Optimal Effective Pair Potential for Charged Colloids.

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Abstract. – The effective interaction between charged colloidal particles in solution both with and without added salt is studied using an *ab initio* theory which includes effective many-body forces induced by the counter- and salt-ions. Fitting these forces with a pair potential, we obtain an optimal pair potential which reproduces the *ab initio* data for the pair correlations correctly. This optimal potential is very close to a screened Coulomb potential, thus justifying the Yukawa-picture, frequently used for the interaction of charged colloids. In general, however, the effective charge and the screening length differ from that of Derjaguin-Landau-Vervey-Overbeek (DLVO) theory and Wigner-Seitz cell models. Moreover, the optimal effective pair potential depends on the thermodynamic phase. The mapping of many-body interactions onto optimal pair-interactions drastically reduces the computing time in simulating large systems.

The interaction between highly charged spherical colloidal particles («macroions») in water or non-aqueous solutions is determined by the screening of the counterions and additional salt ions [1]. For strongly interacting concentrated suspensions, the effective interparticle forces clearly exhibit a many-body character induced by non-linear macroion-configuration–dependent counterion screening. These many-body effects are negligible for highly diluted and weakly interacting suspensions, where the macroion interaction is described in terms of the DLVO potential [2,3], derived from the *linear*-screening theory, with an electrostatic *pair* potential of the Yukawa type:

$$V_{\mathrm{DLVO}}(r) = \frac{Z^2_{\mathrm{DLVO}}}{\varepsilon r} \exp[-\kappa r]. \tag{1}$$

Here, r is the interparticle distance, ε is the dielectric constant of the solvent, $\kappa = \sqrt{4\pi(\sum_i q_i^2 \rho_i)/\varepsilon k_B T}$ the Debye-Hückel inverse screening length, T the temperature, and q_i, ρ_i the charges and concentrations of the counterions and added salt ions. The effective charge Z_{DLVO} is related to the bare macroion charge Z via $Z_{\mathrm{DLVO}} = Z \exp[\kappa R]/(1 + \kappa R)$, where R is the macroion radius. For low macroion packing fractions ϕ and strong interactions, non-linear–screening effects can be partially accounted for by a calculation of the counterion and salt ion profiles in a spherical Wigner-Seitz cell (WSC) for *one* macroion [4]. Comparison of these density profiles with that resulting from a linearized theory at the WSC boundary also yields an effective Yukawa pair interaction $V_{\mathrm{WSC}}(r) =$

$= (Z_{\mathrm{WSC}}^2 / \varepsilon r) \exp[-\kappa_{\mathrm{WSC}} r]$. In general the renormalized charge Z_{WSC} is smaller than the bare charge Z, and κ_{WSC} is somewhat smaller than the Debey Hückel value κ.

Recently, an *ab initio* theory for counterion screening was proposed[5,6] which systematically includes non-linear–screening effects and effective counterion-induced manybody interactions between the macroions within a classical pseudo-potential approximation. It represents a combination of molecular dynamics for the macroions and classical density functional theory for the counterions, incorporating correlations effects between the counterions, and thus is superior to the familiar Poisson-Boltzmann theory. Within this approach, one can directly judge the quality of the traditional Yukawa pair potentials. For high interactions and salt-free suspensions, it was found that the DLVO theory overestimates the structure for low ϕ, whereas it underestimates the static correlations for high ϕ. This failure can be qualitatively understood as follows. For low packing fractions, the non-linear screening, neglected in the DLVO approach, leads to an enhanced counterion concentration at the macroionic surfaces, which screens the bare macroion charge much more effectively than in the linearized approximation. Consequently, the structure of the macroions is overestimated by the DLVO theory. For high ϕ, on the other hand, the space for the counterion screening is missing, due to the excluded volume of the neighbouring particles. Hence, the true repulsion between macroions is even larger than predicted by the DLVO theory. The WSC-Yukawa model was also tested against *ab initio* theory, and it was found that it gives satisfactory agreement for low $\phi < 0.05$[7], but strongly underestimates the structure for $\phi \geq 0.08$[6]. Thus, none of the traditional pairwise Yukawa models reproduces the data for any packing fractions.

The aim of this letter is twofold. First, we show how to extract an *optimal effective pair potential* which is very close to a Yukawa potential $V_{\mathrm{AI}}(r) = (Z_{\mathrm{AI}}^2 / \varepsilon r) \exp[-\kappa_{\mathrm{AI}} r]$, from the data of an *ab initio* simulation. Using this optimal pair potential, all *ab initio* data for the pair structure of the macroions can be correctly reproduced. Clearly, the effective charge Z_{AI} and the inverse screening length κ_{AI} differ in general from the DLVO and WSC expressions. People are used to thinking in terms of effective Yukawa pair potentials in the context of charged colloidal suspensions. The present work gives an *ab initio* justification of the Yukawa picture. Furthermore, we find that the effective potential $V_{\mathrm{AI}}(r)$ depends on the thermodynamic phase: it is a bit different in coexisting solid and liquid phases of the suspension. This was never taken into account in the traditional Yukawa models. The second purpose of the paper is to present, within the theory of ref.[6], explicit *ab initio* results for an *added salt*, which is the usual case in real charged colloidal suspensions. The idea of an optimal effective pair potential also applies to this more complicated situation.

