high Z.) Theories for electrical conduction in classical charged systems such as electrolytes have a long history [31–33]. Unfortunately their generalization to charged colloids is difficult, and therefore simulations such as the ones presented here may offer the best chance for understanding the major features of conduction in such systems. We interpret the results by considering the Nerst-Einstein relation [34] connecting σ with the densities and self-diffusion coefficients of colloidal particles and counterions: $\sigma = e^2 n_C Z_C(D_c + Z_C D_C)/k_BT$, where we employed charge conservation to eliminate the counterions' density and now designate the charge of the colloidal particles by Z_C. With the exception of Z_C, which is open to interpretation, all quantities involved are known or have been determined in the simulations. At the two extremes Z_C can be identified with either the 'bare' charge Z, or the effective one Z_{eff}. As shown in Fig. 3 the first choice does not capture the character of the simulation results, as it predicts a monotonously increasing conductivity. We also note that such an identification is not consistent with the neglect of correlations between the charged colloidal particles and counterions, as *de facto* implied in the above form of the Nerst-Einstein relation [34], and which should be important given the surface 'condensation' of counterions. If on the other hand Z_C is identified with Z_{eff}, this yields an electrical conductivity with a maximum positioned almost identically with the MD simulation results. The renormalization of the colloid charge thus seems to account qualitatively for the behavior of the conductivity, whose maximum appears to be the result of at least two effects: the saturation of the effective colloidal charge and the slowdown of the colloidal particles due to the relaxation effect, operating again at the level of the effective charge. It may seem puzzling that this analysis does not include the electrophoretic effect, which should also be relevant for electrical conduction [31]. We note however that the above phenomenology is incomplete, as it does not include a characterization of the self-diffusion coefficient of the counterions. Somewhat unexpectedly, it appears therefore that electrophoretic retardation would only contribute to conduction indirectly, through the self-diffusion motion of the counterions, but this issue needs further investigation. As observed in Fig. 3, the σ values calculated using Z_{eff} still underestimate significantly the MD results. To obtain better agreement we simply rescale Z_{eff}, and find that a multiplicative factor of 1.4 brings the MD simulations and Nerst-Einstein predictions in close agreement. This factor is essentially identical with the one determined in [30], which compared the effective colloidal charge obtained from structural (shear modulus) and transport (electrical conductivity) measurements. We would like to take advantage of the microscopic details available here to further analyze the difference between Z_{eff} and the effective transported charge. To this end we consider the pair correlation function between colloidal particles and the whole suspending fluid (combined counterions and solvent particles) - $g_{Cc+s}(r)$ - Fig. 4. This function also exhibits strong layering at short distances, and on intermediate length scales converges to $1/(1-\phi_C)$, corresponding to a higher apparent interstitial fluid density. We define the first peak of $g_{Cc+s}(r)$ up to where this density is reached (at distance r_b) as a boundary fluid layer, and calculate the effective charge contained in this shell. We also determine the charge shell boundary r_σ corresponding to the observed transported charge $1.4Z_{eff}$, and find that it agrees well with r_b, particularly at higher Z - Fig. 4 (inset). Both are approximately half an atomic diameter smaller than r_0, the first minimum of $g_{Cc}(r)$, which defines the Stern layer and Z_{eff}.

In sum, MD simulations of a charged colloidal suspension in the salt-free regime reveal that the system exhibits an electrical conductivity maximum as a function of the colloid charge. We attribute this behavior to two main competing effects: colloid effective charge saturation due to counterion 'condensation' and diffusion slowdown due to the relaxation effect. We also find that, in agreement with previous observations, the effective transported charge is larger than the one determined by the Stern layer, and suggest that it corresponds to the boundary fluid layer at the surface of the colloidal particles. Finally, it may be interesting to study such systems at lower solvent dielectric constants, where clustering effects may play an important role [35].

