Interaction between Charged Rodlike Colloidal Particles

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The interactions and correlations of charged rodlike colloidal particles are investigated using an *ab initio* approach which includes many-body inter-rod forces induced by nonlinear counterion screening. It is found that these forces can satisfactorily be described by an effective Yukawa segment model which in general differs from the traditional Derjaguin-Landau-Verwey-Overbeek theory. Whereas no simple analytical expression for the Yukawa parameters is available for the disordered phase, an exactly soluble cylindrical cell model reproduces the *ab initio* data quite well in the liquid-crystalline phase.

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Charge-stabilized colloidal suspensions of rigid rodlike particles represent excellent realizations of liquid-crystalline systems on a mesoscopic length scale [1,2]. There are quite a number of concrete examples ranging from concentrated aqueous suspensions of tobacco-mosaic viruses (TMV) [3] or bacterial *fd* viruses [4] to cylindrical micellar aggregates [5] and ellipsoidal polystyrene latex particles [6]. In 1936 the first experimental proof of liquid-crystalline order was given by Bawden *et al.* [7] using a TMV suspension. Since then a flurry of experimental and theoretical investigations followed. Recent experiments, mainly for TMV, have essentially contributed to our understanding of the structural and dynamical correlations in the disordered phase [8] and have also revealed a complex phase diagram including nematic [9], smectic [10], columnar [11], and crystalline phases. Despite these numerous investigations, the full phase diagram for TMV is still not entirely understood over the full range of densities and added salt concentrations.

Theoretically the knowledge of correlations and the phase diagram of a rodlike charged suspension is rather rudimentary, since the form of the inter-rod forces which is a necessary basic input for any statistical mechanics theory is not known exactly. Up to now theoretical work was directed along two lines. First the screened electrostatic interaction between rods was mapped onto that of hard spherocylinders [10,12] where the phase diagram is known [13]. This idea was first indicated by Onsager [14]. 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 a more realistic description of the rod interaction was introduced and discussed by Klein and co-workers [15]. They studied a model of segments with point charges along the rods interacting via a pairwise Yukawa potential according to the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) [16] theory of linear screening. This model is only justified in the limit of infinite dilution [17] but fails in the regime of strong interaction where liquid-solid phase transformations take place.

In this Letter, *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 Ref. [18] by Hansen and co-workers where it was applied to *spherical* colloidal particles. Combining molecular dynamics (MD) for the rods and classical density functional theory for the counterions, many-body forces and torques between the rods induced by nonlinear counterion screening are systematically included. While these nonlinear screening effects are neglected in DLVO theory, they become essential for strongly interacting charged suspensions. Contrarily an *ab initio* simulation of the *full* primitive model is impossible on present-day computers due to the large charge asymmetry and the corresponding large time scale separation between counterionic and rod motion.

As a result, the interactions and correlations between the charged rods are obtained in the disordered and crystalline phase. Fitting the many-body forces and torques by an effective segment model of point particles interacting via a pair potential, one extracts an *optimal* effective segment model. Interestingly enough the shape of the optimal pair potential is very close to a Yukawa potential. This optimal effective Yukawa segment model satisfactorily reproduces the *ab initio* data for the pair correlations and is thus a reasonable simple model for the rod interaction. Consequently, the Yukawa segment picture used by Klein and co-workers [15] is justified if one uses Yukawa parameters that are *renormalized* with respect to DLVO theory. In order to predict a simple analytical expression for the optimal Yukawa parameters an exactly soluble Poisson-Boltzmann model in a cylindrical Wigner-Seitz cell is proposed which is designed for strongly interacting aligned rods. In the liquid-crystalline phase this model agrees quite well with the optimal effective Yukawa segment model. In the fluid phase, however, a simple expression for the Yukawa parameters is not known such that one has to perform a full *ab initio* calculation.