The central idea in obtaining an optimal pair potential from the *ab initio* data is to store N_c typical configurations of N_m macroion positions $\{R_i^{(j)}, i = 1, \ldots, N_m, j = 1, \ldots, N_c\}$ and their corresponding many-body forces $\{F_i^{(j)}, i = 1, \ldots, N_m, j = 1, \ldots, N_c\}$ during a small–systemsize simulation of N_m macroions in a cubic box with periodic boundary conditions. We then make a least-square fit of all these forces with a pair potential $V(r)$, *i.e.* we minimize the expression

$$\sum_{j=1}^{N_c} \sum_{i=1}^{N_m} \left(F_i^{(j)} - \sum_{k=1;\, k \neq i}^{N_m} \frac{\partial V(r)}{\partial r} \frac{r}{r} \bigg|_{r = |R_i^{(j)} - R_k^{(j)}|} \right)^2 . \tag{2}$$

In the k-sum of (2), the periodic images of particle k must also be included if $V(r)$ is long ranged. By definition, the optimal pair potential $V^*(r)$ minimizes the expression (2). If the interparticle forces were derivable from a pair potential, $V^*(r)$ would exactly reproduce this pair potential. If we represent $V(r) = V(r, a)$ as a function of a small number of variational parameters a, we get an approximation for $V^*(r)$. The quality is governed by the number of variational parameters and

than the bare the explicit form of the α-dependence. We remark that a force fit is much more sensitive and direct than a fit of the structure factor $S(k)$ with different potentials usually carried out in [5,6] which analysing experimental scattering data [8,9], since $S(k)$ is rather insensitive to details of the d manybody interactions.

We made the same runs as in ref. [6] (for a compilation of the parameters, see table I) and tried different ansätze for $V(r,\alpha)$. With a two-parameter Yukawa ansatz $V(r,\alpha) = V_{AI}(r) = (Z_{AI}^2/\varepsilon r)\exp[-\kappa_{AI}r]$, $\alpha \equiv (Z_{AI}, \kappa_{AI})$ we obtain a very good fit of the forces with an average error of less than 3%. The Yukawa fit is much better than a two-parameter soft-sphere fit with $V_{AI}(r,\alpha) = Ar^{-\nu}$, $\alpha = (A,\nu)$. If one uses the four-parameter fit $V_{AI}(r,\alpha) = (Z_{AI}^2/\varepsilon r)(1 + A \exp[-\lambda r])\exp[-\kappa_{AI}r]$, $\alpha = (Z_{AI}, \kappa_{AI}, A, \lambda)$, A is less than 0.05 and the average error does not improve significantly, indicating that the Yukawa form is indeed very close to $V^*(r)$. The of the Yukawa fit are summarized in table I. As a rule, $\kappa_{AI} < \kappa$ for low ϕ, but $\kappa_{AI}\kappa$ for

g this effective optimal Yukawa potential, we have performed standard simulations. The o data for the pair correlation function $g(r)$ are compared in fig. 1, for two different ter combinations (runs A and B), with the ab initio fit and the DLVO theory. The fitted potential reproduces the ab initio pair correlations quite well. Triplet correlations, r, are more sensitive to non-pairwise interparticle forces. In fig. 2, the bond angle tion function $g_3(\theta, R_c)$ of particle triplets that have two interparticle distances smaller is shown for $R_c = 2.5R$ and $R_c = 3.2R$. We have used a finite system with $N_m = 53$ s (run A). For $R_c = 2.5R$, the agreement of the ab initio data and the $V^*(r)$ data is fair. r, the first maximum is not well reproduced for $R_c = 3.2R$. Mainly macroion triplets of eighbouring particles contribute to this peak where non-linear screening drastically their repulsion. Hence, the peak cannot be described in terms of effective pairwise ions. This indicates that the optimal pair potential is a useful description for the pair e, but is less useful for higher-order correlations which depend more sensitively on the nature of the interparticle forces.

advantages of the fitting procedure are obvious. First, in order to fix $V^*(r)$, one typically eds small system sizes with $N_m \approx (10 \div 20)$ macroions. In fact, we performed run A also n = 15 particles (instead of $N_m = 53$) and did not find any significant difference in the ffective pair potential, which indicates that the fit is stable with respect to finite system idying a number of test runs, we found that far fewer configurations are needed to obtain an to compute statistical quantities like $g(r)$. It is much more efficient to first determine ith a small system and a relatively short ab initio run and then use $V^*(r)$ in an ordinary ar or Brownian dynamics simulations for a large system which does not suffer from any ze effects. Second, quantities which are very difficult to obtain in an ab initio calculation,

TABLE I. – Parameters of the different runs and of the associated Yukawa potentials. Here Z is the bare n charge, ϕ the packing fraction, N_m the number of macroions used in the periodically repeated x of the simulations, X the salt concentration, κR the inverse Debye-Hückel screening length VO, $\kappa_{AI}R$, Z_{AI} are the Yukawa parameters. The other parameters were fixed to $T = 300$ K, R = 53 nm, q = e.

