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Charged rod-like colloidal suspensions: what can we learn from *ab initio* simulations?

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Abstract. An *ab initio* approach to simulate the interactions and correlations of charged rod-like colloidal particles is proposed, which combines molecular dynamics for the mesoscopic rods and classical density-functional theory for the microscopic counterions. Many-body inter-rod interactions induced by non-linear counterion screening are systematically included in this approach. It is found that these forces can satisfactorily be described by an effective Yukawa-segment model which, however, differs in general from the traditional Derjaguin–Landau–Verwey–Overbeek theory.

Charge-stabilized colloidal suspensions of rigid rod-like particles represent excellent realizations of liquid-crystalline systems on a mesoscopic length scale [1]. Among quite a number of concrete examples the most-studied systems are aqueous suspensions of tobacco-mosaic viruses (TMVs) [2] or bacterial fd viruses [3]. Recent experiments have revealed a complex phase diagram including nematic, smectic, columnar and crystalline phases. Nevertheless the full phase diagram is still not entirely understood over the full range of densities, temperatures and added salt concentrations.

The knowledge of correlations and the phase diagram of a rod-like charged suspension is rather limited, since the form of the inter-rod forces, which is a necessary basic ingredient for any statistical mechanics theory, is not known exactly. Theoretical work has been directed along two lines. First, following an early idea of Onsager [4], the screened electrostatic interaction between rods was mapped onto that of hard spherocylinders. In view of the fact that the phase diagram depends sensitively on details of the interaction it becomes clear that this approach is too crude if quantitative predictions on correlations and on the complexity of the phase diagram are demanded. Second, in a more realistic description of the rod interaction discussed by Klein and coworkers [5] a model of beads or segments was studied with point charges along the rods interacting via a pairwise Yukawa potential according to the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of linear screening. This model is only justified in the limit of infinite dilution [6] but fails in the regime of strong interaction where liquid–solid phase transformations take place.

In this paper, *ab initio* simulations for charged rods in a salt-free suspension are reported based on the adiabatic 'primitive' model of highly asymmetric electrolytes where the counterionic density field is explicitly taken into account. This approach was recently proposed in [7] by Löwen *et al* where it was applied to *spherical* colloidal particles. The charge distribution of the spherocylindrical rods with total length L and cylindrical radius R is modelled by N_s equal point charges Ze located equidistantly along the rods such that their charge line density is $z = N_s Ze/L$. The point-like counterions carry an opposite charge $-qe$ ($qe \ll zL$) and interact via the Coulomb potential $V_{cc}(r) = q^2e^2/\epsilon r$ where ϵ is the

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dielectric constant of the solvent. Moreover the counterion–rod and inter-rod interactions are modelled to be a combination of the excluded rod volume and the corresponding Coulomb forces. A configuration of N_r rods is characterized by their centre-of-mass positions $\{\boldsymbol{R}_i\}$ and by a set of unit vectors $\{\boldsymbol{\Omega}_i\}$ determining their orientations ($1 \leqslant i \leqslant N_r$). The total Lagrangian $\mathcal{L}$ of the adiabatic 'primitive' model involves molecular dynamics for the rods and density functional theory for the counterions:

$$\mathcal{L} = \sum_{i=1}^{N_r}\left(\frac{1}{2}M\dot{\boldsymbol{R}}_i^{\,2} + \frac{1}{2}\Theta\dot{\boldsymbol{\Omega}}_i^{\,2}\right) - \sum_{i,j=1;\,i<j}^{N_r} V_{rr}(\boldsymbol{R}_i - \boldsymbol{R}_j, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j) - \mathcal{F}([\rho_c(\boldsymbol{r})], \{\boldsymbol{R}_i\}, \{\boldsymbol{\Omega}_i\}) \tag{1}$$

where M and Θ are the mass and the moment of inertia of the rods and $V_{rr}(\boldsymbol{R}_i - \boldsymbol{R}_j, \boldsymbol{\Omega}_i, \boldsymbol{\Omega}_j)$ is the direct inter-rod potential. Furthermore, $\mathcal{F}([\rho_c(\boldsymbol{r})], \{\boldsymbol{R}_i\}, \{\boldsymbol{\Omega}_i\})$ is the free-energy functional of the counterion density field $\rho_c(\boldsymbol{r})$ in the external field made up by the rods. For $\mathcal{F}$ the local density approximation (LDA) plus a mean-field term is adopted [7]. The equations of motion generated by $\mathcal{L}$ are integrated numerically at fixed temperature T under the constraints of global charge neutrality and fixed unit norm of $\boldsymbol{\Omega}_i$ using the Car–Parrinello method and a rod pseudopotential approximation similar to that in [7]. After a sufficient equilibration period statistics are gathered for rod correlations. Inspection of the equations of motion generated by the Lagrangian $\mathcal{L}$ shows that the forces on the centre-of-mass and the torques are not pairwise, in general. It is only in the dilute limit that the forces become pairwise which is equivalent to linear screening or DLVO theory.