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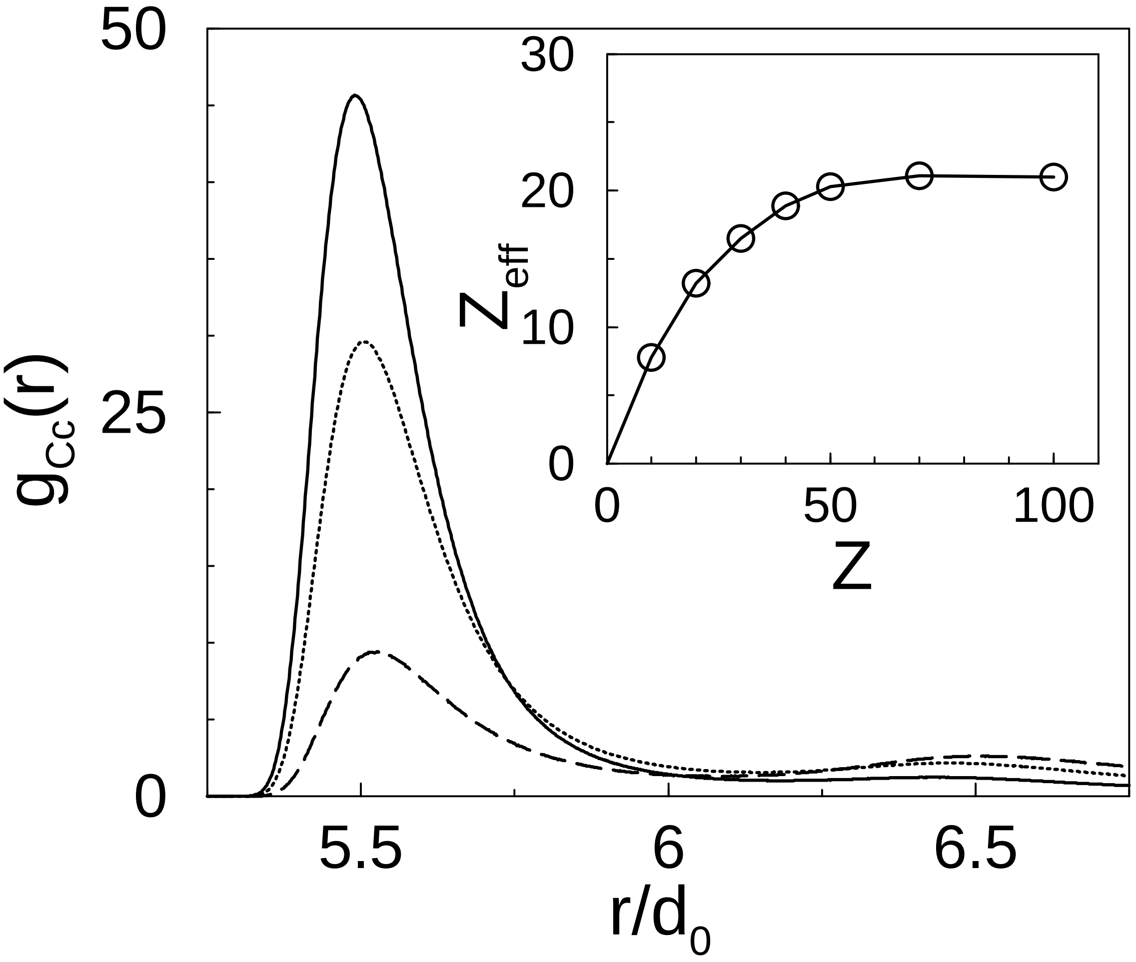

FIG. 1: Colloid-counterion pair correlation function for Z = 10 (dashed line), 50 (dotted line), 100 (solid line). Inset: effective colloidal particle charge Z_{eff} as a function of the 'bare' charge Z.

