Comment on "Attractive Potential between Confined Colloids at Low Ionic Strength"

Recently Kepler and Fraden (KF) reported an attractive component in the experimentally estimated pair potential $U(r)$ in aqueous colloidal suspensions of polystyrene particles which were confined between two glass plates [1]. In spite of getting unphysical numbers for the parameters using the DLVO potential, they failed to consider the well-known counterion mediated attraction [2,3] and went on to speculate the origin of attraction to be in confinement. In this Comment we contradict their hypothesis and provide evidence that the attraction is due to the counterion mediation [2,3] as envisaged in Sogami theory. The effective pair potential in confined geometry within the DLVO framework is earlier shown always to be repulsive [4].

We now show that the Sogami pair potential $U_s(r)$ [2] explains all the qualitative features of the experimental pair potential $U(r)$ obtained by KF. $U_s(r)$ has been extensively used to explain a number of other experimental results in these systems [5]. $U_s(r)$ has a potential minimum at R_m with a depth $U_m = U_s(R_m)$. R_m depends on screening length κ^{-1} and U_m on effective charge fZe and ionic strength. f is degree of dissociation and Ze the titratable charge. Since an *in situ* measurement of these quantities are rather difficult, in most of the cases these are treated as the parameters. $U(r)$ curves of KF are digitized and fitted to the $U_s(r)$. The fits were weighted to emphasize the depth and the minimum of the pair potential. Table I gives the results and Fig. 1 shows $U_s(r)$ for the fitted parameters. Notice from Table I and Fig. 1 a good agreement between Fig. 3 of KF and our results. The effective hard sphere diameters obtained from $U_s(r)$ also agree well with those obtained from Fig. 1 of KF. Further, our simulations with $U_s(r)$ for the surface potential Φ_0 in the range of 2.8 to 6.2 mV show [5] a single peak in $g(r)$ and no rapid aggregation is found as reported by KF in the case of DLVO potential. Thus the fitted parameters are physically reasonable. The curves a–f of KF correspond to successively decreasing ionic strength. This behavior of U_{em} and R_{em} on ionic strength or equivalently κ is *remarkably similar* to the Fig. 2 of Ref. [2]. Thus the good agreement between $U_s(r)$ and results of KF strongly suggest that the origin of attraction arises due to counterion mediation as this has been taken into account in Sogami formalism. The effect of confinement is expected to broaden the potential well hence Sogami's theory for a confined system is expected to give better agreement to the results of KF. A few similar experiments have apparently shown only repulsion [6]. This is because for the reported values of the parameters Z and κ [6], U_m is found to be $\sim 0.02 k_B T$ making its experimental detection difficult. Thus $U_s(r)$ can explain other results in bulk and confined geometries [6]. To conclude, it is shown that the attraction reported by KF arises from counterion mediation as envisaged in Sogami theory.

Table I. Fitted parameters for curves a–f of Fig. 3 of Ref. [1]. Position R_{em} and depth U_{em} correspond to $U(r)$.

Curve[a]	$f(10^{-3})$	$\kappa\sigma$	$\frac{R_m}{\sigma}$	$\frac{R_{em}}{\sigma}$	$-\frac{U_m}{k_B T}$	$-\frac{U_{em}}{k_B T}$
a	2.12	7.68	1.38	1.39	0.198	0.200
b	1.64	5.29	1.56	1.56	0.208	0.207
c	1.36	3.79	1.80	1.80	0.205	0.210
d	1.10	3.12	2.01	2.01	0.152	0.150
e	0.82	2.37	2.41	2.40	0.085	0.085
f	0.59	1.13	4.47	...	0.034	...

[a]The number density and the charge density used in the fitting are the same as those reported by KF. σ is the particle diameter.

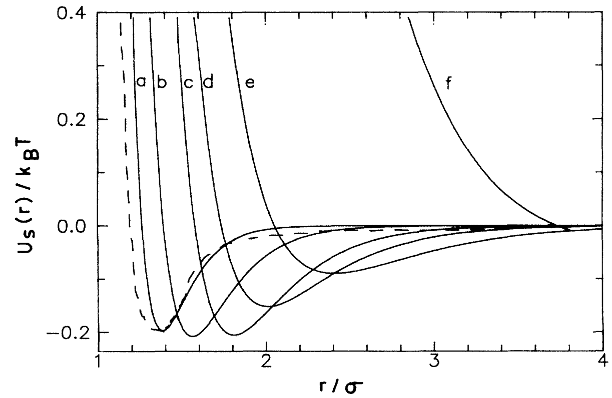

FIG. 1. $U_s(r)$ for the fitted parameters listed in Table I. For the sake of comparison the curve a of Fig. 3 of KF is also shown as the dashed line.

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