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Fast, Robust Evaluation of the Equation of State of Suspensions of Charge-Stabilized Colloidal Spheres

Yannick Hallez*[ORCID] and Martine Meireles

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

S *Supporting Information*

ABSTRACT: Increasing demand is appearing for the fast, robust prediction of the equation of state of colloidal suspensions, notably with a view to using it as input data to calculate transport coefficients in complex flow solvers. This is also of interest in rheological studies, industrial screening tests of new formulations, and the real-time interpretation of osmotic compression experiments, for example. For charge-stabilized spherical particles, the osmotic pressure can be computed with standard liquid theories. However, this calculation can sometimes be lengthy and/or unstable under some physicochemical

conditions, a drawback that precludes its use in multiscale flow simulators. As a simple, fast, and robust replacement, the literature reports estimations of the osmotic pressure that have been built by adding the Carnahan−Starling and the cell model pressures (CSCM model). The first contribution is intended to account for colloid−colloid contacts, and the second, for electrostatic effects. This approximation has not yet been thoroughly tested. In this work, the CSCM is evaluated by comparison with data from experiments on silica particles, Monte Carlo simulations, and solutions of the accurate Rogers−Young integral equation scheme with a hard-sphere Yukawa potential obtained from the extrapolated point-charge renormalization method for a wide range of volume fractions, surface charge densities, and interaction ranges. We find that the CSCM is indeed perfectly adequate in the electrostatically concentrated regime, where it can be used from vanishingly small to high surface charge because there is error cancellation between the Carnahan−Starling and cell model contributions at intermediate charge. The CSCM is thus a nice extension of the cell model to liquid-like dense suspensions, which should find application in the domains mentioned above. However, it fails for dilute suspensions with strong electrostatics. In this case, we show that, and explain why, perturbation methods and the rescaled mean spherical approximation are good alternatives in terms of precision, ease of implementation, computational cost, and robustness.
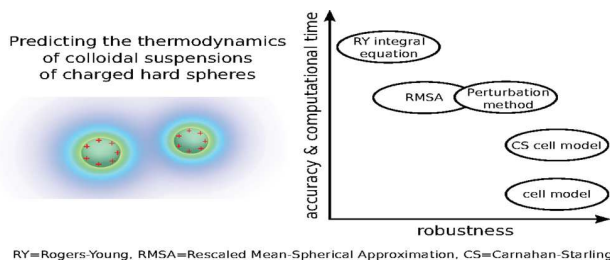
1. INTRODUCTION

The equation of state (EOS) of a colloidal dispersion is a macroscopic, thermodynamic signature of the physical and chemical phenomena at play on the particle scale. For example, the examination of an EOS has proven useful in showing that some latex particles release small polymers under dilute, high-pH, low-salt conditions[1] and in understanding the link between the dynamic yield stress and the formation of a slip layer in silica suspensions[2] or again in determining the conditions under which casein micelles in suspension make the transition from separate, incompressible entities to a percolated compressible network.[3] The understanding that can be gained by studying the EOS of a suspension relies on the knowledge of a set of typical EOSs for a few canonical, simpler, well-documented suspensions. If quantitative models exist for the latter EOSs, then matching them with experimental data even allows physical quantities to be measured.

The EOS is also an essential ingredient required to build continuous models of out-of-equilibrium suspensions. It can be used to derive quantities such as the gradient diffusion coefficient or the particle stress in flowing suspensions if the microstructure is close to equilibrium (particle Péclet number

<1, which is often verified in practice).[4] In this case, the physicochemical parameters may change continuously in space and time because of variations of the colloid and ion concentrations (including the pH). Multiscale simulation codes intended to compute colloidal flows should therefore either be able to evaluate millions of values of the pressure on the fly or have access to these values in precomputed lookup tables. In both cases, a large number of osmotic pressure or compressibility values have to be computed for a broad range of physicochemical parameters as fast as possible and in a robust manner and, in particular, without human intervention.

In this work, we discuss the determination of such a model of EOS for a suspension of charged hard spheres in a liquid containing both salt ions and the counterions of the colloids. Accurate models do exist to compute the EOS of such suspensions. Unfortunately, they suffer from two major drawbacks in the context mentioned above. First, they may be prohibitively computational-time-consuming, like primitive

model molecular dynamics or Monte Carlo simulations, because they require a few hours to obtain one pressure value. Second, they may be fast but unreasonably human-time-consuming, like some spectral solvers of integral equation schemes requiring the tweaking of a few numerical parameters to achieve and accelerate convergence. This lack of robustness is also incompatible with any kind of on-the-fly calculation in a multiscale solver.

Models that are simple and fast already exist, with various associated precisions, computational times, and robustnesses. The cell model (CM) is able to produce accurate predictions of the osmotic pressure in "effectively concentrated" dispersions, i.e., suspensions in which the mean intercolloid distance is smaller than a few times the interaction range.[5,6] The cell model is relatively simple to implement, always converges, and accounts for nonlinear effects in strongly charged suspensions. It is therefore often very attractive, but by construction, it accounts only for the ion contribution to the pressure, which indeed dominates in effectively concentrated suspensions,[7] and it ignores the direct colloid–colloid interactions essential in dilute suspensions. For uncharged spheres, the Carnahan–Starling (CS) expression is very accurate up to volume fractions ϕ of about 0.5. Between these two extremes, predicting the thermodynamics of charged sphere suspensions requires a knowledge of an effective pair potential of interaction u. The effective parameters entering this potential can be computed from the real screening length and surface charge (obtained by titration, for instance) with various methods, a procedure termed renormalization. Several of these renormalization methods are based on the cell model solution.[8−10] If this route is chosen, calculating an equation of state without fitting experimental data inevitably starts with a CM resolution to determine u. Thermodynamics can then be predicted with perturbation methods or through a calculation of the suspension structure with statistical theories. This second step adds computational time to the equation of state calculation and, sometimes, significant numerical instability, depending on the method.