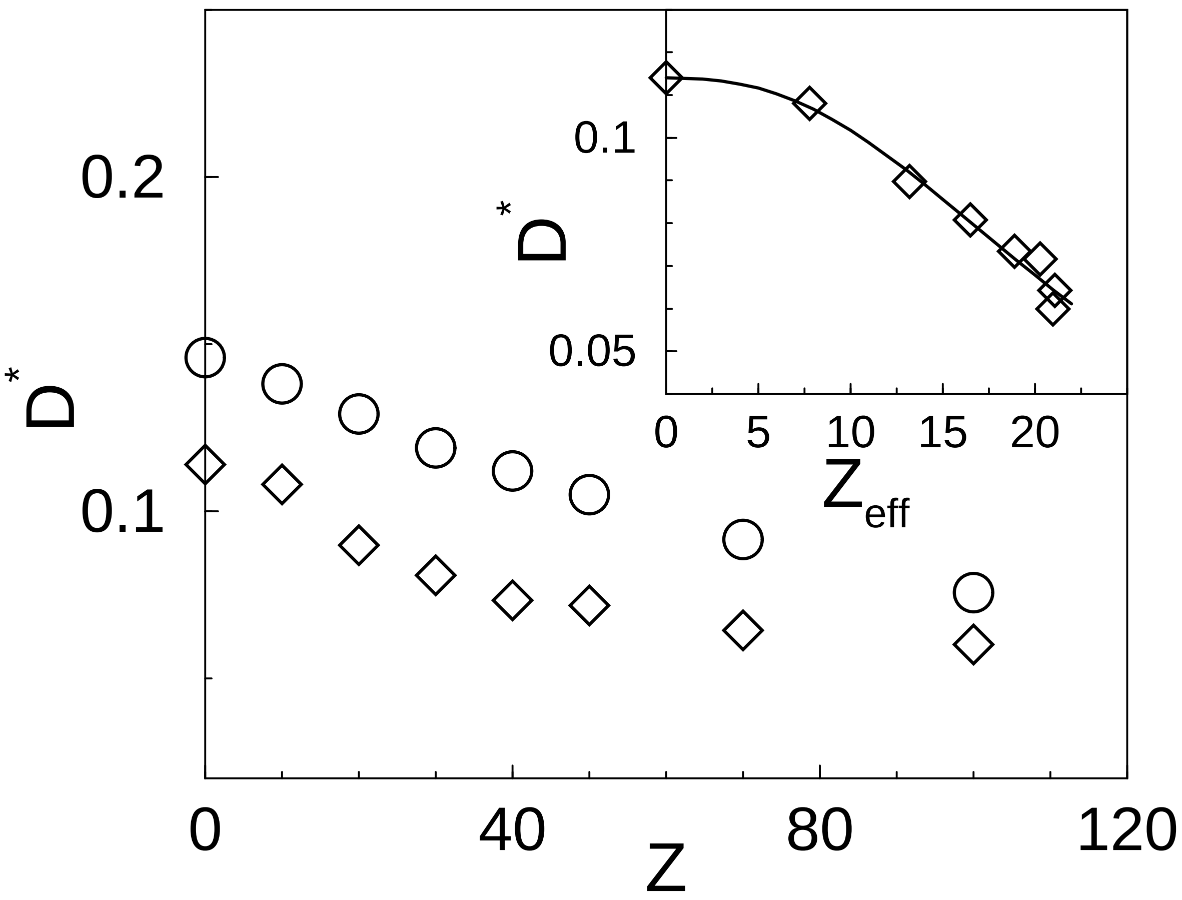

FIG. 2: Self-diffusion coefficients of counterions (circles) and colloidal particles (diamonds) as a function of colloid charge Z; $D^* = D_\alpha d_\alpha / D_0 d_0$, $D_0 = d_0^2/t_0$, $\alpha = c, C$. Inset: Colloidal particle self-diffusion coefficient as a function of the effective charge Z_{eff} (symbols) and Onsager relaxation effect relation (solid line).

