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

B. V. R. Tata[1] and Norio Ise[2]

[1]*Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India*

[2]*Central Laboratory, Rengo Company Ltd., Ohhiraki, Fukushima, Osaka 553, Japan*

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In the Comment by Grier and Crocker (preceding paper) the authors tried to refute our criticism [Phys. Rev. E **58**, 2237 (1998)] on their work [J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **77**, 1897 (1996)] by simply fitting once again their old experimental data. Grier and Crocker claim that their pair-potential measurements on aqueous dilute suspension of charged colloidal particles confined between charged glass walls at gap of about 8 μm provide evidence for the failure of Sogami-Ise (SI) theory and demonstrate the applicability of the Dejaguin, Landau, Vervey, and Overbeek (DLVO) theory. Grier and Crocker do not provide additional experimental proof to counter our criticism. We continue to claim here based on our conductivity and conductometric titration measurements, which allow estimating the effective charge and determining the number and nature of the dissociable sites respectively, that their measurements using not well-characterized samples cannot provide clear evidence for the failure of SI theory. With the evidences available in literature, we refute all of the Grier and Crocker comments, including the effect of charged wall confinement on the measured colloidal interactions.

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In the Comment [1] by Grier and Crocker (GC) the authors try to defend against our criticism [2] on their previously published measurements [3]. We point out the main drawbacks in CG's experiments here. These are (i) improper choice of uncharacterized samples. GC have not characterized their samples for the effective charge Ze and for the nature of dissociable groups on the particles. (ii) The suspension parameters used by GC do not favor the conditions to verify the validity of Sogami-Ise (SI) theory. (iii) In fitting the experimental data GC assume that the effective charge number Z and the inverse Debye screening length κ are independent. But the SI theory models a suspension where the counterion concentration in the medium is determined by the charge on the particle and hence Z and κ are *not independent* in the SI formalism. In other words, the Sogami theory is for multiparticle systems while the DLVO theory is for two-particle systems. (iv) GC's $U(r)$ data measured for a gap of 8 μm between charged glass walls is not entirely free from the effect of confinement due to the presence of charged wall. Neither the Sogami theory nor the DLVO theory is derived for such a geometry.

Before we elaborate the above mentioned limitations in this reply, we point out that GC fail to present new data to refute our criticism on their work. The old data (see Fig. 1 of Ref. [3]), which was fitted earlier to expressions of SI potential and DLVO potential with Z and Debye screening length κ^{-1} as independent parameters, is once again fitted to the same expressions. They repeat the fitting in such a way that the fitting to SI potential should appear worse than earlier (compare the fitted values presented in Table I of Ref. [1] and Table I of Ref. [3]) but not for fitting to DLVO potential. This exercise is rather biased and does not add any new physics to resolve the ongoing controversy on the existence of long-range attraction in charged colloidal systems [4,5].

Choice of suspensions: GC have given in their Comment [1] the expressions for the DLVO potential $U_{\mathrm{DLVO}}(r)$ [Eq. (1) of Ref. [1]] and the SI potential $U_{\mathrm{SI}}(r)$ [Eq. (2) of Ref. [1]] but not for κ. To have consistency with our notation we write the expression for $U_{\mathrm{SI}}(r)$ as

$$U_{\mathrm{SI}}(r)=2\frac{(Ze)^2}{\epsilon}\left(\frac{\sinh(\kappa d/2)}{\kappa d}\right)^2\left(\frac{A}{r}-\kappa\right)\exp(-\kappa r), \quad (1)$$

where $A=2+\kappa d\coth(\kappa d/2)$ and the inverse Debye screening length κ is given as

$$\kappa^2=4\pi e^2(n_pZ+n_i)/(\epsilon k_BT), \quad (2)$$

where d is the diameter of the particle, n_p the particle concentration, n_i the concentration of impurity ions, T the temperature, ϵ the dielectric constant of water, and k_B the Boltzmann constant. The effective charge Ze is related to the surface charge density σ on the particle by $\sigma=Ze/\pi d^2$. The position of the potential minimum R_m is given as

$$R_m=\{A+[A(A+4)]^{1/2}\}/2\kappa \quad (3)$$

and the well depth by $U_m=U_{SI}(R_m)$. R_m as well as U_m strongly depends on κ (see Fig. 1.4 of Ref. [4]) which in turn depends on Ze and n_i.

