

Supporting Material for
Effects of valences of salt ions at various concentrations on
charged dendrimers

Wen-de Tian^a and Yu-qiang Ma^{a,b,*}

^a *National Laboratory of Solid State Microstructures and Department of Physics,
Nanjing University, Nanjing 210093, China*

^b *Laboratory of Soft Condensed Matter Physics and Interdisciplinary Research,
Soochow University, Suzhou 215006, China*

* *E-mail: myqiang@nju.edu.cn.*

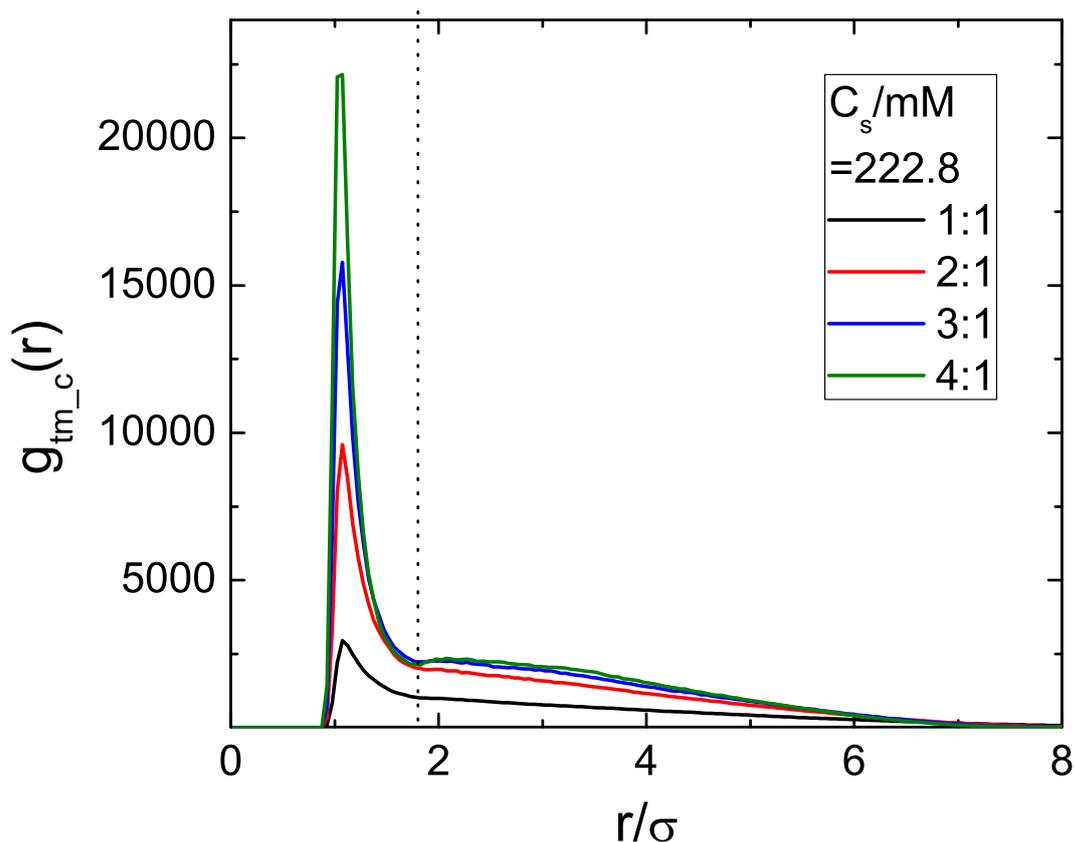


Fig. S 1: Radial distribution functions(RDFs) between terminal monomers of dendrimer and the added cations for different valences of salt ions as a function of the distance from each charged monomer of dendrimer at C_s^* . The first minima of RDFs is at $r \sim 1.75\sigma$, which is used as cutoff distance (denoted by dotted line) to calculate the mean effective charge of dendrimer.

