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Yannick Hallez, Martine Meireles. Surface and extrapolated point charge renormalizations for charge-stabilized colloidal spheres. European Physical Journal E: Soft matter and biological physics, 2018, 41 (5), pp.1-6. 10.1140/epje/i2018-11676-9 . hal-03510674

HAL Id: hal-03510674

<https://hal.science/hal-03510674>

Submitted on 4 Jan 2022

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To link to this article : DOI : [10.1140/epje/i2018-11676-9](https://doi.org/10.1140/epje/i2018-11676-9)
URL <https://doi.org/10.1140/epje/i2018-11676-9>

To cite this version : Hallez, Yannick and Meireles-Masbernat, Martine
: *Surface and extrapolated point charge renormalizations for charge-stabilized colloidal spheres* (2018), pp. 1-6

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Surface and extrapolated point charge renormalizations for charge-stabilized colloidal spheres

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Abstract. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is widely used to model interactions between weakly charged spheres in dilute suspensions. For particles bearing a higher charge, the linearized electrostatics underlying the DLVO theory is no longer valid but it is possible to map the real colloidal system to an auxiliary one that still obeys linear electrostatics but which involves a different, effective pair potential. This procedure, termed renormalization, can be performed in various ways, the most widely used being surface charge renormalization (SCR) based on the cell model. SCR is still limited to dilute suspensions since the auxiliary system is made of spheres interacting through a DLVO-like pair potential. The recent extrapolated point charge (EPC) renormalization overcomes this limitation by using point charges in the auxiliary system and has indeed been shown to produce better results than the SCR in dense suspensions. Here, we recall that the DLVO-like potential used in the SCR can be modified to account for many-body ion-colloid core exclusion effects (a model termed SCR_X here); we show that the accuracy of the EPC and SCR_X renormalizations is virtually identical, and conclude by explaining why the EPC method is still the most attractive option of the two in many cases.

1 Introduction

Electrostatic interactions between particles play a major role in a variety of natural and industrial colloidal suspensions, particularly as a stabilization mechanism. These interactions have usually been modeled with the Debye-Hückel treatment in the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1, 2]. However, by construction, this treatment is restricted to low surface charges and dilute systems.

The low charge constraint is imposed by the use of the linearized Poisson-Boltzmann (PB) theory instead of the original one. This constraint can be removed by using charge renormalization methods. The general idea is to map the real system of strongly charged colloids obeying PB theory to a fictitious, auxiliary, system of charged objects designed to maintain certain properties of the original system when they are treated with the linearized PB theory. Various choices for this auxiliary system define various renormalization models [3]. One of the most famous is the surface charge renormalization (SCR) method based on the cell model [4, 5]. This procedure leads to an effective DLVO-like pair potential that is valid for a pair of colloids in an otherwise infinite medium, and is thus only valid in dilute suspensions.

In *concentrated* suspensions, the form of the classical DLVO potential exerted between spheres with a finite radius is incorrect because of the inappropriate treatment of the deformation of the electric double layer (EDL) of a given pair of colloids by the core of their neighbors. Therefore, independently of the quality of the SCR renormalization itself, structure and thermodynamic calculations are still delicate for the auxiliary system at high volume fraction. Boon *et al.* [6] designed a renormalization method termed extrapolated point charge (EPC) renormalization. It involves an auxiliary system of point charges instead of colloidal spheres, so that no core exclusion effect is encountered in this auxiliary system whatever the volume fraction of the real system. Dense suspensions can be dealt with in a straightforward manner, since the auxiliary system is now always infinitely dilute. Their comparison of the EPC method with primitive model (PM) molecular dynamics shows a very good quantitative agreement and, indeed, better pressure predictions than SCR at high volume fraction.

It is nevertheless worth remembering that a correction to the DLVO potential exists to account for the many-body effect mentioned above. It involves a rescaling of the effective point charge depending on the radial distribution function (rdf) [7, 8] and can be implemented relatively easily in iterative Ornstein-Zernike (OZ) equation solvers. In

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the present work, the coupling between the effective potential obtained with SCR and this correction is termed SCR_X.

The aim of this “Tips and Tricks” article is to show that the EPC produces results virtually identical to those of the SCR_X for a wide range of experimentally relevant physico-chemical conditions and to discuss why the EPC method seems, however, generally more attractive than SCR_X for practical calculations.