In fitting experimental data GC have assumed that Z and κ are independent. This is valid only if the counterion concentration $n_pZ\ll n_i$. This condition can be met easily in experiments designed for measuring the pair-potential $U(r)$ between colloidal particles, by choosing very dilute suspensions. Further, meeting this condition satisfies the assumptions of DLVO theory and ideally suited for testing the existence of screened Coulomb repulsion given by DLVO potential. It may be mentioned here that the DLVO theory [6] models a very dilute suspension consisting of charged colloidal particles immersed in an electrolyte [7]. Thus the dominant contribution to screening parameter κ is due to the ions of the electrolyte rather than the counterions dissociated from colloidal particles. In other words $n_p Z \ll n_i$, hence Z and κ can be taken as independent parameters when the measured $U(r)$ data is fitted to DLVO potential.

On the other hand, the SI theory [8] models a suspension consisting of a number of charged colloidal particles with its counterions. The charging of colloidal particle was achieved by the release of the counterions by the colloidal particle. Thus counterion concentration ($n_p Z$) in the medium is directly related to the charge on the particle. Hence in the SI theory Z and κ are *not independent*. The ideal experimental condition for verifying the SI theory is dilute suspensions of highly charged particles, where the counterion concentration is much larger than the impurity ion concentration n_i. In other words, dilute suspensions which satisfy the condition $n_p Z \gg n_i$ are ideally suited for testing the validity of SI theory and measurements of $U(r)$ performed on such suspensions can be fitted with either Z or κ as the parameter.

In the case of GC experiments, they have not made any attempt to determine suspension parameters viz. n_p and Z of their samples. Hence, they do not know the conditions that are appropriate to verify the SI theory. We made an attempt to estimate these quantities. GC used very dilute suspensions [3], hence the values of n_p are expected to be of the order of 10^7–10^8 cm^{-3}. It is known that in deionized suspensions the background 1:1 electrolyte concentration to be about 1.2 μm and GC also mention this value [3], which corresponds to $n_i = 7.2\times10^{14}$ cm^{-3}. To satisfy the condition $n_p Z \gg n_i$, the Z values on the particles used by GC should be of the order of 10^8–10^9.

Since GC have not verified whether their particles have these charge numbers or not, we made an attempt to estimate Z values. Using the same suspensions (same catalog number and same size of the same company) Yamanaka [9] carried out conductivity and conductometric titration measurements. The samples were cleaned initially with mixed ion-exchange resins, followed by dialysis against milli-Q water for 10 days. Then the suspensions were kept with mixed ion-exchange resins for more than a week.

These deionized samples with diameters of 0.65, 0.97, and 1.53 μm having volume fractions ($\phi = \pi d^3 n_p/6$) of 0.84, 0.95, and 1.09%, respectively did not show significant conductivity K as compared to the background conductivity $\sim$0.9 μS/cm which arises from ions in the water that have been remained unexchanged due to the finite capacity of the mixed-bed used for deionization. The small values of K strongly suggest that the particles have low charge. We conclude this from the experience of earlier conductivity measurements on 0.18 μm particles, which showed a conductivity of 1.37 μS/cm at a volume fraction of 0.18% and had charge about 1594*e* [10]. Yamanaka concentrated (by ultrafilteration) the 0.65 and 0.97 μm diameter suspensions to a ϕ of 2.2 and 4.7, respectively, with an aim to increase the conductivity K of the suspensions above the background conductivity. The K values are found to be still not meaningfully larger than the background for determining accurately the effective charge on these particle. Further the conductivity being low even in concentrated samples suggests that the charge numbers are small. The sedimentation and associated precipitation caused problem to increase the volume fraction of 1.53 μm size particles, and hence no conductivity measurements were carried out. These conductivity measurements on the three particles reveal that the Z values are too small to satisfy the condition $n_p Z \gg n_i$. Thus applying the $U_{\rm SI}(r)$ to fit experimental $U(r)$ data is inappropriate. The numbers for Z and κ obtained by such a fitting do not have any physical meaning. Hence the GC's conclusion based on such data does not constitute clear evidence for failure of the SI theory.

GC mentioned that their measurements are on polystyrene *sulfate* spheres. This is untrue. If their particles have a large amount of sulfate groups (strong acid groups), then the particles are expected to have a large amount of effective charges due to their strong dissociation. Yamanaka [9] carried out conductometric titration measurements on deionized concentrated samples using 0.01 N NaOH. In both cases the presence of a large amount of weak acid groups could be detected but *not* strong acid groups. Since the particles have only weak acid groups, the dissociation of these groups under ambient conditions is very small leading to a small amount of effective charges. Thus the small values of Z on the particles used by GC is understandable.