To avoid these additional constraints, some authors have made the choice of building an approximate equation of state by simply adding the Carnahan–Starling pressure to the cell model pressure.[4,11,12] The motivation stems from the observation that the ion-induced CM pressure is much larger than the CS pressure at high effective volume fraction and that the CS pressure dominates the electrostatic contribution for vanishingly small surface charges. This simple model, termed CSCM here, is fast, unconditionally stable, and accurate within these two limits by construction. It completely avoids the computational overhead and instability introduced by the effective potential-based methods mentioned above. Although it was satisfactory in the contexts where it was used, to have any general reach, it needs to remain acceptable in other regions of the parameter space. The aims of this article are to determine the extent to which this is the case and to propose alternative schemes when necessary.

The different models involved in this work are presented in section 2. Their predictions are compared to experimental and Monte Carlo data in section 3 and show in particular that the renormalized integral equation scheme considered as a reference is actually an accurate and predictive tool. The performances of the simple CSCM are discussed in section 4 by means of a systematic comparison with reference data throughout the parameter space. Finally, alternative methods

are compared to this model in terms of precision, cost, and ease of use. Note that a list of abbreviations is provided in the Abbreviations section if needed.

2. MODELS

For future use, let us recall that the osmotic pressure of a suspension of charged hard spheres can be decomposed into $\Pi = \rho kT + \Pi_C + \Pi_E^{col} + \Pi_E^{ions}$, where ρ is the colloid density, k is the Boltzmann constant, T is the temperature, Π_C is the contribution of colloid−colloid contacts, Π_E^{col} is the contribution of direct colloid−colloid electrostatic interactions, and Π_E^{ions} is the contribution of the small ions. Because Π_E^{ions} is induced by electrostatics, the total electrostatic contribution to the pressure is $\Pi_E \equiv \Pi_E^{col} + \Pi_E^{ions}$.

The equation of state of uncharged hard spheres is very well modeled by the Carnahan−Starling expression $\Pi_{CS} = \rho kT(1 + \phi + \phi^2 - \phi^3)/(1 - \phi)^3$ up to volume fractions ϕ of about 0.5. On the other hand, strongly charged, interacting spheres arrange themselves on a solid-like structure, which permits the use of the cell model:[13] the suspension is split into identical, electroneutral, usually spherical cells, each containing one colloid of radius a. Conserving the global volume fraction defines the cell radius $R = a\phi^{-1/3}$. The osmotic pressure of the suspension is related to the total ion density at the boundary of the cell $n(R)$ by $\Pi_{CM} = 2n(R)kT - 2n_{res}kT$. Here, $2n_{res}$ is the ion density in an ion reservoir assumed to be in equilibrium with the suspension. $n(R)$ can be obtained from a Monte Carlo simulation in the primitive model or from a 1D resolution of the Poisson−Boltzmann equation valid at low electrostatic coupling. In the latter case, the resulting 1D spherically symmetric problem can be solved numerically in a fast, accurate, and robust manner even for nonlinear electrostatics. More details on the construction of the cell model can be found in refs 9 and 13−15. The drawback of this model is that it takes only the osmotic pressure contribution of the ions, Π_E^{ions}, into account and not the contribution Π_E^{col} from the colloids themselves. It produces a good estimate of the full electrostatic contribution Π_E only when the former largely dominates the latter. This is the case when the interaction range is large compared to the intercolloid distance, which is sometimes called the "electrostatically concentrated" regime.[5−7,16]

The equation of state of colloidal suspensions is often required for volume fractions varying by orders of magnitude. These suspensions can then be in either the electrostatically dilute or the electrostatically concentrated regimes. For the reasons mentioned in the Introduction, this led some authors[4,11,12] to use the simple approximation $\Pi \simeq \Pi_{CSCM} \equiv \Pi_{CS} + \Pi_{CM}$, termed CSCM here. To some extent, it can be seen as a cell model approximation patched for colloid−colloid correlations by adding, in a crude way, Π_{CS} instead of the true contribution $\rho kT + \Pi_C + \Pi_E^{col}$. For low colloidal charges Ze, Π_E and Π_{CM} (scaling as Z^2) are much smaller than Π_C so that the CSCM reduces to Π_{CS} and remains accurate. In the electrostatically concentrated limit, Π_E^{ions} is much larger than every other contribution, so the CSCM pressure reduces to the accurate cell model prediction. However, to be of any practical use, the CSCM has to remain acceptable between these two limits. The aim of this work is to determine if this is the case.

To this end, the colloidal osmotic pressures given by the simple CSCM will be compared to predictions of alternative methods. In this work, the latter are all based on a one-component model (OCM) of the suspension: the small ions are not considered explicitly, but their effect is accounted for

implicitly through the definition of an effective potential of interaction between the colloids. The effective pair potential considered here is of the hard-sphere Yukawa type,

$$\beta u(r) = \begin{cases} Q^2 l_{\mathrm{B}} \dfrac{e^{-\kappa_{\mathrm{eff}} r}}{r}, & r \geq 2a \\ \infty, & r < 2a \end{cases} \tag{1}$$

where $\beta = 1/kT$ and $l_{\mathrm{B}} = e^2/4\pi\epsilon kT$ is the Bjerrum length. Q and κ_{eff} are the effective point charge and the effective screening length determined following the extrapolated point charge (EPC) renormalization method.[10] This scheme involves a preliminary resolution of the cell model. Then the effective screening length is defined as $\kappa_{\mathrm{eff}} = \kappa\sqrt{\cosh\psi_{\mathrm{D}}}$, where $\kappa = \sqrt{8\pi l_{\mathrm{B}} n_{\mathrm{res}}}$ is the inverse screening length in the ion reservoir and ψ_{D} is the dimensionless electric potential at the cell boundary. In the EPC, the real system of spheres is replaced by a fictitious system of point charges with charge[10]

$$Q = \frac{\tanh\psi_{\mathrm{D}}}{\kappa_{\mathrm{eff}} l_{\mathrm{B}}} [\kappa_{\mathrm{eff}} R \cosh(\kappa_{\mathrm{eff}} R) - \sinh(\kappa_{\mathrm{eff}} R)] \tag{2}$$