The different renormalization models are briefly introduced in sect. 2 and a thorough comparison between them, involving the screening of a large range of physico-chemical parameters, is presented in sect. 3. Comments on the use of both strategies are proposed in the conclusion.

2 Models

The effective pair potential considered here is of the usual hard-core Yukawa type,

$$\beta u(r) = \begin{cases} Q^2 l_B \frac{e^{-\kappa r}}{r}, & r \geq 2a, \\ \infty, & r < 2a, \end{cases} \quad (1)$$

where a is the colloid radius, $\beta = 1/kT$, $l_B = e^2/4\pi\epsilon kT$ is the Bjerrum length, k is Boltzmann’s constant, T is the temperature, e is the elementary charge, and ϵ is the permittivity of the solvent. Q and κ are an effective point charge and an effective inverse screening length. Before continuing, note that the form of this potential is correct at low to moderate density, but it is questionable at high densities [8, 9]. Remember also that it is not valid at too short separation distances.

The various renormalization models available in the literature differ by the way they compute the values of the effective parameters in eq. (1). In this work, Q and κ are determined following either the EPC [6] or the SCR method. The precise SCR implementation used here is the one described by Trizac and coworkers [5]. Both renormalization schemes rely on the cell model, defining a single effective screening length as $\kappa = \kappa_{\text{res}} \sqrt{\cosh \psi_D}$, where $\kappa_{\text{res}} = \sqrt{8\pi l_B n_{\text{res}}}$ is the inverse screening length in an ion reservoir with constant ion density n_{res} in equilibrium with the suspension, and ψ_D is the dimensionless electric potential at the cell boundary. Here we stick with the original EPC and SCR prescriptions of Boon *et al.* [6] and Trizac *et al.* [5]. Note however that there is no rigorous theoretical link between the form of the interaction potential (1) and the cell model. Therefore, choosing a value of κ for the effective potential from the cell model necessarily involves some level of heuristics and, indeed, even the original authors of the SCR [4] qualify their method of “recipe”. Instead of basing the effective screening length on the ion density at the edge of the cell as in the EPC and SCR, it is also possible to base it on the effective average ion density in the cell to obtain the value κ' [10, 11]. This may look more consistent with theories for effective potentials derived for weakly charged colloids with the MSA

closure for instance [7]. Note however that the present choice κ for the screening factor reduces to κ' when the surface charge is weak [5] and that there is no reason for the MSA result to hold true for strongly charged colloids.

The value of Q depends on the renormalization method. In the EPC method, the auxiliary system contains only point charges with [6]

$$Q = \frac{\tanh \psi_D}{\kappa l_B} [\kappa R \cosh \kappa R - \sinh \kappa R], \quad (2)$$

where $R = a\phi^{-1/3}$ is the cell radius and ϕ is the volume fraction.

In the SCR model, the auxiliary system contains only spheres with the same finite radius a and a DLVO-like effective charge

$$Q = Z^* e^{\kappa a} / (1 + \kappa a + X), \quad (3)$$

where [5]

$$Z^* = \frac{\tanh \psi_D}{\kappa l_B} [(\kappa a \kappa R - 1) \sinh(\kappa R - \kappa a) + (\kappa R - \kappa a) \cosh(\kappa R - \kappa a)] \quad (4)$$

and $X = 0$. This is valid for two weakly charged spheres at not too small distance in an otherwise empty medium.

For suspensions of weakly charged spheres at non-vanishing density, Khan and coworkers [7] derived the effective interaction potential between two colloids with the assumption of point-like ions and the MSA closure in the PM Ornstein-Zernike description (same hypotheses as the Debye-Hückel theory). At large separation distance, this effective potential is of the Yukawa form and the effective charge is (3) with κ replaced by κ' and

$$X = e^{-\kappa' a} (\sinh \kappa' a - \kappa' a \cosh \kappa' a) \times \rho \int g(r) \frac{e^{-\kappa' (r-2a)}}{\kappa' r} d\mathbf{r}, \quad (5)$$