We strongly refute GC statement in their comment that ‘‘the inability of Tata, Ise, and their collaborators to determine the charge on the spheres with bulk conductivity measurements does not alter this conclusion.’’ It is not our inability but it is the lack of strong acid groups in their samples, which makes their samples unfit for verifying the applicability of SI theory. Thus, our present measurements require GC to alter their conclusions.

Thus, it is clear from our conductivity and conductometric titration measurements that characterization of samples with respect to nature of the dissociable groups and determination of effective charge is very important. The prior knowledge of suspension parameters helps in creating favorable conditions to test the validity of a particular theory.

GC experiments are more tuned to verify screened Coulomb repulsion but not the existence of long-range attraction in $U(r)$ as inferred from several evidences reported in bulk suspensions [4,5,10–12]. Even if one observes the long-range attraction in $U(r)$, it is not going to be a conclusive proof for evidence of SI theory till the measurements verify the κ dependence of R_m and U_m [see Eq. (3) and Fig. 1.4 [4]] as predicted by SI theory [8]. If the objective is to test the existence of long-range attraction in $U(r)$ of isolated pairs, then the right experiments should be done on well characterized suspensions of highly charged particles far away from uncharged walls. Hence, we completely disagree with the GC statement that they provide compelling evidence against the SI theory correctly describing the interactions between isolated pairs of charged colloidal spheres [3] or SI theory fails both quantitatively and qualitatively to describe their data [1]. In fact we have shown by performing simulations that $U_{\rm SI}(r)$ correctly describes several experimental phenomena such as vapor-liquid condensation [13,14] void structure [15,16], gas-solid coexistence [10,17], reentrant transition [18,19], and reentrant solid-liquid transition [11,12] observed in bulk suspensions.

Effect of confinement. The DLVO theory and SI theory have been derived for unconfined suspensions. The confinement could be due to a hard wall or due to a charged (charges on the wall could be like or opposite to that on the ticles in the suspension) wall. In GC's experiment there exists a negatively charged wall confining the negatively charged polystyrene particles in the suspension. GC argue that the $U(r)$ measurements made at 8 μm away from the glass wall are free from the confinement effect. We argue here based on the following measurements reported in the literature that their $U(r)$ measurements corresponding to 8 μm gap are not completely free from confinement effect.

The charge density as reported by GC [3] on the glass wall is one electron equivalent per 10 nm^2, which is about 1.6 $\mu\mathrm{C/cm}^2$ and is not a very small charge density. If this value is correct, it is anticipated from Muramoto *et al.* [20] experiments that there exists considerable electrostatic interaction between the charged plate and the charged particle apart from the particle-particle interaction. These experiments are on gaslike ordered suspensions and Muromoto *et al.*'s [20] observation that the particle concentration is high close to the wall and decreases gradually is a consequence of charged-wall–charged-particle interaction, but not due to the many-body structure of bulk colloidal fluids as conjectured by GC. Further, the charged-wall–charged-particle interaction is found to persist to distances as high as 5–50 μm depending on the charge on the plate and charge on the particle. So the GC's conclusion viz. ''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'' is not true.

It is clear from the above discussion that there exists a possibility of finite amount of wall-particle interaction over and above the interparticle interaction. GC neither measure nor estimate the charged wall-charged particle interaction as a function of wall-particle separation. In the absence of such data, making a conclusion [1] such as ''the interaction energy at a separation of 8 μm from the wall is negligible,'' does not have any scientific validity. GC make statements based on their belief. So their statement that ''there is simply no possibility for an electrostatic coupling between the spheres and the charged walls'' should not be taken seriously. GC make measurements with particles having different charges (by using different sizes). The fitted values presented in Table I [1] need correction for the possible charged-wall–charged-particle interaction.

To summarize, GC have not made any attempt to characterize the samples. We carried out the characterization and our measurements show that the polystyrene particles have a large number of weak acid groups, and hence the effective charge on the particle is not sufficiently high favoring the conditions for verifying the validity of SI theory. Based on the evidences available on the long-range electrostatic effect of charged wall on the charged particles we argued that the GC's $U(r)$ data, measured at 8 μm away from the charged glass wall, is not entirely free from confinement. We have clearly brought out the experimental conditions in very dilute suspensions that are favorable for observing the long-range attraction and testing the validity of SI theory.

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