Comment on ''Monte Carlo study of structural ordering in charged colloids using a long-range attractive interaction''

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A recent theoretical analysis [B. V. R. Tata and N. Ise, Phys. Rev. E **58**, 2237 (1998)] of interactions and phase transitions in charge-stabilized colloidal suspensions made reference to our previously published measurements [J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **73**, 352 (1994); **77**, 1897 (1996); A. E. Larson and D. G. Grier, Nature (London) **385**, 230 (1997)] of colloidal interactions. Tata and Ise claim that our measurements cannot distinguish between predictions of the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory and those of the competing theory due to Sogami and Ise (SI). We demonstrate that the DLVO theory accurately describes the measured interactions between isolated pairs of like-charged spheres, while the SI theory fails both quantitatively and qualitatively to describe our data.

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Tata and Ise [1] recently revisited the outstanding problem of electrostatic interactions between charged colloidal spheres dispersed in aqueous electrolytes. Even qualitative features of the intersphere interaction are still under contention despite more than a century of intense scrutiny. The long-accepted theory due to Derjaguin, Landau, Verwey, and Overbeek (DLVO) predicts a purely repulsive electrostatic interaction between pairs of like-charged spheres [2–4]. This intuitively satisfying prediction is at odds, however, with a large and rapidly growing body of experimental evidence that colloidal electrostatic interactions include a long-ranged attractive component, at least under some circumstances. Tata and Ise suggest [1] that the observed attractions *can* be explained by the alternative theory due to Sogami and Ise (SI) [5,6]. We argue in this Comment that direct measurements of the interaction potential for charged colloidal spheres rule out the SI theory as a possible description for colloidal electrostatic interactions while highlighting limitations of the DLVO theory.

Both the DLVO and SI theories are derived from the nonlinear Poisson-Boltzmann equation describing the electric potential in a solution of ions. Both theories solve for the electric potential outside a highly charged sphere by linearizing the otherwise intractible Poisson-Boltzmann equation. They both also invoke the linear superposition approximation to estimate the energy cost for bringing two spheres into proximity. Thus, both theories are intended to describe the interactions between an isolated pair of charged colloidal spheres surrounded by pointlike simple ions. The extention to larger many-body systems follows in both theories from linear superposition of the pairwise results.

Both the DLVO and SI theories include terms accounting for van der Waals interactions. The van der Waals attractions are negligibly small for polymer spheres separated by more than 200 nm of water [7] and so will not be considered in the following discussion.

The DLVO theory predicts that the interaction potential between two spheres of radius a each carrying an effective charge Ze has the form

$$\frac{U_{\text{DLVO}}(r)}{k_B T} = Z^2 \left(\frac{e^{\kappa a}}{1+\kappa a} \right)^2 \lambda_B \frac{e^{-\kappa r}}{r}, \qquad (1)$$

where $\lambda_B = e^2/(\epsilon k_B T)$ is the Bjerrum length for the solvent whose dielectric constant at temperature T is ϵ, and the Debye-Hückel screening length κ^{-1} is given by $\kappa^2 = 4\pi\lambda_B n$. λ_B is the characteristic lengthscale at which the electrostatic interaction between a pair of monovalent ions has magnitude $k_B T$. κ^{-1} sets the distance over which electric fields are screened by a total concentration n of monovalent ions. For pure water at $T=24°$, $\lambda_B = 0.71$ nm, and $\kappa^{-1}=0.97$ μm. The term in parentheses in Eq. (1) accounts for the exclusion of simple ions from the spheres' interiors.

The SI potential has the form

$$\frac{U_{\text{SI}}(r)}{k_B T} = Z^2 \frac{\sinh^2 \kappa a}{(\kappa a)^2} \left(1 + \kappa a \coth \kappa a - \frac{\kappa r}{2} \right) \lambda_B \frac{e^{-\kappa r}}{r}, \qquad (2)$$

and differs qualitatively from the DLVO potential in that it contains a long-ranged attractive tail in addition to a screened-Coulomb repulsion at intermediate range. Considerable debate has arisen regarding the derivation of Eqs. (1) and (2). We will not address these theoretical concerns here, but will focus instead on how these results compare with experimentally measured interaction potentials.

