Electronic Supplementary Material (ESI) for Soft Matter.
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On the stability of aqueous dispersions with conducting nanoparticles

Ryan Szparaga*, Clifford E. Woodward** and Jan Forsman*
Theoretical Chemistry, Lund University
P.O.Box 124, S-221 00 Lund, Sweden
*School of Physical, Environmental and Mathematical Sciences
University College, University of New South Wales, ADFA
Canberra ACT 2600, Australia

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1 Supporting Information

1.0.1 Size and n_{max} convergence

The investigated systems display a rather slow convergence, in terms of size, and the number of included reflections. We will discuss the problems of choosing an odd-numbered value for n_{max} below, but even when this is even, a rather large value is typically required. In Figure 1, we illustrate the poor convergence properties that these systems display. Here we see that a very large number of reflections are needed, as well, a surprisingly large system size is often required. A single reliable pressure data point measurement required single-processor simulation times of the order of weeks! We were surprised by the computational demands for a, seemingly simple, primitive model system. It is likely that these two requirements are linked. That is, large numbers of reflections means that relevant distances perpendicular to the walls is large. These long-range reflections will exert their influence over large distances in the lateral directions.

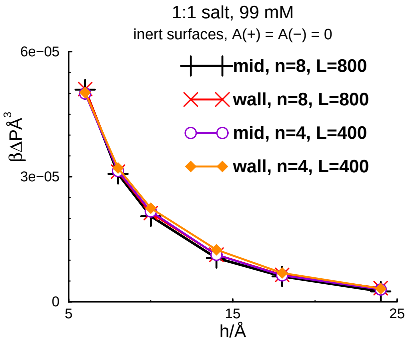

Figure 1: Evaluating dependence on system size, as well as the number of included image reflections, in simulations at 99 mM salt.

1.0.2 Comparing results for hard and softly repulsive surfaces

One problem with hard wall models is that the wall pressure evaluations require density extrapolations. This can lead to poorer statistics (especially at low salt concentrations), and possibly also systematic errors, since the curvature of the density profile might change with separation. It is therefore of interest to consider the use of softly repulsive surfaces, with negligible contact densities. In Figure 2 we verify that one obtains similar interactions with hard as with softly repulsive walls.

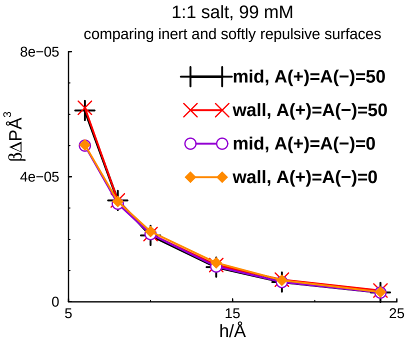

Figure 2: Comparing simulation results obtained with hard ($A_+ = A_- = 0$) and softly repulsive ($A_+ = A_- = 50$) conducting walls, respectively.

1.0.3 Long-range tail part, with ion-specific surfaces

For completeness, we present the long-ranged tail, also for the cases with ion-specific surface interactions. As we can see in Figure 3, the latter will lead to a slower convergence towards the limiting long-range (continuum-electrostatic) behaviour. Nevertheless, this limit is approached at sufficiently large separations. The existence of this salt-independent long-range interaction relies upon our intial *ansatz* for R_d, eq. (**??**).

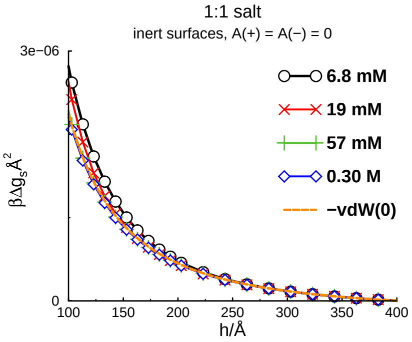

Figure 3: iPB predictions for the long-range part of the interactions between ion-discriminating ($A_+ = -A_- = 4.5$) and conducting surfaces, i.e. those shown at short separations in Figure **??**.

1.1 Poor convergence with odd-numbered reflections.

Here we will try to illustrate how and why the convergence, in terms of total reflection number, is poor when this number is odd. In other words, if n_{max} is an odd number, then n has to be very large to produce convergent results. This is worse than it might first appear, because the "non-convergent" results one obtains for modest and odd values of n_{max} are *very* far from being convergent. In fact, if we use our standard grand canonical simulations, these systems fill up with an absurd amount of salt, orders of magnitude too high. If we instead constrain the system to have the same average salt concentration as a grand canonical simulation with an even n_{max} would give, we still end up with highly unphysical results. Specifically, the system demixes, forming separate phases only containing cat- and anions, respectively. This is illustrated in graph(a) of Figure 4, where $n_{max} = 5$. In graph (b) of the same Figure, we see how the simulation box is filled up seemingly without bounds [1]. This is for $n_{max} = 11$, which actually is high enough to produce reasonable values *provided that the number of salt pairs is constrained*, i.e. that the simulation is performed canonically. We also note how the system spontaneously splits up into separate positively and negatively charge phases, in a clearly unphysical manner. The periodic boundary conditions playe a role, but this phase separation also occurs in an analogous "closed" system, without periodic boundary conditions (not, shown, but the phase boundary is then along the diagonal).