Solving the Ornstein−Zernike (OZ) equation with the effective pair potential (eq 1) yields the microstructure of the colloids, from which the pressure P_{OCM} can be computed, for example, with the virial equation

$$P_{\mathrm{OCM}} = \rho kT - \frac{\rho^2}{6} \int g(r)\, u'(r)\, r\, \mathrm{d}r \tag{3}$$

The pressure P of the true multicomponent system involves an additional ion contribution stemming from the so-called volume term in the free energy arising from the mapping of the multicomponent system to the one-component equivalent system.[17−19] The osmotic pressure $\Pi \equiv P - 2n_{\mathrm{res}}kT$ of the true multicomponent system is then[10]

$$\Pi = P_{\mathrm{OCM}} + kT \frac{\kappa_{\mathrm{eff}}^2}{8\pi l_{\mathrm{B}}} \left[1 - \left(\frac{\kappa}{\kappa_{\mathrm{eff}}} \right)^2 \right]^2 \tag{4}$$

The last contribution in eq 4 is important only when the screening length is significantly renormalized, which happens at a large effective volume fraction and surface charge.

From this point, the different models considered in this work diverge in the way P_{OCM} is calculated in eq 4. The Rogers−Young (RY) closure[20] of the OZ equation is renowned for its accuracy concerning hard-sphere Yukawa systems. This scheme is an interpolation between the hypernetted chain and Percus−Yevick closures, with the interpolation coefficient being determined in such a way as to ensure that the isothermal compressibilities computed with the virial equation and with the compressibility equation are identical. This is known to yield very accurate results for charged hard spheres but involves significant computational time to determine the interpolation coefficient.[21,22]

The rescaled mean-spherical approximation[23] (RMSA) is much faster because it does not involve an iterative spectral solver such as the Rogers−Young scheme. It is based on the semianalytical MSA solution of the OZ equation with potential (eq 1). We use the MSA solution of Hayter and Penfold.[24] It still requires the iterative determination of a rescaling parameter and some calls to an FFT algorithm to switch from structure factor $S(q)$ to $g(r)$, which constitutes the main computational

effort of the method. Extensions of the RMSA scheme have been proposed to correct for the overlap between the ion background and the colloid core if necessary,[21,25] but here, because of the use of the extrapolated point charge renormalization, ions can, by construction of the effective potential, occupy the space inside colloids, so we consider only the unmodified RMSA scheme.

Finally, the pressure P_{OCM} will also be computed with a perturbation method. The excess free energy of the system F_{exc} obeys the Gibbs−Bogoliubov inequality[26]

$$F_{\mathrm{exc}} \leq F_{\mathrm{exc}}^* + \left\langle \sum_{i<j} [u(r_{ij}) - u^*(r_{ij})] \right\rangle^* \tag{5}$$

where F_{exc}^* is the excess free energy of a reference system in which colloids interact through the arbitrary potential u^* and $\langle...\rangle^*$ is the thermodynamic average in this system. If u^* has a free parameter, then minimizing the right-hand side of eq 5 with respect to this parameter makes it the best estimate of F_{exc}. Here we consider a reference system of (uncharged) hard spheres with the diameter d^* used as a free parameter so that eq 5 gives an estimate of the excess free energy per colloid as

$$\beta f_{\mathrm{exc}} = \min_{d^*} \left\{ \frac{4\phi - 3\phi^2}{(1 - \phi)^2} + 2\pi\rho \int_{d^*}^{\infty} r^2 g^*(r,\, d^*)\, \beta u(r)\, \mathrm{d}r \right\} \tag{6}$$

where g^* is the radial distribution function of a suspension of hard spheres with diameter d^* and βu is given by eq 1. The analytical expression for g^* used here was developed in ref 27 and is too long to be reported. However, it is available in the program in Supporting Information. The OCM pressure is then $\rho kT + \rho^2(\partial f_{\mathrm{exc}}/\partial\rho)$ at fixed N, T, and effective potential. The integral in eq 6 is easily evaluated, and the minimization can be performed with standard packages. Hence, this method is quite simple to implement and is even faster than the RMSA scheme.

Attractive forces, such as van der Waals forces, may exist between colloids at short distance. They are not considered in the models described in this section. In experimental systems, this is justified if the long-range repulsions are strong enough to prevent colloids from coming too close to contact. It will be shown to be the case for the data considered in this work.

3. COMPARISON WITH REFERENCE DATA

The predictions of the models discussed in the previous section are compared to two sets of results available in the literature: experimental measurements on silica spheres and numerical data obtained with Monte Carlo simulations.

Many osmotic compression experiments have been conducted on Ludox HS40 silica spheres. In Figure 1, we report the osmotic pressure values measured by Goehring et al.[12] and Li et al.,[28] with the latter authors correcting the values obtained earlier by Chang et al.[29] and Persello et al.[2] These data are particularly interesting because they cover a range of regimes from electrostatically dilute to concentrated, they correspond to highly charged particles so that charge renormalization is necessary, and the volume term plays an important role but they are still within the weak coupling limit where the (nonlinear) Poisson−Boltzmann theory is fully valid.

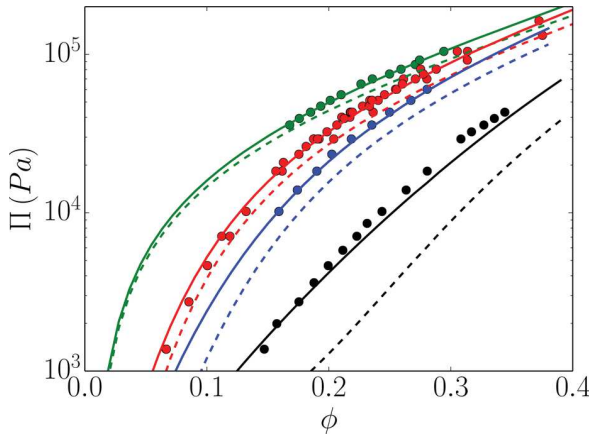A first noteworthy feature of Figure 1 is the excellent agreement between the RY predictions and the experimental