In the *ab initio* calculations, the charge distribution of the spherocylindrical rods with total length L and cylin-

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drical radius R is modeled by N_s equal point charges Ze located equidistantly along the rods such that their charge line density is $z=N_sZe/L$. The pointlike 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 dielectric constant of the solvent. Moreover, the counterion-rod and inter-rod interactions are modeled to be a combination of the excluded rod volume and the corresponding Coulomb forces. A configuration of N_r rods is characterized by their center-of-mass positions $\{\mathbf{R}_i\}$ and by a set of unit vectors $\{\mathbf{\Omega}_i\}$ determining their orientations ($1 \le i \le N_r$). The total Lagrangian $\mathcal{L}$ of the adiabatic "primitive" model involves MD for the rods and density functional theory for the counterions

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

where M and Θ are the mass and the moment of inertia of the rods and $V_{rr}(\mathbf{R}_i-\mathbf{R}_j,\mathbf{\Omega}_i,\mathbf{\Omega}_j)$ is the direct inter-rod potential. Furthermore, $\mathcal{F}([\rho_c(\mathbf{r})],\{\mathbf{R}_i\},\{\mathbf{\Omega}_i\})$ is the free energy functional of the counterion density field $\rho_c(\mathbf{r})$ in the external field made up by the rods. For $\mathcal{F}$ the local density approximation (LDA) plus a mean-field term is adopted [18]. The equations of motion generated by $\mathcal{L}$ are integrated numerically at fixed temperature T under the constraints of global charge neutrality (with fixed mean counterion density $\bar{\rho}_c$) and fixed unit norm of $\mathbf{\Omega}_i$ using the Car-Parrinello method [19] and a rod-pseudopotential approximation similar to that in Ref. [18]. After a sufficient equilibration period statistics are gathered for rod correlations. In addition to the direct pairwise inter-rod forces on the center of masses $-\nabla_{\mathbf{R}_k}\sum_{i,j=1;i<j}^{N_r}V_{rr}(\mathbf{R}_i-\mathbf{R}_j,\mathbf{\Omega}_i,\mathbf{\Omega}_j)$ there are counterion-induced many-body forces $-\nabla_{\mathbf{R}_k}\mathcal{F}([\rho_c^{(0)}(\mathbf{r})];\{\mathbf{R}_i\},\{\mathbf{\Omega}_i\})$ where $\rho_c^{(0)}(\mathbf{r})$ is the configuration-dependent equilibrium counterion density obtained from minimization of $\mathcal{F}$. In analogy also the torques acting on the rods exhibit a many-body character induced by the counterions.

During the *ab initio* simulations, a number of typical rod configurations and the associated forces $\{\mathbf{F}_i\}$ and torques $\{\mathbf{M}_i\}$ 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. Since force and torque enter into the equations of motion and thus determine the correlations, this direct fit is superior to a fit of the free energy by an effective two-particle potential. Performing this fit procedure for several runs and parameter combinations the following results were obtained: First, the *ab initio* many-body forces and torques are reproduced within an averaged error of less than 3%. Second, the fit is robust against small system size ($N_r \gtrsim 8$) indicating that a simulation of a small system is already sufficient to get the optimal $V_{\text{eff}}(r)$. Comparing different *Ansätze* with two variational parameters, a Yukawa form $V_{\text{eff}}(r)=Z^{*2}e^2\exp(-\kappa^* r)/\epsilon r$ with an inverse screening length κ^* and an effective segment charge Z^* is an acceptable fit superior, e.g., to an inverse power-law *Ansatz*. As will be shown below this optimal Yukawa segment model reproduces the *ab initio* data for the rod pair correlations satisfactorily. However, for a highly interacting system, the optimal Yukawa parameters κ^* and Z^* differ strongly from their DLVO values

$$\kappa_D=\sqrt{4\pi e^2q^2\bar{\rho}_c/\epsilon k_BT},$$

$$Z_D=zL\exp(\kappa_D R)/(1+\kappa_D R)N_se.$$

In order to establish a simple connection of κ^* and Z^*, κ^* to the rod parameters and rod concentration ρ_r, a model is proposed where the nonlinear Poisson-Boltzmann (PB) equation [20] for one infinitely long rod in its cylindrical Wigner-Seitz cell of radius $R_0=1/\sqrt{\pi L\rho_r}$ is considered [21]. The equilibrium counterion density can be calculated analytically in this geometry [22]. Linearizing the PB equation at the Wigner-Seitz cell boundary one obtains the two Yukawa parameters of the Poisson-Boltzmann cell (PBC) model, κ_P and Z_P, as follows

$$\kappa_P=\kappa_D\left(\frac{1+\beta^2}{2\pi l_BR_0^2\bar{\rho}_c}\right)^{1/2}, \tag{2}$$

where $l_B=e^2q^2/\epsilon k_BT$ is the Bjerrum length and β is the zero of $\arctan[(l_Bz/e-1)/\beta]/\beta+\arctan(1/\beta)/\beta-\ln(R_0/R)$. For the effective segment charge Z_P one gets

$$Z_P=\frac{LR(1+\beta^2)}{l_BR_0^2\kappa_PN_s}\frac{K_1(\kappa_PR)I_1(\kappa_PR_0)-K_1(\kappa_PR_0)I_1(\kappa_PR)}{I_1(\kappa_PR_0)K_0(\kappa_PR_0)+I_0(\kappa_PR)K_1(\kappa_PR)}. \tag{3}$$