where ρ is the colloid number density and $g(r)$ is the colloid-colloid rdf [7, 8]. Note that in this correction derived at low surface charge with the MSA, the inverse screening length involves the average effective ion density. In an attempt to extend the SCR scheme to more concentrated suspensions, we propose here the recipe tagged SCR_X consisting in using the effective potential based on (1), (3) and (5) with the effective parameters derived from the original SCR [5], *i.e.* Q and κ , and not κ' . Whether or not using κ' instead of κ in all these models would lead to better results concerning the structure and thermodynamics of a strongly charged colloidal suspension still needs to be established. The present arbitrary choice already allowed us to reproduce accurately and without fitting parameters experimental equations of state of salty silica suspensions and of salt-free suspensions simulated with a PM Monte Carlo method [12]. It will also allow us to compare the results of the SCR_X scheme to those of the original SCR and EPC schemes in this article.

The equilibrium structure of a suspension of particles interacting through (1) can be obtained by solving the Ornstein-Zernike (OZ) equation with the Rogers-Young closure [13] (RY), which is known to produce very accurate results for charged hard spheres [14, 15].

This calculation yields $g(r)$ in the one-component model, from which the pressure P_{OCM} can be computed, for example with the virial equation. Considering the potential u as explicitly depending on density (choice I), the OCM pressure reads

$$\beta P_{\text{OCM}} = \rho - \frac{2\pi}{3} \rho^2 \int_0^\infty dr r^2 g(r) \left(r \frac{\partial \beta u(r)}{\partial r} - 3\rho \frac{\partial \beta u(r)}{\partial \rho} \right). \quad (6)$$

Alternatively, considering the effective potential as some optimal effective interaction at a *prescribed, fixed* density $\rho = \rho_d$ (calculated possibly for a set of different ρ_d) the density derivative term in (6) is absent and the state-independent form is recovered (choice II). Which option is the best is a fundamental and difficult question that is not resolved and that is outside the scope of this paper. Note however that $g(r)$ and the structure factor $S(q)$ are independent of this choice of viewpoint because the structure of a suspension with prescribed number of colloids, volume and temperature depends only on the effective potential in these conditions and cannot depend on whether the effective potential would change if the volume were changed [16]. Therefore, using the fully density-dependent viewpoint I, the isothermal compressibility calculated from (6) is not equal to the one computed from $S(q \rightarrow 0)/\rho kT$ [16, 17]. As the standard RY scheme relies precisely on the enforcement of this equality it cannot be used with this viewpoint. In this work, we therefore chose to neglect the density derivative term in (6) for simplicity. The reader is referred to refs. [16–18] for more details on the thermodynamics of systems involving density-dependent potentials.

The pressure, P , of the true multi-component system involves an additional ion contribution stemming from the so called volume term in the free energy. The latter is a consequence of the mapping of the multi-component system to the equivalent one-component system with effective parameters [19–21]. The actual osmotic pressure $\Pi \equiv P - 2n_{\text{res}}kT$ of the true multi-component system is then [6]

$$\Pi = P_{\text{OCM}} + kT \frac{\kappa^2}{8\pi l_B} \left[1 - \left(\frac{\kappa_{\text{res}}}{\kappa} \right)^2 \right]^2. \quad (7)$$

The last contribution in (7) is common to both the EPC and the SCR(X) schemes by construction.

3 Comparison of EPC and SCR(X) renormalizations

Boon and co-workers [6] compared structures and pressures obtained with the RY scheme and either the SCR or the EPC renormalization with the predictions of PM molecular dynamics simulations. The EPC scheme proved

