

Charge Renormalization, Thermodynamics, and Structure of Deionized Colloidal Suspensions

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Abstract. In charge-stabilized colloidal suspensions, highly charged macroions, dressed by strongly correlated counterions, carry an effective charge that can be substantially reduced (renormalized) from the bare charge. Interactions between dressed macroions are screened by weakly correlated counterions and salt ions. Thermodynamic and structural properties of colloidal suspensions depend sensitively on the magnitudes of both the effective charge and the effective screening constant. Combining a charge renormalization theory of effective electrostatic interactions with Monte Carlo simulations of a one-component model, we compute osmotic pressures and pair distribution functions of deionized colloidal suspensions. This computationally practical approach yields close agreement with corresponding results from large-scale simulations of the primitive model up to modest electrostatic coupling strengths.

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1 Introduction

Charge-stabilized colloidal suspensions [1–3] exhibit rich thermodynamic phase behavior and tunable materials properties (e.g., thermal, mechanical, optical, rheological) that are the basis of many industrial and technological applications. Thermally excited (Brownian) motion of nm- μ m-sized particles dispersed in a fluid medium drives the self-assembly of ordered phases. Important examples are nanoscale structures [4] and colloidal crystals, whose diverse crystalline symmetries and variable lattice constants can conveniently template photonic band-gap materials [5–7].

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Interparticle interactions and correlations determine the distribution of microions (counterions and salt ions) around the colloidal macroions and thereby govern microion-mediated electrostatic interactions between macroions. As explained by the landmark theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) [8,9], repulsive interactions between like-charged macroions can stabilize a suspension against aggregation induced by van der Waals attractive interactions [10,11]. Equilibrium and dynamical properties of charged colloids depend sensitively on electrostatic interactions, which can be widely tuned by adjusting system parameters: size, charge, and concentration of ion species; pH and dielectric constant of solvent.

A powerful approach to modeling charged colloids is molecular simulation of either the primitive model, which includes all ions explicitly, or all-atom models, which include even individual solvent (e.g., water) molecules. At such microscopic resolution, simulations can potentially yield valuable insights into the thermodynamic, structural, and dynamical properties of real suspensions. Currently available processors and algorithms are limited, however, to relatively small systems and low ion size and charge ratios. Furthermore, simulations of microscopically detailed models do not necessarily elucidate the physical mechanisms underlying complex cooperative behavior.

An alternative to brute-force modeling is simulation of a one-component model, derived by pre-averaging over the microion coordinates to obtain *effective* interactions between macroions, screened by implicitly modeled microions. This coarse-grained strategy finesses the computational challenges that plague more explicit models, but relies on practical and accurate approximations for the effective interactions. A previous simulation study [12] validated the one-component model — implemented with linear-response and mean-field approximations — by direct comparison with pressure data from primitive model simulations at modest electrostatic couplings. The eventual breakdown of the model at higher couplings was attributed to failure of linear-screening approximations to account for nonlinear counterion association near macroions.

A recently proposed charge renormalization theory of effective interactions in charged colloids [13] addresses limitations of linear-screening approximations by incorporating an effective (renormalized) macroion charge into the one-component model. Calculations based on a variational approximation for the free energy indicated the potential of the theory to accurately predict thermodynamic properties of suspensions well into the nonlinear-screening parameter regime. The present paper describes complementary Monte Carlo simulations designed to test predictions for both thermodynamics (osmotic pressure) and structure (pair distribution function) of deionized suspensions of highly charged colloids.

The remainder of the paper is organized as follows. Section 2 first reviews the primitive and effective one-component models of charged colloids. Section 3 outlines the charge renormalization theory, which predicts renormalized system parameters: effective macroion charge, volume fraction, and screening constant. Section 4 describes our Monte Carlo simulations, which take as input the renormalized effective interactions. Section 5 compares our results for the pressure and pair distribution function of deion-