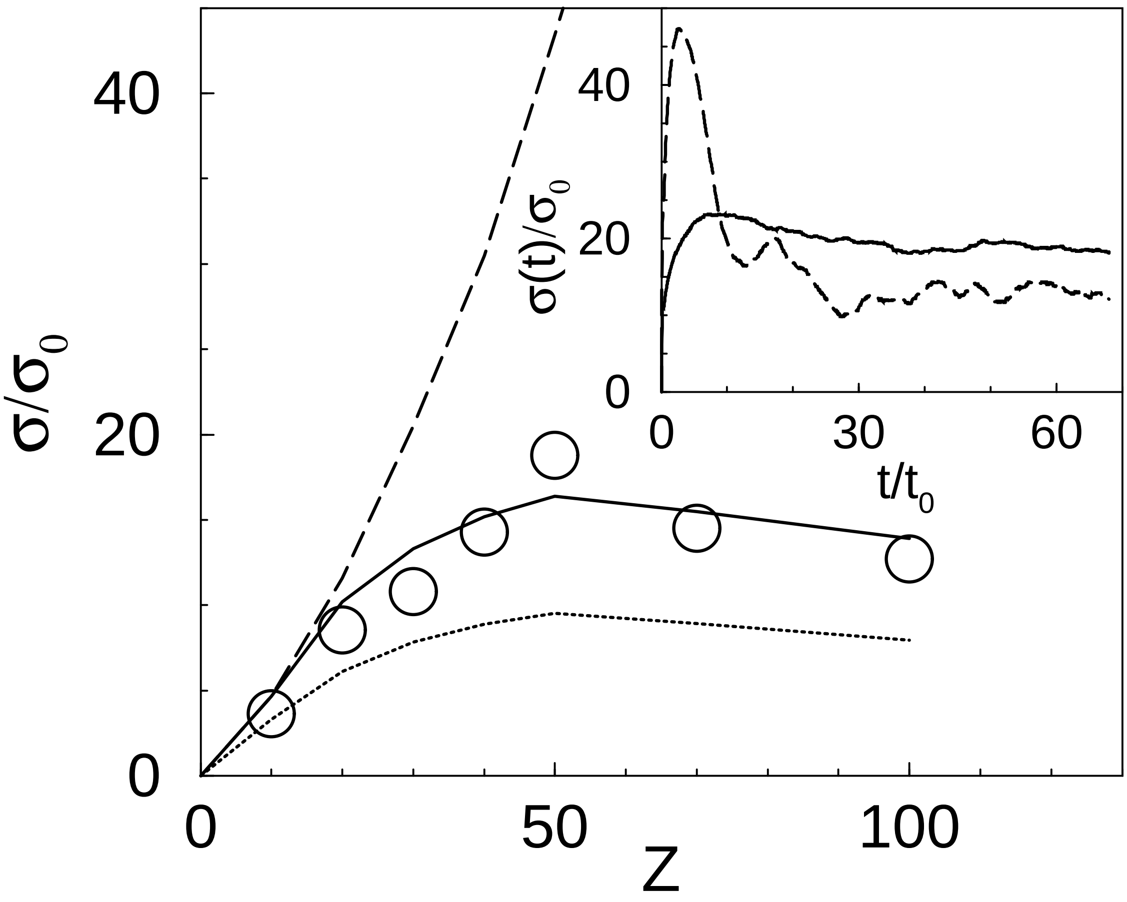

FIG. 3: Electrical conductivity of the suspension: simulations (triangles) and Nerst-Einstein relation with 'bare' charge Z(dashed line), effective charge Z_{eff} (dotted line) and $1.4Z_{eff}$ (solid line). Inset: time dependent electrical conductivity for $Z = 50$ (solid line) and $Z = 100$ (dashed line).