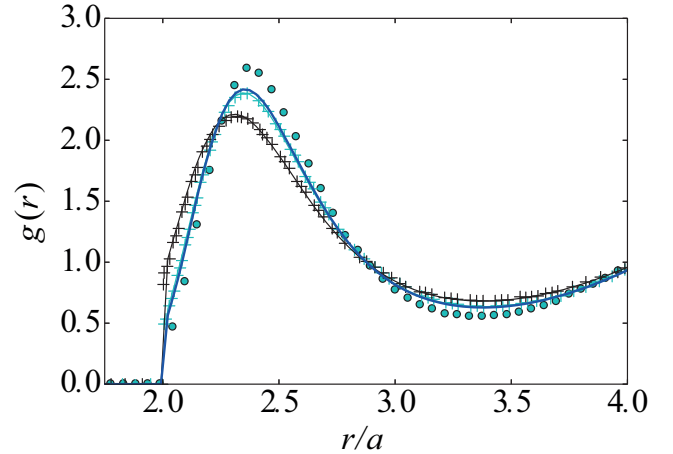


Fig. 1. Colloid-colloid radial distribution function obtained for $Z = 80$, $a = 37.5$ nm, $\phi = 0.3682$, $\kappa a = 1.3444$. Data from ref. [6]: primitive model MC (circles), RY with SCR (black crosses), RY with EPC (cyan crosses). Present data: RY with SCR (thin black line), RY with EPC (thin cyan line), RY with SCR(X) (thick blue line). For every method, $\kappa/\kappa_{\text{res}} = 1.309$. $Z^*/Z = 0.9972$ for SCR(X) and 1.21 in EPC.

to be of excellent quality and was superior to the SCR scheme at high volume fraction both for a salt-free system and for a suspension with added salt. This was expected since the many-body term (5) was not used with the SCR. If the auxiliary system of charged spheres involved in the SCR is treated with this correction (approach termed SCR(X) here), the two methods should produce closer results. In a previous work, we compared the EPC and SCR(X) predictions with experimental pressure data obtained by compression of Ludox silica spheres and with numerical PM data for a salt-free suspension and we found very good agreement for both renormalization methods, without any fitting parameter [12]. The predictions of EPC and SCR(X) were actually indistinguishable.

To confirm this, the rdf calculations reported in fig. 2 of ref. [6] were reproduced with our implementation of the EPC, SCR, and SCR(X) methods. The results are displayed in fig. 1. The agreement between the present EPC (and SCR) results and Boon and coworkers' ones is excellent. But, most importantly, this figure reveals that the SCR(X) and EPC schemes produce almost indistinguishable rdfs. The EPC and SCR pressure values corresponding to the data of fig. 1 differ by about 11%, while the EPC and SCR(X) values differ by only 1.7% (Note that the scale is off by a factor 10 in fig. 2 of ref. [6]¹). This test case is somewhat peculiar since the effective charge is very close to the bare charge (see caption of fig. 1). Only the screening parameter is really renormalized. The difficulty when using SCR instead of EPC here is not the renormalization itself, but rather to deal with the auxiliary system. Indeed, the usual DLVO form is not valid at high particle volume fraction and the potential in the auxiliary system has to include the correction (5) to obtain good predictions. On the other hand, the EPC auxiliary system containing only

¹ Private communication with Niels Boon.