Figure 1. Osmotic pressure of Ludox HS40 suspensions dialyzed against osmolyte solutions with various ionic strengths I: from top to bottom, I = 0.5, 5, 10, and 50 mM. Symbols: measurements by osmotic compression[2,12,28,29] as reported in refs 12 and 28. Solid lines: RY-EPC theory. Dashed lines: CSCM.
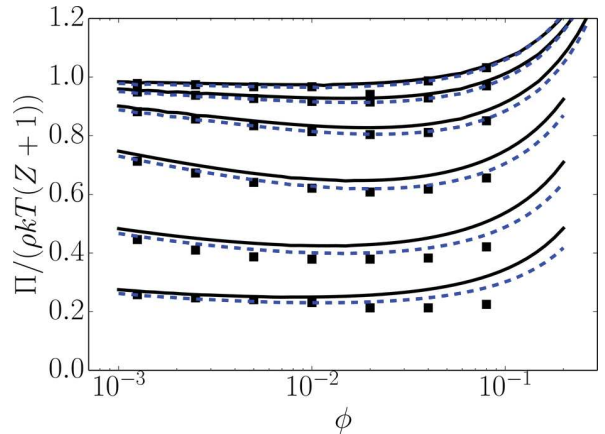

Figure 2. Osmotic pressure of charge-stabilized spheres without added salt. Symbols: primitive model Monte Carlo simulations.[31] Solid line: RY-EPC theory. Dashed line: CSCM. In both models, l_B = 7.312 × 10^{-10} m and Z = 40. The coupling parameter, $\Xi = 2\pi z^3 \sigma' l_B^2/e$ (where z is the valency of an ion), is from top to bottom 0.00986, 0.0396, 0.158, 0.633, 2.532, and 10.24.

data obtained without any fitting parameter. Colloid size a = 8 nm was measured by small-angle X-ray scattering, and the bare surface charge density σ' = 0.5 e/nm^2 was determined from titration at the pH of the experiments.[12,30] Note that the precise value of this bare charge does not affect the equations of state significantly because in this high-charge regime the effective surface charge reaches a plateau value almost independent of the bare charge.[8] To obtain agreement such as that in Figure 1 over this wide range of physicochemical conditions, every ingredient introduced in the previous section is necessary: the renormalization at high charge and the volume term when renormalization is significant. Figure 1 proves, in particular, that the hard-sphere Yukawa (HSY) potential is perfectly suited to these colloids and physicochemical conditions and that the van der Waals interactions can safely be ignored. As an examination of the radial distribution function reveals, colloids never enter into contact even at the highest salt content investigated (0.05 M).

The CSCM osmotic pressure predictions are reported as dashed lines in Figure 1. For most parameters, this model performs quite satisfactorily. The only significant discrepancy is encountered for the highest salt concentration and is most dramatic for intermediate volume fractions. This is a parameter domain in which colloid−colloid correlations are indeed expected to play an important role. More details will be provided in section 4.

The experimental system presented above corresponds to a case with added salt. The parameter κa ranges between 0.6 and 6 here. The behavior of suspensions with $\kappa a > 6$ will be similar to the κa = 6 case: the structure of the suspension is liquid-like and can be modeled with DLVO-like theories. It is interesting to explore the other limit of the interaction range parameter, $\kappa a \rightarrow 0$, corresponding to suspensions without added salt. In this case, the interaction range is infinite, so a solid-like structure is quite probable and the CSCM should be very precise. However, this is a stringent test for theories based on a renormalized pair potential because renormalization is expected to work, by construction, only for particles separated by a distance larger than $O(\kappa^{-1})$.[8]

As a reference set of data, we consider the primitive model Monte Carlo simulations of Linse[31] reproduced in Figure 2.

Because our calculations are carried out in the μVT ensemble, we set a reservoir ion concentration such that $\kappa a = 10^{-3}$. This is sufficiently low to reach the salt-free limit and ensure results independent of κa. Both the RY-EPC theory and the CSCM reproduce the simulation data quite well. The agreement is especially good for the four upper curves in Figure 2 but less so for the two lower curves. This was to be expected from the coupling parameter values, which indicate that the lowest two curves are in the moderate to high coupling regime, out of reach of the mean-field Poisson−Boltzmann theory underlying every model employed in this work.

Considering the aforementioned reserve about the use of renormalization methods in electrostatically dense suspensions, the RY-EPC scheme is very accurate in this salt-free test. This is made possible by correctly accounting for the volume term, which contributes approximately half the osmotic pressure value in the calculations reported in Figure 2. A similar evaluation of the RY-EPC approach has been conducted by Boon et al. on a different set of Monte Carlo simulation data[10] and also shows its good prediction capabilities.

As expected in the salt-free limit, the simple CSCM yields data in excellent agreement with Monte Carlo simulations, actually better than the RY theory.

