Structure and cluster formation in size asymmetric soft electrolyte systems

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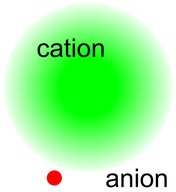
System definition



We consider an electrolyte system with no excluded volume interactions. The cations are Gaussian charge distributions with width α and total charge +*q*. The anions are points with charges -*q*. The key dimensionless parameters for this system are l_B/α, where l_B is the Bjerrum length, and the reduced ion density $\rho\alpha^3$.

charge density:

$$Q_+(\mathbf{r}-\mathbf{R}) = \frac{q}{(2\pi\alpha^2)^{1/2}} \exp\left(-\frac{|\mathbf{r}-\mathbf{R}|^2}{2\alpha^2}\right)$$

$$Q_-(\mathbf{r}-\mathbf{R}) = -q\delta^d(\mathbf{r}-\mathbf{R})$$

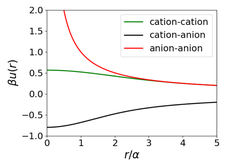
interaction potential:

$$\beta u_{++}(r) = \frac{l_B}{r}\mathrm{erf}\left(\frac{r}{2\alpha}\right)$$

$$\beta u_{--}(r) = \frac{l_B}{r}$$

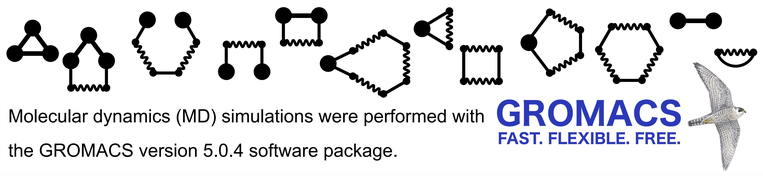
$$\beta u_{\pm}(r) = \frac{l_B}{r}\mathrm{erf}\left(\frac{r}{\sqrt{2}\alpha}\right)$$

An interesting feature of this model is that the repulsive energy of two overlapping cations is less than the attractive energy of an overlapping cation-anion pair. In fact, a single anion can "glue" together three cations.



Theory and simulation

This system is analyzed within the context of the variational perturbation theory, where it is considered a collection of particles interacting with a randomly fluctuating field with a mean and correlation that are are treated as variational parameters. Within the cumulant expansion, this theory recovers the Debye-Huckel (DH) or mean-spherical approximation. Within a diagrammatic analysis, it recovers the hypernetted chain (HNC) approximation when only chain and loop diagrams are included (see L Lue, *Soft Matter* **14**, 4721 (2018)).



Molecular dynamics (MD) simulations were performed with the GROMACS version 5.0.4 software package.

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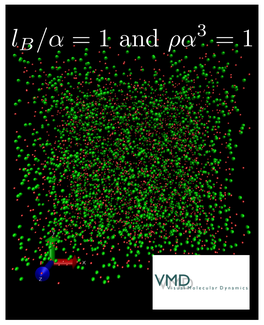
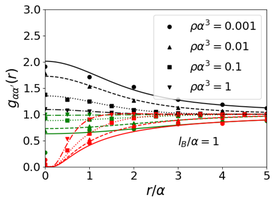
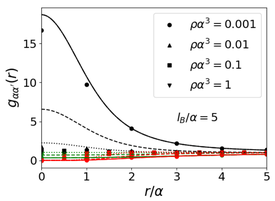
Structure



A typical configuration of a system is shown on the left. The green particles are cations, and the red particles are anions. The pair correlation functions for systems with l_B/α=1 and l_B/α=5 for a range of densities are shown in the two figures below. The symbols are from MD simulations, and the lines are predictions of the HNC approximation. Green denotes the cation-cation correlations, red denotes the anion-anion correlations, and black denotes cation-anion correlations.

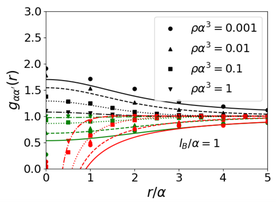
At low densities, the cations and anions are generally correlated; however, as the density increases, this correlation decreases. There is a strong correlation "hole" between anions, which shrinks as the density increases. There is also a correlation "hole" between cations, but this is fairly weak and essentially disappears with increasing density. The positions of the cations appear to be uncorrelated with the rest of the system. For these conditions, we might expect that the system behaves as a classical one-component plasma (OCP).



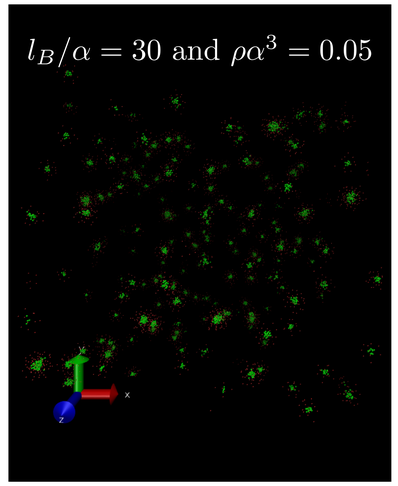


The HNC approximation provides a good description of the structure of the system at low to intermediate couplings. Interestingly, it captures the cation-anion pairing at low densities, but it does not describe the rapid decorrelation of their interactions with increasing density, which becomes more severe at higher electrostatic couplings. In the case where aggregates begin to form (at high electrostatic couplings or at high ion densities), this approximation breaks down.

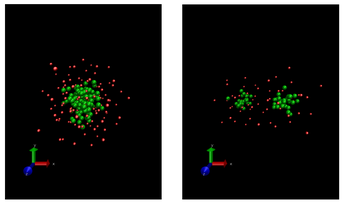
The MSA does reasonably well in describing the cation-cation and cation-anion correlations at low to moderate couplings, however, it fails to describe the anion-anion correlations at short distances. This can be corrected by introducing a correlation hole, as done for the OCP.

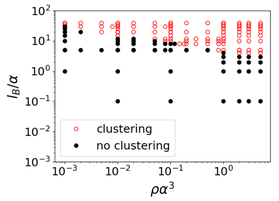


Cluster formation



The system begins to form clusters as the Bjerrum length or the density ibecomes sufficiently large. An example configuration of a clustering system is shown in the image to the left. A more detailed view of some clusters are shown below.





A "phase" diagram of state points where MD simulations were performed is given on the left. Conditions where clusters were observed are denoted by the open red symbols.

The clusters appear to be stable, with a relatively compact, fluid core of cations that is surrounded by a cloud of point anions. In general, these clusters are electrically neutral. As the density increases, the clusters will generally grow in aggregation number.

The pair correlation function for systems in the clustering regime are shown on the right at reduced ion densities of 0.01 (solid lines), 0.05 (dashed lines), and 0.1 (dotted lines). The size of the clusters appears to be relatively insensitive to the electrostatic coupling.