Three methods have been developed over the past five years to measure the electrostatic interactions between micron-scale colloidal spheres with sub-$k_B T$ resolution. One [8–10] extracts the pair potential, $U(r)$, from measurements of the spatial distribution of spheres at equilibrium in a low density suspension. Another [11–14] extracts $U(r)$ from two spheres' trajectories using the Fokker-Planck formalism for interacting Brownian particles. The third [15] gauges $U(r)$ by measuring two spheres' displacements in calibrated optical traps as a function of their separation. All three approaches reveal that the DLVO theory quantitatively describes the interactions between isolated, unconfined pairs of spheres [8,11–15]. The first two techniques also have been used to demonstrate that confined spheres experience long-ranged attractions not explained by the DLVO theory
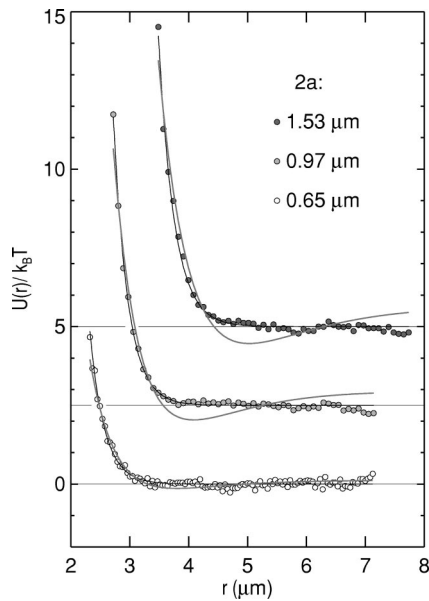

FIG. 1. The electrostatic interaction measured between pairs of colloidal spheres from three different-radius populations mixed together in the same electrolyte (from Ref. [14]). The solid curves are fits to the DLVO theory, Eq. (1), and the shaded curves are fits to the SI theory, Eq. (2). By making all three measurements in the same solution, we can ensure that they all correspond to the same ionic strength and Debye-Hückel screening length. Data sets were offset vertically for clarity.

[9,10,12,13]. Quantitative results from the latter two methods effectively rule out the SI theory as a possible explanation for the interactions between isolated pairs of spheres [12,15]. This point was made explicitly in Ref. [12] but was rejected by the authors of Ref. [1] who claim instead that the experimental results are inconclusive.

Tata and Ise argue that interpretation of measured pair interactions is rendered ambiguous because of the practical difficulty of independently measuring the spheres' charge Z and the electrolyte's screening length κ^{-1} under the experimental conditions of Refs. [11] and [12]. Both Z and κ have to be treated as free fitting parameters in comparisons with theoretical predictions. Based on fits [16] of Eq. (2) to the data of Ref. [11], Tata and Ise claim that the SI theory models the pair interaction potential as successfully as the DLVO theory, although with quantitatively different results for Z and κ.

The methodology of the experiments reported in Ref. [12], was intentionally designed to circumvent such ambiguities. We measured the pair interactions among three populations of polystyrene latex spheres, of diameters 0.65, 0.97, and 1.53 μm, mixed together in the same dilute suspension. Using optical tweezers to select and isolate two spheres of particular diameters, we were able to independently measure the pair potential for all six combinations of the three sphere sizes. The potentials measured for like-sized pairs appear in Fig. 1. While Z and κ still cannot be determined independently, the values of κ^{-1} obtained from fits to the data must be consistent with each other since all measurements were carried out at the same time in the *same electrolyte*.

Nonlinear least squares fits to both the DLVO and SI theories appear as solid lines overlaid on the data in Fig. 1.

TABLE I. Interaction parameters obtained by nonlinear least-squares fits of the data in Fig. 1 to Eq. (1) for the DLVO theory and Eq. (2) for the SI theory. The parameters obtained from the least-squares fit to Eq. (2) must be viewed with considerable caution given the qualitatively poor agreement between the model and the data. We include them for completeness' sake.

	DLVO		SI	
$2a$ (μm)	Z	κ^{-1} (nm)	Z	κ^{-1} (nm)
0.65	6000	272	665	768
0.97	13 800	268	1330	805
1.53	22 800	289	1750	957

Both theories were fit with Z, κ and a physically insignificant additive offset as free parameters. Numerical results are presented in Table I. Details of error estimation for these fits are reported in Refs. [11,12,14].

Both theories offer comparably good fits for the smallest spheres in the study, $2a = 0.65$ μm. Indeed, these spheres' interactions were reported in Ref. [11] and were interpreted as being consistent with the SI theory in Refs. [16] and [1]. As emphasized by Tata and Ise [1], the minimum predicted by the SI theory is comparable to the experimental energy resolution.

The same cannot be said for the larger spheres' data, however. As can be seen in Fig. 1, nonlinear least-squares best fits to the SI theory systematically deviate by up to 1 k_BT from the data for both 0.97 and 1.53 μm diameter spheres. These deviations are well outside the 0.1 k_BT resolution of the experimental technique [11,12,14]. The DLVO theory, on the other hand, fits all data sets equally well.