The most important conclusion of this section is that the RY scheme used with a hard-sphere Yukawa potential renormalized with the extrapolated point charge method simulates charge-stabilized hard-sphere suspensions very precisely without any fitting parameter and whatever the physicochemical conditions. This was shown in the weak coupling limit ($\Xi < 1$) for dilute and concentrated systems ($\phi \in [10^{-3}, 0.4]$), short- and long-range interactions ($\kappa a \in]0, 6]$), and low and high surface charges ($Zl_B/a \in [1, 35]$). In addition, the simple CSCM is very accurate in the salt-free limit as expected. In suspensions with added salt, it was able to give satisfactory predictions for a wide range of parameters, but it was inefficient at intermediate volume fractions when the screening length was moderate. This issue is studied in more detail in section 4 through a systematic comparison of RY-EPC and CSCM results throughout the parameter space. Note that the RY-EPC has been chosen as a reference method to evaluate the CSCM because the Rogers−Young closure is known for its good accuracy and because the
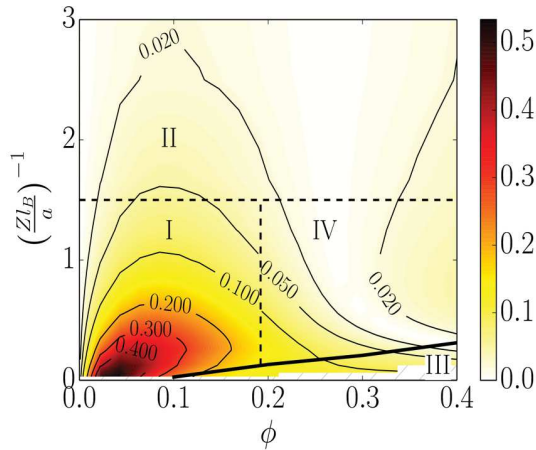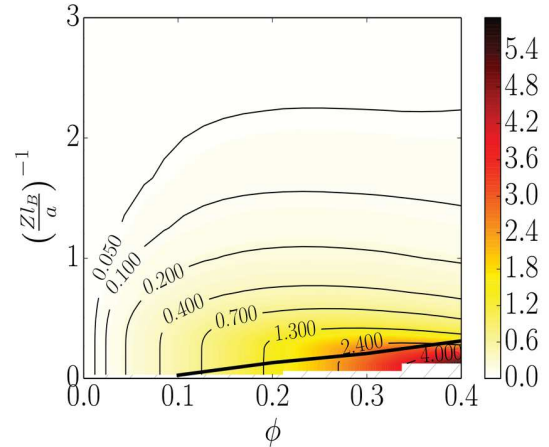
(a) Relative difference in osmotic pressure between the RY-EPC and CSCM schemes: $|\Pi - \Pi_{CSCM}|/\Pi$.
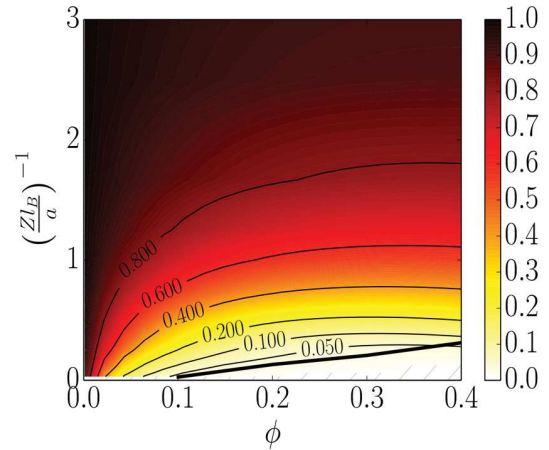
(b) Relative contribution of the contacts to the osmotic pressure in the RY-EPC theory: Π_C/Π.
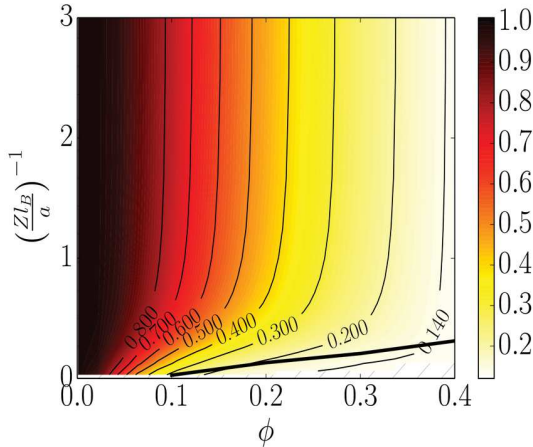
(c) Relative difference between the electrostatic contributions to the osmotic pressure evaluated with the RY-EPC and CSCM: $|\Pi_E - \Pi_{CM}|/\Pi_E$.

(d) Relative difference between the ideal + contact contribution to the osmotic pressure evaluated with the RY-EPC and CSCM: $|\rho kT + \Pi_C - \Pi_{CS}|/(\rho kT + \Pi_C)$.

Figure 3. Comparison of different quantities involved in the equation of state calculation for $\kappa a = 2$. (See the caption of each panel for the precise definition of the quantity evaluated.) In all of these maps, the osmotic pressure denoted Π and its components denoted Π_E and Π_C are computed with the RY-EPC theory, and the osmotic pressure Π_{CSCM} and its components denoted Π_{CM} and Π_{CS} are computed with the CSCM.

EPC renormalization proved to be very precise in salty suspensions and quite precise even in electrostatically concentrated suspensions. It is important to keep in mind, however, that the CSCM was better than the RY-EPC by a few percent in the salt-free case of Figure 2. Therefore, a few percent difference between the two methods should not be automatically associated with an error in the CSCM in the comparisons presented hereafter.

4. DISCUSSION

The results reported in section 3 reveal a loss of quality of the CSCM in suspensions with added salt, indicating an effect of the interaction range. In the following text, we consider systems with long-range ($\kappa a = 0.5$) and short-range ($\kappa a = 2$) interactions. The volume fraction and the surface charge are varied systematically for both types of systems. The volume

fraction ranges between 10^{-3} and 0.4. The average interparticle distance $\kappa d = 2\kappa a(\phi^{-1/3} - 1)$ is thus between 0.36, an effectively concentrated regime with strongly overlapping electrical double layers, and 36, an effectively dilute regime with double layers very small compared to the interparticle distance. The dimensionless charge Zl_B/a is also varied continuously between 0.05 and 32 in order to sample both low-charge regimes, in which renormalization is not necessary, and high-charge regimes, in which it plays a central role. (The dimensionless charge $\sigma = (Zl_B/a)/\kappa a$ ranges between 0.1 and 16.)