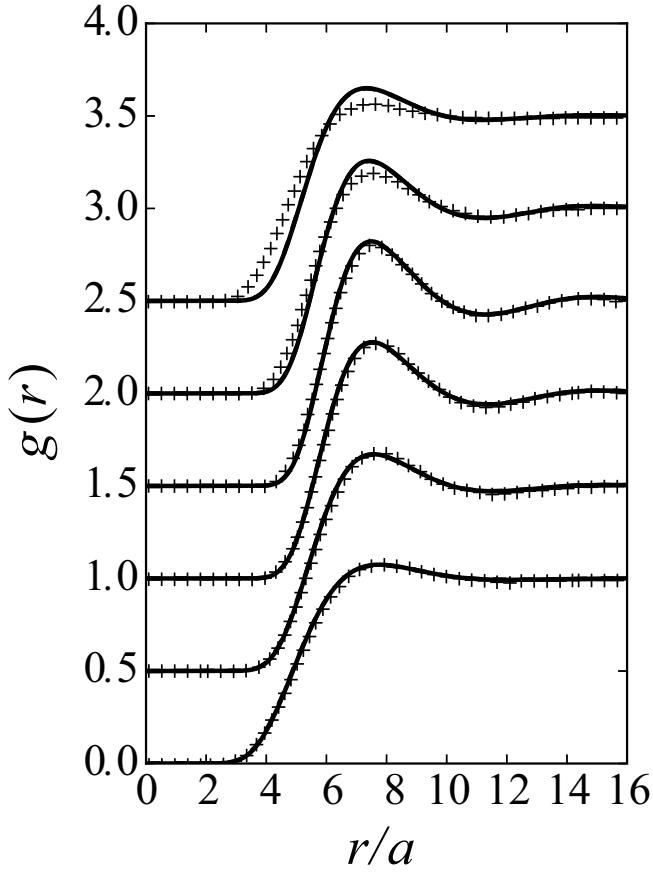


Fig. 2. Colloid-colloid radial distribution function of a salt-free suspension obtained for $Z = 40$, $\phi = 0.01$ and increasing coupling parameters from bottom to top (see values in table 1). Each subsequent $g(r)$ is shifted by 0.5 for clarity. Crosses: primitive model MC data from [22]. Lines: present RY calculations using $\kappa_{\text{res}}a = 0.001$ (SCR(X) and EPC curves are indistinguishable).

Table 1. Renormalized parameters associated to the RY calculations in fig. 2. The coupling parameter Γ is defined here as $z^2 l_B/a$ where z is the ion valency. The inverse screening length in the salt-free system is $\kappa_0 = \sqrt{4\pi l_B Z \rho}$. The colloid effective valencies Z^* computed with the SCR or the EPC differ by less than one percent for the present data set.

Γ	κ/κ_0	Z^*/Z
0.0222	0.98	1
0.0445	1.35	0.99
0.0889	1.80	0.935
0.1779	2.22	0.77
0.3558	2.48	0.51
0.7115	2.60	0.28

point charges, it is always at infinite dilution and its treatment is easier.

It is also interesting to compare the SCR and EPC renormalization schemes in a system requiring a more significant renormalization. Structure calculations corresponding to a salt-free system are presented in fig. 2, with

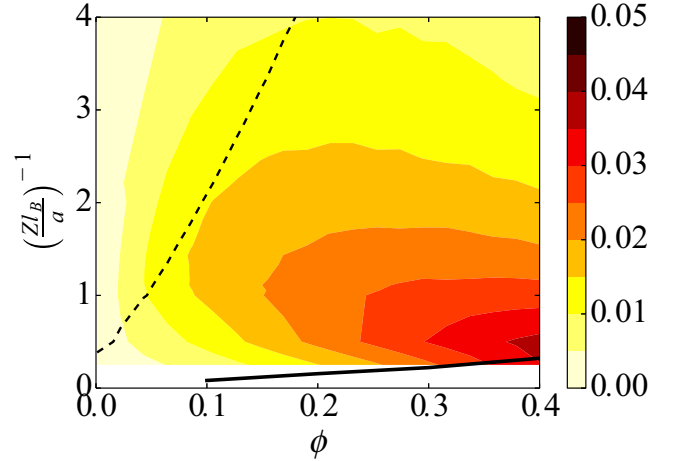


Fig. 3. Map of the relative difference in the osmotic pressure value obtained by solving the OZ-RY model with the EPC or SCR(X) charge renormalization approaches ($|\Pi_{\text{EPC}} - \Pi_{\text{SCR(X)}}|/\Pi_{\text{EPC}}$) for $\kappa a = 0.5$. The dashed line delimits the linear and non-linear electrostatic regimes, and the continuous line is the freezing line (see text for more details).

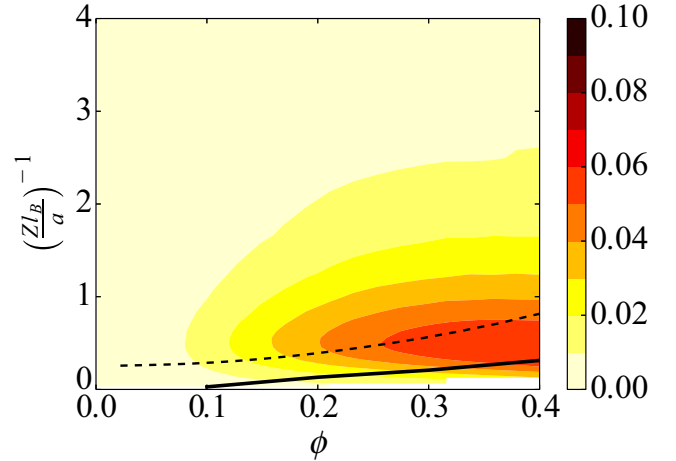


Fig. 4. The same as fig. 3 but for $\kappa a = 2$.