Not only does the SI theory fail to account for the functional form of the measured pair potentials, but values for κ^{-1} obtained from these fits reveal further failings of the SI theory. In the first place, the screening length obtained from the SI theory for the 1.53 μm diameter spheres extends to 960 nm. This is within experimental error of the theoretical upper limit set by the dissociation of water itself. Achieving such a long screening length is extremely difficult in practice, and impossible in the presence of highly charged spheres and their counterions. Furthermore, the three values of the screening length obtained from fits to the SI theory differ from each other by as much as 20%. By contrast, the DLVO theory yields consistent values for κ^{-1}, independent of sphere size. The DLVO theory's values correspond to an ionic strength of 1.2 μm, a plausible value. We ruled out the possibility that the ionic strength could have drifted substantially during the six-hour-long series of measurements by repeating the first measurement at the end. Values obtained from both SI and DLVO theories changed by less than 5% during this time. Thus, drifting ionic strength cannot explain the inconsistent values obtained from the SI theory.

Tata and Ise state [1] that our spheres are so weakly charged that the attraction predicted by the SI theory is unmeasurably small. Examination of Fig. 1 shows immediately that whatever the larger spheres' charge states, the SI theory cannot account for the range of their observed repulsions without erroneously introducing a sizeable long-ranged attraction. Furthermore, our measurements show that the pair interaction is comparable to k_BT even when the spheres are 2

diameters from contact. Such long-ranged repulsion is simply inconsistent with their assertion that the spheres are too weakly charged to show an attractive tail. The inability of the Tata, Ise, and their collaborators to determine the charge on the spheres with bulk conductivity measurements does not alter this conclusion.

Tata and Ise also suggest that the charged glass walls of our sample chambers may have distorted the results of our measurements. Indeed, we find that moving the spheres to within 2 or 3 μm of even one wall qualitatively induces a long-ranged attractive tail in the pair potential not accounted for by the DLVO theory [12,13]. This is consistent with results from other measurement techniques which show pure repulsion between unconfined spheres [8,15] and long-range attraction between confined spheres [9,10]. The measurements reported in Ref. [12] and reproduced in Fig. 1 were performed with the spheres more than 8 μm from the nearest wall. This is at least eight screening lengths separation, assuming the largest possible value for κ^{-1}, and probably more than 20 screening lengths, assuming a more realistic value. There is simply no possibility for an electrostatic coupling between the spheres and the walls strong enough to distort our measurements significantly. Measured hydrodynamic coupling [17] similarly is too weak at these separations to affect our potential measurements.

Tata and Ise cite a report of correlations induced in bulk colloidal fluids by proximal walls extending to 50 μm [1] as evidence for a possible wall-induced influence on our measurements. These correlations, however, reflect the many-body structure of bulk colloidal fluids at relatively high concentrations, and not the behavior of an otherwise isolated pair of spheres. This observation, therefore, is irrelevant to the present discussion and leaves us with no evidence that the walls, at more than 8 μm separation, affect our measurements.

The consistent picture emerging from the various measurements of colloidal electrostatic interactions is that the DLVO theory accurately describes the behavior of isolated pairs of spheres, but fails to account for the long-ranged attractions apparently induced by nearby charged walls. Such a failure should not be surprising since the DLVO theory is formulated for isolated pairs of spheres with relatively weak interactions. The SI theory, on the other hand, fails to describe even isolated pairs' interactions. If the SI theory fails for two spheres, it cannot be used to explain the properties of many-sphere systems.

The authors of Ref. [1] and their collaborators have built a strong case over the years that the DLVO theory fails to explain many phenomena in monodisperse charge-stabilized colloidal suspensions. There is little disagreement remaining that these anomalous phenomena arise from or are characterized by long-range attractions among the spheres and that these attractions are mediated by the surrounding simple ions.

What remains to be understood, then, is the mechanism for the attraction. Even though the SI theory describes long-ranged electrostatic attractions among like-charged spheres mediated by simple ions, it appears to do so incorrectly at the most basic level, as we have argued in this Comment. Rejecting the SI theory does not require rejecting the experimental evidence for like-charge colloidal attractions. Quite the contrary, it mandates renewed efforts to identify the correct mechanism for this effect. A variety of theories, including those described in Refs. [18–24], are currently under investigation as possible explanations. These extend the DLVO formulation by including effects of nonlinearity and relaxing the assumption of linear superposition. Another possibility is that these attractions cannot be explained within the mean-field formalism of the Poisson-Boltzmann equation. Only when further efforts yield a verifiably correct explanation for the attractions observed among colloidal spheres will an explanation for the complex behavior of bulk charge-stabilized colloidal suspensions be possible.

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