Data are represented in phase-diagram-like maps (Figures 3 and 4), with the axes being the volume fraction ϕ and a temperature scaled by the interaction strength $(Zl_B/a)^{-1}$. The solid phase is found below the thick black line (region III) computed with the Hansen–Verlet criterion, $S_{max} = 2.85$.
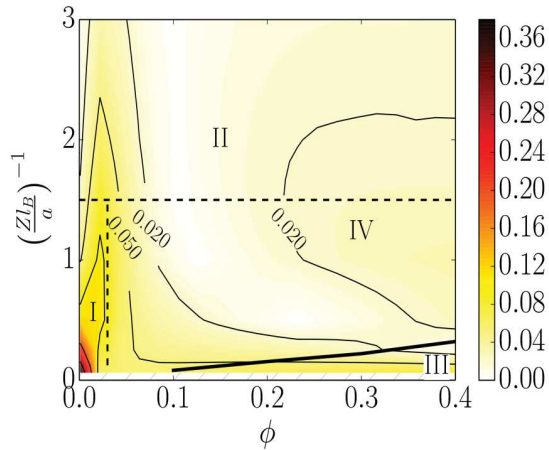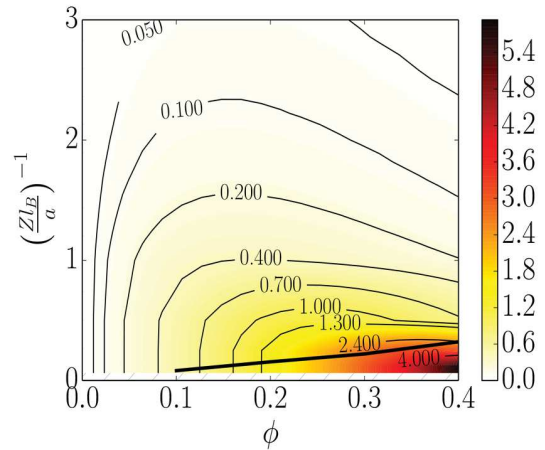
(a) Relative difference in osmotic pressure between the RY-EPC and CSCM schemes: $|\Pi - \Pi_{CSCM}|/\Pi$.
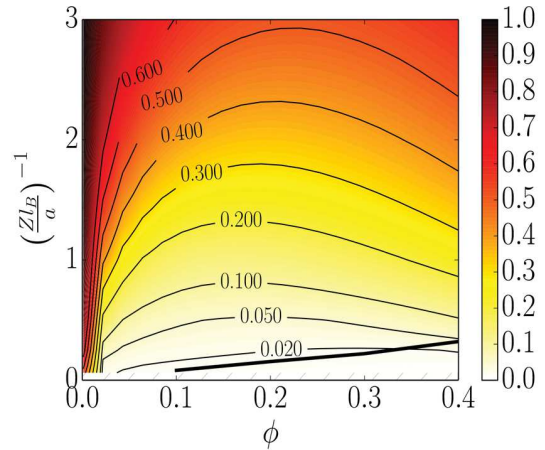
(b) Relative contribution of the contacts to the osmotic pressure in the RY-EPC theory: Π_C/Π.
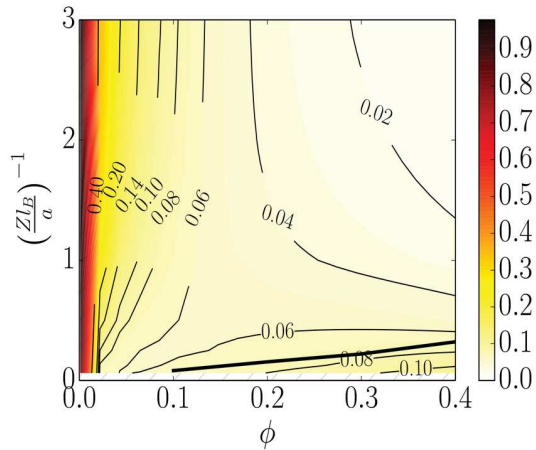
(c) Relative difference between the electrostatic contributions to the osmotic pressure evaluated with the RY-EPC and CSCM: $|\Pi_E - \Pi_{CM}|/\Pi_E$.

(d) Relative difference between the ideal + contact contribution to the osmotic pressure evaluated with the RY-EPC and CSCM: $|\rho kT + \Pi_C - \Pi_{CS}|/(\rho kT + \Pi_C)$.

Figure 4. Comparison of different quantities involved in the equation of state calculation for $\kappa a = 0.5$. (See the caption of each panel for the precise definition of the quantity evaluated.) In all of these maps, the osmotic pressure denoted Π and its components denoted Π_E and Π_C are computed with the RY-EPC theory, and the osmotic pressure Π_{CSCM} and its components denoted Π_{CM} and Π_{CS} are computed with the CSCM.

Although sufficient for the present discussion, this is a qualitative boundary because the value of S_{max} at freezing actually varies slightly with the type of interactions, from 2.85 for hard spheres up to 3.3 for pure Yukawa systems with long-range interactions. (See, for example, Heinen et al.[21] and references therein.)

The CSCM and RY-EPC osmotic pressure predictions are compared in Figure 3a for $\kappa a = 2$ and in Figure 4a for $\kappa a = 0.5$. Overall, the accuracy of the CSCM is quite good for the broad range of parameters investigated. The maximum error is about 30−40% and is found for intermediate volume fractions and high surface charges (region I), in line with the observations of section 3. In all of the other regions (II, III, and IV), the CSCM predicts osmotic pressures within 10% of the actual values. This can be explained in the following way.

In the very low charge regime and whatever the volume fraction value (zone II in Figures 3a and 4a), the total osmotic pressure Π is dominated by its contact contribution Π_C as shown in Figures 3b and 4b. Because electrostatic effects are weak in this regime, the contact pressure is well approximated by the Carnahan−Starling equation of state, as proven in Figures 3d and 4d: in the parameter region where Π_C is at least 70% of Π, the Carnahan−Starling expression matches Π_C within 10%. Note that systems benefiting from good modeling in region II must have very low van der Waals interactions even at contact. They are essentially systems with purposely matched optical indexes.