During the *ab initio* simulations, a number of typical rod configurations and the associated forces and torques were stored. A least-squares fit of these forces and torques with an effective pair potential $V_{\text{eff}}(r)$ on N_s segments along the rods then yields an *optimal* pair interaction between the rods [8]. Performing this fit procedure for several runs and parameter combinations it turns out that the *ab initio* many-body forces and torques are reproduced within an averaged error of less than 3%. Interestingly enough, a Yukawa form $V_{\text{eff}}(r) = Z^{*2}\exp(-\kappa^* r)/\epsilon r$ with an inverse screening length κ^* and an effective segment charge Z^* is an acceptable fit. For a highly interacting system, the optimal Yukawa parameters κ^* and Z^* differ strongly from their DLVO values $\kappa_D^2 = 4\pi e^2 q^2 \bar{\rho}_c/\epsilon k_B T$, $Z_D = zL\exp(\kappa_D R)/(1+\kappa_D R)N_s$ where $\bar{\rho}_c$ is the mean counterion density.

Preliminary *ab initio* results are presented for one run in the disordered phase. The temperature is fixed to $T = 300$ K (room temperature) and the solvent dielectric constant is that of water, $\epsilon = 78$. $N_r = 108$ rods are put into a periodically repeated cubic simulational box. Each rod has a total length $L = 295$ nm, a cylindrical radius $R = 47$ nm and was composed of $N_s = 3$ segments with a segment charge $Z = 45$, having a distance of $d = 101$ nm along the rods. The rod density is $\rho_r = 3.55/L^3$ corresponding to a concentrated system with a relatively high volume fraction $\phi = 0.25$. Orientational pair correlations are conveniently measured by the function

$$g_P(r) = \sum_{i,j=1;\,i\neq j}^{N_r} \langle P_2(\cos\theta_{ij})\delta(\boldsymbol{r} - (\boldsymbol{R}_i - \boldsymbol{R}_j))\rangle \Big/ \sum_{i,j=1;\,i\neq j}^{N_r} \langle\delta(\boldsymbol{r} - (\boldsymbol{R}_i - \boldsymbol{R}_j))\rangle \tag{2}$$

where θ_{ij} is the angle between two orientations $\boldsymbol{\Omega}_i$ and $\boldsymbol{\Omega}_j$ and $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial. $\langle ... \rangle$ denotes a canonical average. Results for $g_P(r)$ are shown in figure 1 together with those of the optimal *ab initio* fit and the DLVO segment model. It

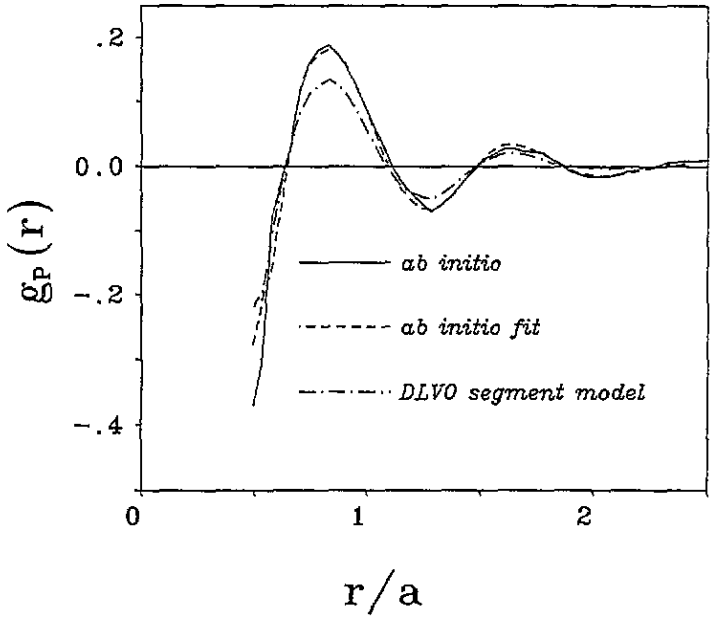

Figure 1. Orientational pair correlation function $g_P(r)$ versus centre-of-mass separation r measured in terms of the mean distance $a = \rho_r^{-1/3}$ for run A: *ab initio* data (solid line), *ab initio* fit (dashed) and DLVO theory (dot-dashed).

can be seen that the DLVO model underestimates the structure considerably whereas the *ab initio* results are fairly well reproduced by the optimal Yukawa-segment model.

In conclusion, based on an *ab initio* calculation, the Yukawa-segment model used by Klein and coworkers [5] is justified if one uses Yukawa parameters that are *renormalized* with respect to DLVO theory. This should motivate a detailed theoretical study of the Yukawa-segment model involving computer simulation or density functional theory of freezing in order to predict qualitatively and quantitatively the phase diagram of a TMW suspension.

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