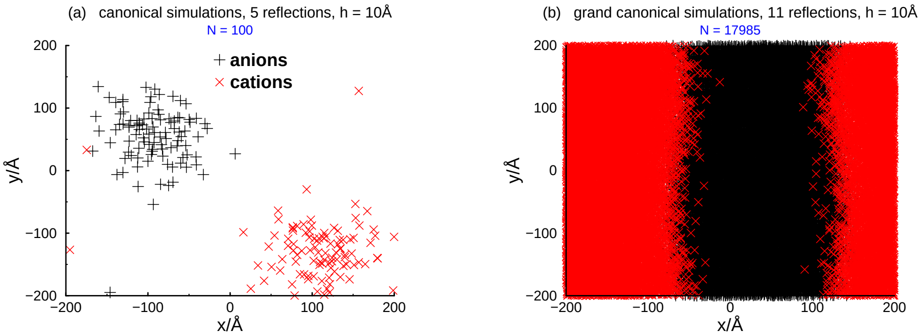

Figure 4: x, y-coordinate snapshots, from simulations using an odd, and not very large, value of n_{max}.
(a) Canonical system, with $n_{max} = 5$. The number of salt pairs is constrained to be 100, which is a typical average value fro grand canonical simulations with an even-valued n_{max}.
(b) Grand canonical simulations, with $n_{max} = 11$. This is *not* a system in complete grand canonical equilibrium. If continued, the grand canonical steps would lead to an even further increase of N. We stopped at this stage, because this suffices for illustrative puroposes, and the simulations naturally become very sluggish.

Converged results *can*be obtained also with an odd n_{max}, but then n_{max} needs to be very large. In graph(a) of Figure 5 we see how $n_{max} = 41$ is large enough to produce sensible results, even from grand canonical runs. However, as seen in graph (a), we get reasonable, though not fully converged, data also with $n_{max} = 2$, where the crucial aspect of course is that this is an even number.

So, how can these results be rationalized? We have constructed very simplified system to illustrate what we believe i the origin of these problems. Let us simply consider the bare self-interaction, $V_{self}(z, h)$. In Figure 6, we have plotted how the self-interaction varies with z, at $h = 10$ Å, depending upon the choice of n_{max}. We see how the limiting values of $V_{self}(z, h)$

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[1] If the simulation had continued, even more salt pairs would have been added

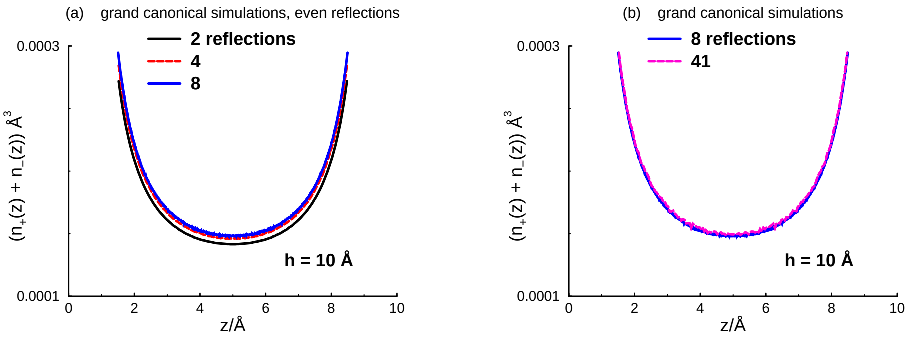

Figure 5: Density profile dependencies on n_{max}, using grand canonical simulations.
(a) Even-valued n_{max}.
(b) Comparing profiles for $n_{max} = 8$ and $n_{max} = 41$. In the latter case, n_{max} is large enough to provide reasonable density profiles, even from grand canonical simulations.

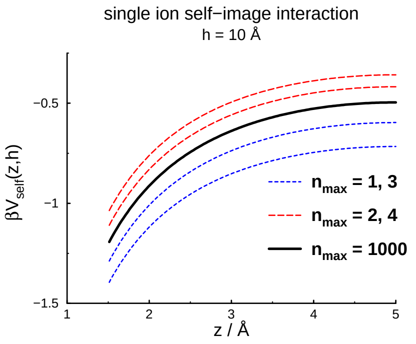

Figure 6: Self-interaction energies, for various choices of n_{max}, at $h = 10$ Å. Hard, non-discriminating ($A_+ = A_- = 0$) and conducting surfaces.

are approach, as n_{max} increases, which of course is expected. However, for odd values of n_{max} the strength self-interaction is always *overestimated*, whereas the opposite is true for even values of n_{max}. This problem is alleviated by a similar overestimation (for odd n_{max}) of repulsive interactions with images stemming from ions of opposite sign, but only partly so. Furthermore, the observed overestimations, for odd values of n_{max} combine to form a strong driving force for phase separation, where positive and negative ions condense into separate regions at the surfaces (Figure 4. This driving force is absent for even-numbered values of n_{max}.

1.2 Consistency checks of iPB predictions.

Here, we briefly report an important thermodynamic consistency check for the iPB calculations, namely that pressures evaluated at the mid plane, $\Delta P(mid)$, across a wall, $\Delta P(wall)$, and via discrete free energy differentiation, $-\partial \Delta g_s / \partial h$ all agree. An example is given in Figure 7, for ion-discriminating conducting surfaces, at a bulk salt concentration of about 19 mM. This is just

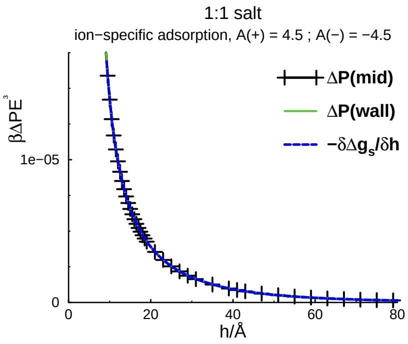

Figure 7: Checking agreememt between various ways to calculate the normal pressure. Ion-discriminating ($A_+ = -A_- = 4.5$) condicting surfaces, immersed in a 19 mM 1:1 salt solution. Only salt-induced pressures, P_s, are shown.

one illustrative example; similar agreements are of course found for all other cases.