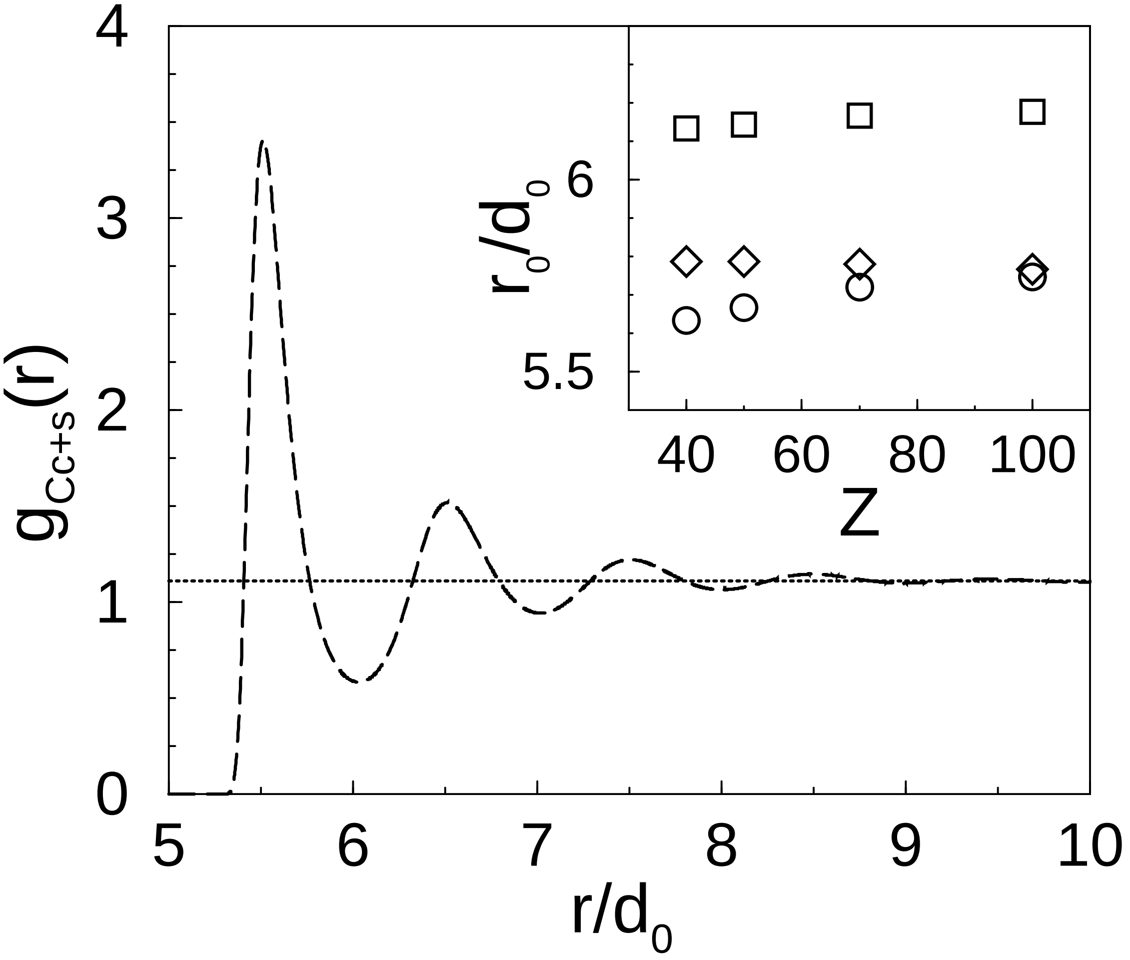

FIG. 4: Colloid-fluid (solvent+counterions) pair correlation function $g_{Cc+s}(r)$ - dashed line; dotted line corresponds to $1/(1-\phi_C)$. Inset: first minimum of $g_{Cc}(r)$ - r_0 (squares), fluid layer boundary - r_b (see text) (diamonds), and charge shell boundary corresponding to $1.4Z_{eff}$ - r_σ(circles).