the effective parameters reported in table 1. Our implementation of the cell model being in the μVT ensemble we chose to work with a small ion reservoir concentration corresponding to $\kappa_{\text{res}}a = 0.001$, which is sufficiently small to obtain data corresponding to the salt-free case. The SCR, SCR(X), and EPC schemes yield indistinguishable structures for this system. This is due to the low volume fraction ($\phi = 0.01$) which makes the auxiliary systems of spheres (SCR) or point charges (EPC) virtually identical. The agreement of the present schemes with the primitive model data of Linse [22] is perfect but for the two highest coupling parameter values. The latter discrepancy was expected for these strong coupling cases in which even the form of the Yukawa potential is not valid. The pressures associated to the structure calculations of fig. 2 were reported in a previous work [12] and were found to be also in good agreement but for these two highest couplings.

Motivated by these observations, we considered a more thorough comparison of the EPC and SCR(X) methods,

with a systematic variation of volume fraction (range 10^{-3} to 0.4) and dimensionless charge ($Zl_B/a \in [0.1, 32]$), and for short-range interactions ($\kappa a = 2$) and long-range interactions ($\kappa a = 0.5$). The osmotic pressure predictions of these two methods are compared in the $(\phi, (Zl_B/a)^{-1})$ plane in figs. 3 and 4. The vertical axis is a dimensionless temperature scaled by the repulsive interactions. The region below the dashed line is the region where renormalization actually takes place due to a significant surface charge and volume fraction. It is defined as the points in the parameter space where the LPB and PB cell models yield osmotic pressures differing by more than 10%. The continuous line is the freezing line calculated with the Hansen-Verlet criterion $S_{\max} = 2.85$ applied to the EPC results. Note that 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, *e.g.*, Heinen *et al.* [14] and references therein). The criterion $S_{\max} = 3.1$ has been reported to be suited for suspensions with a vanishing $g(r = 2a^+)$ [15]. Calculations with the latter value produced freezing lines slightly below the ones displayed in figs. 3 and 4 and hardly distinguishable from them so they are not represented for clarity.

In the linear regime, above the dashed line, the renormalization schemes are not active. In the SCR_X, the auxiliary system is the same as the real one and, in the EPC system, point charges are considered with the real DLVO charge. The two models agree within a few percent in this region. This is the order of the accuracy of the numerical OZ solver. This observation suggests *a posteriori* that the treatment of the many-body effect by EPC is equivalent in precision to the modification of the sphere DLVO potential with (5).

In the solid phase, the volume term common to both the EPC and SCR_X models becomes large and the global error on the osmotic pressure therefore automatically decreases. The maximum discrepancy is found in the liquid phase, *i.e.* above the continuous line in figs. 3 and 4. It is, however, at most about 6% for the full range of parameters investigated. Once again, this is close to the numerical solver accuracy so we can conclude the EPC and SCR_X are actually virtually identical in terms of precision. The apparent discrepancy between the two models reported in ref. [6] was due to the neglect of ion-core exclusion in the RY scheme based on the SCR potential ($X = 0$ in (3)).

4 Conclusion

It has been shown that the EPC and SCR_X renormalization methods are almost perfectly equivalent in terms of precision for a wide range of physico-chemical parameters. This is not a proof of validity for either of them but, considering they are built following different routes, this is quite reassuring.

There are nonetheless strong advantages associated with using the EPC in practice. The many-body correction to the DLVO potential in the SCR_X requires an estimate of $g(r)$, which itself depends on this pair potential.

The correction can thus only be applied by an iterative procedure while computing the structure. When the OZ equation is solved numerically, this is not an issue because the method is already iterative. However, using this correction is more complicated in semi-analytical OZ solutions like the (R)MSA, or with perturbation methods to obtain a pressure value. Using correction (5) would also be quite impractical in one-component Monte Carlo or molecular dynamics simulations since the pair potential would have to be modified on the fly based on sliding averages of $g(r)$, thus increasing the computational time significantly. Defining an effective pair potential independent of the structure with the EPC renormalization method therefore tends to be a sound and simple choice if finite concentration effects are expected.

Author contribution statement

YH developed the numerical code and performed the simulations. Both authors (YH and MM) contributed to the final version of the manuscript.

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