In the very dilute regime, here $\phi < 1-2\%$, for short-range interactions and whatever the surface charge (left of zones I and II in Figure 3a), the suspension once again behaves mostly as a liquid of hard spheres and the CSCM performs well for the
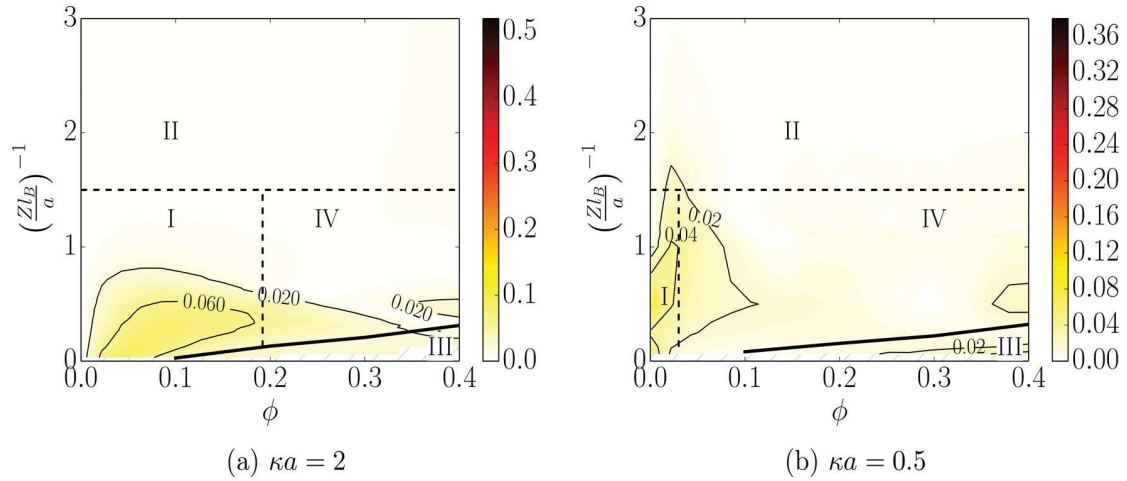
Figure 5. Relative difference between osmotic pressure predictions from perturbation theory Π_{perturb} and from RY-EPC theory Π: $|\Pi - \Pi_{\text{perturb}}|/\Pi$.
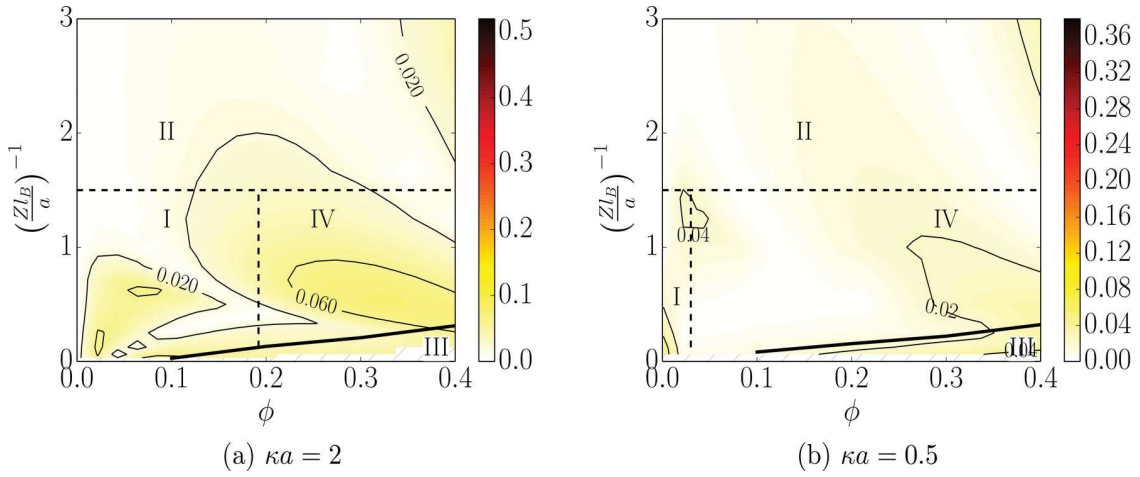

Figure 6. Relative difference between osmotic pressure predictions from RMSA-EPC theory Π_{RMSA} and from RY-EPC theory Π: $|\Pi - \Pi_{\text{RMSA}}|/\Pi$.

same reasons as before. Here a model of equivalent hard spheres with a radius increased by one Debye length would be appropriate.

In the solid phase (high charge and volume fraction; region III in Figures 3a and 4a), the suspension is jammed by electrostatic interactions in a Wigner glass or crystal. The electrostatic contribution to the pressure is high, but the contact contribution vanishes (Figures 3b and 4b). The electrostatic contribution is well approximated by the cell model, as expected by construction and as shown in Figures 3c and 4c. In a previous work, we have shown that the cell model pressure is a good approximation of Π_E for mean intercolloid half distances $\kappa a(\phi^{-1/3} - 1)$ smaller than a value between 1.5 for low charges and 3.2 in the effective charge saturation regime (Figure 4 in ref 6). Applied to the present data, this criterion is consistent with the 40% error isocontour in Figures 3c and 4c. It also corresponds fairly well to the boundaries between regions I and IV, and I and III in Figure 3a and between regions I and IV in Figure 4a.

The general idea found in the literature that the cell model is efficient in solid-like suspensions corresponds well to the phase diagrams computed here. The CSCM can, however, also be precise in liquid-like suspensions provided the interaction range is large compared to the intercolloid distance. The CSCM performs very well in liquid regions IV and II at high volume

fraction and moderate charge. In this case, electrostatic interactions are not strong enough to trap colloids in a solid-like structure, but the interaction range is comparable to or larger than the mean intercolloid distance so the electrostatic potential can be high between colloids. As a consequence, the average concentration of counterions is high and their contribution to Π_E, which is precisely what the CM evaluates, is expected to dominate the direct colloid–colloid contribution Π_E^{col}. The latter is, however, not vanishingly small, and the true electrostatic contribution Π_E is thus slightly underestimated. Meanwhile, an examination of the radial distribution function in this same region reveals a significant contact value at moderate and low charge, although not as high as what would be expected in the pure hard-sphere case. Hence, using Π_{CS} instead of the true contact contribution $\rho kT4\phi g(2a)$ is fairly relevant but tends to overestimate the actual contact contribution Π_C. The two errors in Π_E and Π_C therefore tend to cancel each other out so that the pressures obtained with the CSCM are actually precise for any surface charge at high volume fraction. This is one of the main results of this work.