Here, $I_n(x)$ and $K_n(x)$ are Bessel functions of imaginary argument of order n. This cell model is designed for long aligned rods which are strongly interacting since only the boundary of the cell is treated adequately, but it is not expected to work in the disordered phase.

Ab initio results are presented for two different runs in the disordered and crystalline phase. The temperature is fixed to $T=300$ K (room temperature) and the solvent dielectric constant is that of water, $\epsilon=78$. As for the run in the disordered phase (run *A*), $N_r=108$ rods are put into a periodically repeated cubic simulational box with $\mathcal{N}=96^3$ grid points to resolve the counterion density field [23]. Each rod has a total length $L=295$ nm, a cylindrical radius $R=47$ nm and is 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

$$g_P(r) = \frac{\sum_{i,j=1;i\neq j}^{N_r} \langle P_2(\cos\theta_{ij})\delta(\mathbf{r}-(\mathbf{R}_i-\mathbf{R}_j))\rangle}{\sum_{i,j=1;i\neq j}^{N_r} \langle \delta(\mathbf{r}-(\mathbf{R}_i-\mathbf{R}_j))\rangle}, \quad (4)$$

where θ_{ij} is the angle between two orientations $\mathbf{\Omega}_i$ and $\mathbf{\Omega}_j$ and $P_2(x) = (3x^2-1)/2$ is the second Legendre polynomial. $\langle \cdots \rangle$ denotes a canonical average. If $g_P(r)$ is positive, the averaged orientation of two rods at a given center of mass distance r is parallel whereas it is perpendicular for $g_P(r) < 0$. *Ab initio* results for $g_P(r)$ are shown in Fig. 1 together with that of three different Yukawa segment models based on standard MD simulations: the optimal *ab initio* fit, the DLVO, and the PBC model. In general, $g_P(r)$ is negative for small distances, becomes positive with a maximum roughly at mean distance $a = \rho_r^{-1/3}$, and finally tends oscillatorily to zero as $r \to \infty$. It can be seen that the DLVO and the PBC model underestimate the structure considerably whereas the *ab initio* results are fairly well reproduced by the optimal Yukawa segment model. The same trend can be seen for other pair correlations and in data for single-rod properties as the mean force $\bar{F} = \sqrt{\langle \mathbf{F}_j^2 \rangle}$ or the mean torque $\bar{M} = \sqrt{\langle \mathbf{M}_j^2 \rangle}$. The *ab initio* fit deviates only 3% from the *ab initio* data whereas DLVO (PBC) theory strongly underestimates these quantities by 21% (37%). In conclusion, single particle and pair correlations are satisfactorily reproduced by the *ab initio* fit in the disordered phase, but both simple segment models fail: the DLVO theory because of the high rod concentration, and the PBC model since an infinite cylindrical cell is not an adequate description for the fluid phase of relatively short rods.

Ab initio simulations for long rods become increasingly difficult since one needs a large system size to avoid finite-size effects. As the whole counterion density has to be stored and moved, one rapidly reaches the limitations of present-day computers. Inspired by the success of the *ab initio* fit and keeping in mind that the optimal Yukawa parameters do not strongly depend on system size, an *ab initio* simulation of one smectic layer of $N_r = 9$ long rods with $N_s = 52$, $L = 1664$ nm, $R = 37$ nm, $z = 2.9e$ nm^{-1}, $\rho_r = 45.8/L^3$, $\phi = 0.07$ was performed in a rectangular simulational box with periodic boundary conditions (run *B*). The rod area density in the smectic layer was $0.026/R^2$. A line charge density z^* and an inverse screening length κ^* were fitted as optimal Yukawa parameters. In order to visualize the different interactions, the forces per unit length between two infinitely long parallel rods are shown in Fig. 2 as a function of the rod separation. These forces which are proportional to $f(r) = z^{*2}\kappa^* K_1(\kappa^* r)/\epsilon$ essentially govern the MD equations and are thus a direct measure of the structural order in the rod suspension. The DLVO theory strongly underestimates the interaction but the PBC model yields fairly good agreement for any relevant rod separation.