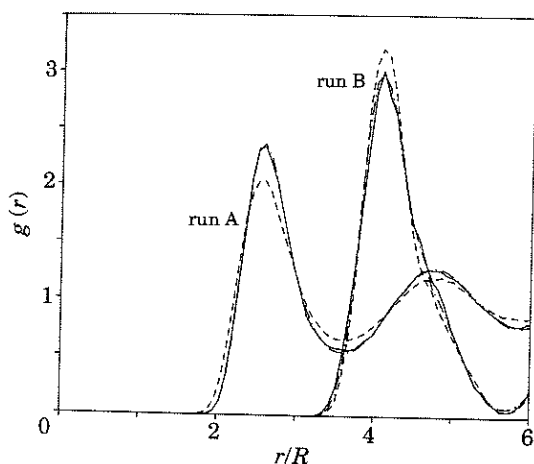| Z/e	ϕ	N_m	X	κR	Z_{DLVO}	$\kappa_{AI}R$	Z_{AI}
100	0.3	53	0	1.10	142	1.29	191
300	0.08	16	0	0.98	404	0.97	380
230	0.08	16	0	0.863	293	0.84	281
230	0.08	15	0	0.863	293	0.79	266
100	0.3	31	0.5	1.85	223	1.63	172

Fig. 1. – Macroion-macroion pair correlation function $g(r)$ vs. reduced distance r/R for runs A and B: comparison of the *ab initio* data (solid lines), DLVO theory (dashed lines) and the *ab initio* Yukawa fit (dot-dashed lines). In run B the system is a b.c.c. solid and $g(r)$ is the spherically averaged pair correlation function.
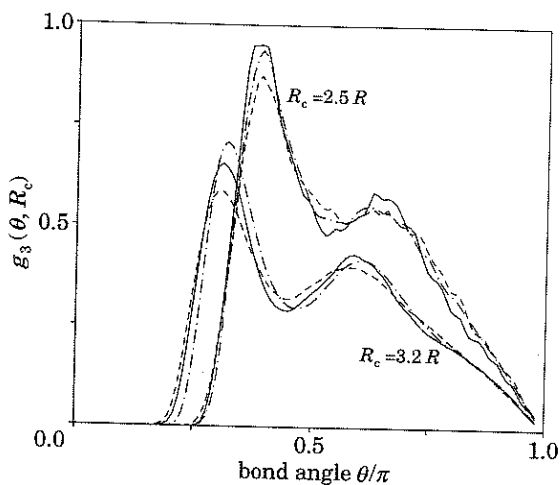

Fig. 2. – Bond angle distribution function $g_3(\theta, R_c)$ vs. reduced bond angle θ/π for $R_c = 2.5R$ and $R_c = 3.2R$ (run A). The curves are normalized so that the integral of $g_3(\theta, R_c)$ over θ is 1 for $R_c = 2.5R$ and 0.75 for $R_c = 3.2R$. The line types are as in fig. 1.

such as the osmotic pressure, the phase diagram or dynamical quantities, such as self-diffusion, can now be approximately determined with a simulation using $V^*(r)$. However, the configuration dependence of the interactions is averaged out by the fit procedure, so that fluctuations will not be correctly reproduced in simulations using the effective pair potential.