The domain in the parameter space where the CSCM is less accurate corresponds to intermediate volume fractions and high surface charges (region I in Figures 3a and 4a). In this region, electrostatic effects are important because of the high charge,

Table 1. Summary of the Characteristics of the Models Investigated

model	RY	RMSA	perturbation	CM	CSCM
ease of implementation	*	**	****	***	****
ease of convergence	*	**	***	****	****
computational time	*	***	***	**	**
structure prediction	yes	yes	no	no	no
numerical tools involved	iterative method, FFT	FFT, nonlinear equation solver	minimization	nonlinear ODE solver	nonlinear ODE solver
domain of validity and precision	precise in the full parameter space	a priori quite precise in the full parameter space with EPC renormalization	precise if the potential of interaction is close to the reference one	precise in solidlike regime	precise for an interaction range larger than the interparticle distance in liquidlike or solidlike regimes

and the interaction range is smaller than the mean intercolloid distance. The ion contribution to the pressure is thus small compared to the direct colloid−colloid contribution, so the CM pressure is irrelevant. In the CSCM, the Carnahan−Starling contribution involves colloid−colloid correlations but erroneous ones because it ignores electrostatics. In particular, the CS modeling implies a nonzero radial distribution function at contact while the high surface charge imposes a vanishing value. Hence, the CSCM is definitely not suitable for such suspensions. They have to be modeled in a better way.

To sum up this systematic evaluation of the CSCM, we can state that (i) it works well for systems with long-range interactions, whatever the volume fraction and surface charge, because the electrostatic contribution to the osmotic pressure is dominant, comes from the ions, and is thus well approximated by the cell model part of the CSCM, (ii) it works for weak charges if van der Waals interactions can be ignored thanks to the dominant contribution of contacts to the osmotic pressure and the good approximation of the latter by the Carnahan−Starling part of the CSCM, and (iii) it is not very efficient in the electrostatically dilute but electrostatically dominated regime that is encountered for high surface charges and interaction ranges smaller than the average interparticle distance. In this case, other methods should be preferred.

The equations of state reported in Figure 1 were also computed with the perturbation method and the RMSA theory presented in section 2 (they are not represented for the sake of clarity). They could both reproduce all of the RY results almost perfectly, with deviations of at most one line width. They were therefore clearly superior to the CSCM for this system in terms of precision. However, the convergence of the RMSA scheme was difficult to obtain for the highest salt content. The performances of these two methods were also investigated in the phase-diagram-like maps used for the CSCM. They produce very good results for the full range of parameters investigated, as shown in Figures 5 and 6. The maximum error never exceeds 10% and is often below a few percent. Once again, the convergence of the RMSA scheme was difficult to obtain for the highest charge with short-range interactions.

These two methods, besides being accurate, are quite fast. Our implementations of the perturbation and RMSA and RY schemes converged in about 0.2, 1.1, and 29 s, respectively, on a standard laptop. Note that the codes were not overly optimized. These values were obtained with fine grids so that the same grids could be used for every surface charge, volume fraction, and salt content. The comparison of computational times is thus qualitative. The important point is that the renormalization step preceding these computations to determine the effective potential involves a cell model resolution, the convergence of which requires about 3 s. Hence, whereas the Rogers−Young scheme involves a significant overhead, the perturbation method gives a nice pressure estimation virtually for free and the RMSA calculation requires only a modest additional effort.

To conclude, the perturbation method and the RMSA scheme are reasonably easy to implement, and their stability does not depend too much on numerical details. The bounds provided for the hard sphere diameter $d*$ in the minimization procedure involved in the perturbation theory (section 2) and the initial value of the rescaling parameter in the RMSA may still have to be modified to ease the convergence under some specific physicochemical conditions.

A summary of the characteristics of the models investigated in this work is provided in Table 1.

5. CONCLUSIONS

The ways to compute the equation of state of a suspension of charged hard spheres in a fast and robust manner were investigated, with particular focus on the CSCM model. This approximation resulting from the simple addition of the Carnahan−Starling (CS) and the cell model (CM) pressure estimations was compared to experimental and Monte Carlo data and to the solution of the Ornstein−Zernike equation with an extrapolated point charge renormalization method applied to a hard-sphere Yukawa potential (RY-EPC scheme).

It was first shown that the RY-EPC scheme could predict osmotic pressures perfectly well without any fitting parameter for silica suspensions in equilibrium with a salt reservoir. Good agreement was also obtained with the results of primitive model Monte Carlo simulations of a salt-free system. The CSCM performed very well by construction in the salt-free system, actually better than the RY-EPC scheme. Comparisons with RY-EPC data throughout the parameter space revealed that the CSCM was satisfactory in concentrated suspensions even for moderate surface charges, thus extending the possibilities of the cell model toward the liquid phase. This is due to an error cancellation between a slightly underestimated electrostatic contribution to the pressure and a slightly overestimated contact contribution to the pressure occurring when the mean intercolloid distance is smaller than a few times the screening length. However, the CSCM is not satisfactory in dilute systems dominated by electrostatic interactions when the radial distribution function at contact vanishes.

Under the last mentioned conditions, perturbation methods and the RMSA scheme (also based on the effective potential determined with the extrapolated point-charge method) can actually produce good results, with a limited loss of robustness and only a small computational overhead compared to the CSCM because the cell model has to be solved anyway to determine the effective potential of interaction. To compute a large number of equations of state of charged hard spheres for arbitrary physicochemical conditions and if robustness is actually an issue, we would thus recommend first solving the cell model to determine this potential and then attempting a pressure prediction with a perturbation method or the RMSA and using the CSCM approximation as a fallback plan if this computation fails. For applications in which the interaction range can be anticipated to be larger than the mean colloidal distance, the CSCM is sufficient, being easy to implement, fast, and perfectly robust for any surface charge. This is of interest in rheological studies, flow calculations of concentrated suspensions, screening tests of new formulations, or the real-time interpretation of osmotic compression data, for example.

ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b02209.

A program containing an implementation of all of the models used in this article (TXT)

AUTHOR INFORMATION

Corresponding Author
*E-mail: yannick.hallez@univ-tlse3.fr.

ORCID ⓘ
Yannick Hallez: 0000-0001-5172-439X

Notes
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ABBREVIATIONS

EOS   equation of state
CM   cell model
CSCM   Carnahan−Starling cell model
EPC   extrapolated point charge
OZ   Ornstein−Zernike
RY   Rogers−Young
MSA   mean spherical approximation
RMSA   rescaled MSA
FFT   fast Fourier transform
OCM   one-component model
HSY   hard-sphere Yukawa

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