Furthermore, standard MD simulations with $N_r = 144$ rods (4 smectic layers with 36 rods) were performed using the different Yukawa segment models. The system was in the crystalline phase. As summarized in Table I, fluctuations in the orientations defined via $\chi_\Omega = 1 - \langle \mathbf{\Omega}_j \rangle^2$, the Lindemann parameter L (i.e., the root-mean-square displacement in the 2D layer measured in terms of the triangular lattice constant a_Δ) as well as the mean force and torque were calculated. Again, the PBC

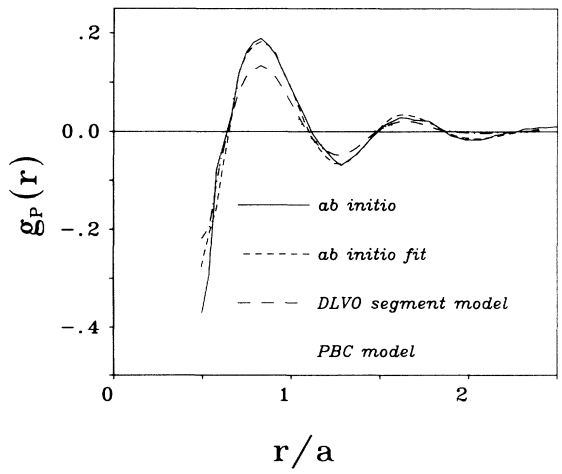

FIG. 1. Orientational pair correlation function $g_P(r)$ versus center-of-mass separation r measured in terms of the mean distance $a = \rho_r^{-1/3}$ for run *A*: *ab initio* data (solid line), *ab initio* fit (dashed), DLVO theory (dot-dashed), and PBC model (dotted).

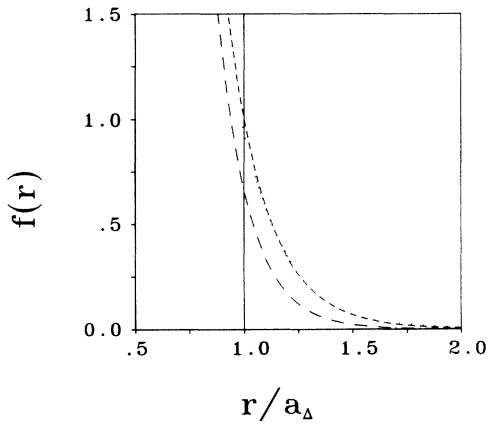

FIG. 2. Force $f(r)$ between two infinitely long parallel rods as a function of the rod distance r for run *B* within three different Yukawa segment models: *ab initio* fit (dashed line), the DLVO (dot-dashed), and the PBC segment model (dotted). The distance r is measured in units of the triangular lattice constant a_Δ. $f(r)$ is measured in units of $f(a_\Delta)$ of the *ab initio* fit data. The most relevant distance for the interaction is $r \simeq a_\Delta$.

TABLE I. Orientational fluctuations $\chi\Omega$, Lindemann parameter L, mean force $\bar{F}$, and mean torque $\bar{M}$ for the different Yukawa segment models (run *B*).

Model	$10^4\chi\Omega$	L	$\bar{F}/k_BT\rho_r^{1/3}$	$\bar{M}/k_BT$
ab initio fit	4.0	0.06	198	199
DLVO	6.5	0.09	189	190
PBC	4.3	0.06	197	198

model yields fairly good agreement with the *ab initio* fit data.

In conclusion, based on an *ab initio* calculation, an interaction-site model with Yukawa point charges along the rods was justified as a simple picture for the interaction between charged rodlike colloidal particles. In phases where the rods are at least partially aligned (like crystals, columnars, smectics, and nematics), a simple exactly soluble PBC model makes reasonable predictions for the Yukawa parameters while the DLVO theory fails for such strongly interacting systems. 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, e.g., of a TMW suspension. As a final comment, also dynamical properties can be addressed by combining the *ab initio* approach with Brownian dynamics for the rods.

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