An interesting point is whether $V^*(r)$ depends on the thermodynamic phase. It has been commonly assumed that the pair potential is independent of the nature of the thermodynamic phase (*i.e.* liquid or solid). We did an *ab initio* simulation for thermodynamic and system parameters close to solid-liquid coexistence (see table I, run C and D). Run C was performed with $N_m = 16$ particles and was started with macroionic positions on a b.c.c. lattice which exactly fits
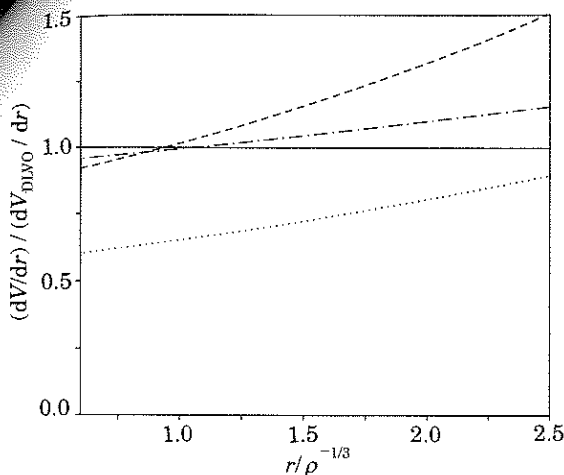
Fig. 3. – Ratio of the forces $\mathrm{d}V(r)/\mathrm{d}r$ (for runs C and D) and that of DLVO theory *vs.* reduced distance $r/\rho^{-1/3}$, where ρ denotes the macroion number density. *Ab initio* Yukawa fit for the solid (dot-dashed line) and the liquid state (dashed line), DLVO theory (solid line) and WSC model (dotted line) are shown. The parameters of the WSC model are $Z_{\mathrm{WSC}} = 217.8$ and $\kappa_{\mathrm{WSC}} R = 0.805$.
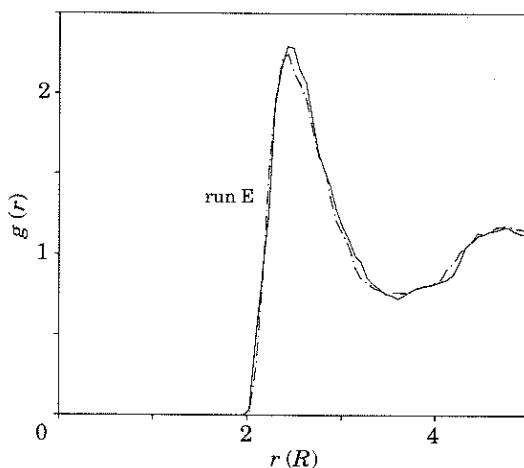

Fig. 4. – Same as fig. 1, but now for added salt (run E): comparison of the *ab initio* data (solid line) and the *ab initio* Yukawa fit (dot-dashed line).

in the cubic simulation box. The system remained solid during the whole simulation. In run D, on the other hand, we used $N_{\mathrm{m}} = 15$ particles and a disordered starting configuration. The system did not freeze during the simulation, since this value of N_{m} was incompatible with b.c.c. freezing in a cubic box. Results for $V^*(r)$ are displayed in fig. 3, where the ratio of the derivative $\mathrm{d}V/\mathrm{d}r$ and the derivative of the DLVO potential are shown. For comparison, the WSC results are also given in fig. 3. Although the thermodynamic and system parameters are exactly equal, the optimal effective potentials are clearly different in the solid and liquid phase. In the ordered solid, a stronger force is required to bring a particle closer to its neighbour in the liquid, whereas, for large distances, the «screening» of the ordered solid is more effective than in the liquid phase. At the nearest-neighbour distance, the forces are nearly equal. The difference in the interparticle

forces between the liquid and solid phase is a small effect on the $(5 \div 10)\%$ level but is significantly larger than the statistical error within the runs, which were estimated by doing different runs and comparing the fitted potential. This effect may, however, shift the solid-liquid coexistence line of a real colloidal suspension significantly with respect to that of a phase-independent Yukawa model [10].

Finally, we present some results for the case of added salt. The *ab initio* simulation can be generalized (as for details see ref. [11]) to include non-linear screening effects from both counter- and salt-ions. We have chosen the same parameters as run A (see table I) and added a monovalent salt with concentration ratio $X = \rho_{co}/\rho_c = 0.5$, where ρ_{co} is the co-ion and ρ_c is the total counterion concentration. Since screening is more effective than in the salt-free case, we introduced a steep soft-core repulsion (with range $2R$) for the macroions to avoid overlapping macroionic configurations. The results for $g(r)$ from the *ab initio* run and the Yukawa fit are summarized in fig. 4. Again fair agreement is found. The DLVO potential also gives a good description of $g(r)$, while the WSC model underestimates the structure significantly. Whereas for run A the DLVO theory underestimated the structure, due to the lack of the screening volume occupied by the neighbouring particles, the effective volume where screening takes place is much smaller for the case of added salt, since $1/\kappa$ is smaller. Thus, the excluded-volume effect is less dominant, and DLVO gives a better description than in the salt-free case. We believe, however, that the success of the DLVO theory is accidental. More details and further results on the added-salt case will be published elsewhere.

To summarize, we have justified, within an *ab initio* approach to counter- and salt ion screening, the Yukawa pair potential picture frequently used in the description of charged colloids. An optimal mapping of a system interacting via many-body forces, onto an effective Yukawa potential was described, which in general deviates from the classic DLVO and WSC model. The approach is quite general and also permits simulations of the pair structure in formerly inaccessible parameter regimes, since one only needs to simulate small system sizes to obtain the optimal effective Yukawa potential.

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