We explore the effect of valence of cations on the attraction between the cations and dendrimer through calculating the radial distribution functions (RDFs) between salt cations and terminally charged monomers of dendrimer. Fig. S1 shows the RDFs between terminal monomers of dendrimer and cations with different valences at $C_s = 222.8\text{mM}(C_s^*)$. It is shown that the main peaks of all four curves are located at $r \sim 1.1\sigma$. However, the height of the peak falls from 22000 in the tetravalent solution to 16000 in the trivalent solution further to 9500 in the divalent solution and finally to 2500 in the monovalent solution. This indicates that the binding of dendrimer to oppositely charged cations depends strongly on the valence of salt ions. With increasing the cation valence, the electrostatic attraction between the

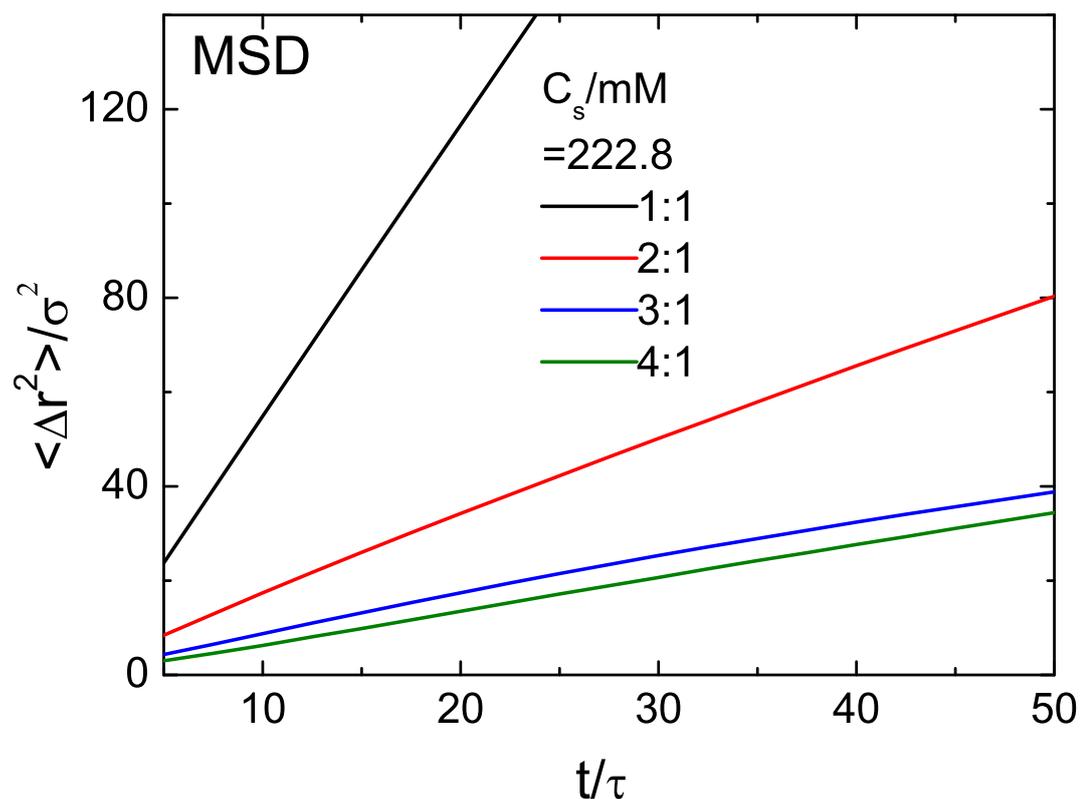


Fig. S 2: Mean-square displacement(MSD) of salt cations with various valences at C_s^* .

cations and the dendrimer becomes stronger, namely the binding of high-valence cations is more strong than that low-valence cations. Thus, the multivalent cations are absorbed and condensed on the dendrimer.

We also plot the mean-square displacement(MSD) of monovalent, divalent, trivalent, and tetravalent cations in Fig. S2. It is found that the slope of MSD vs time sharply decreases with the increase of salt ion valence due to the stronger electrostatic interaction. In other words, the strong multivalent cation-dendrimer correlation leads to the condensation of multivalent cations on the dendrimer, which also causes a reduced mobility of added cations. This implies that the strong condensation of high-valence cations lead to the fact that the osmotic pressure of high-valence cations within the domain of dendrimer is smaller than that of low-valence cations.

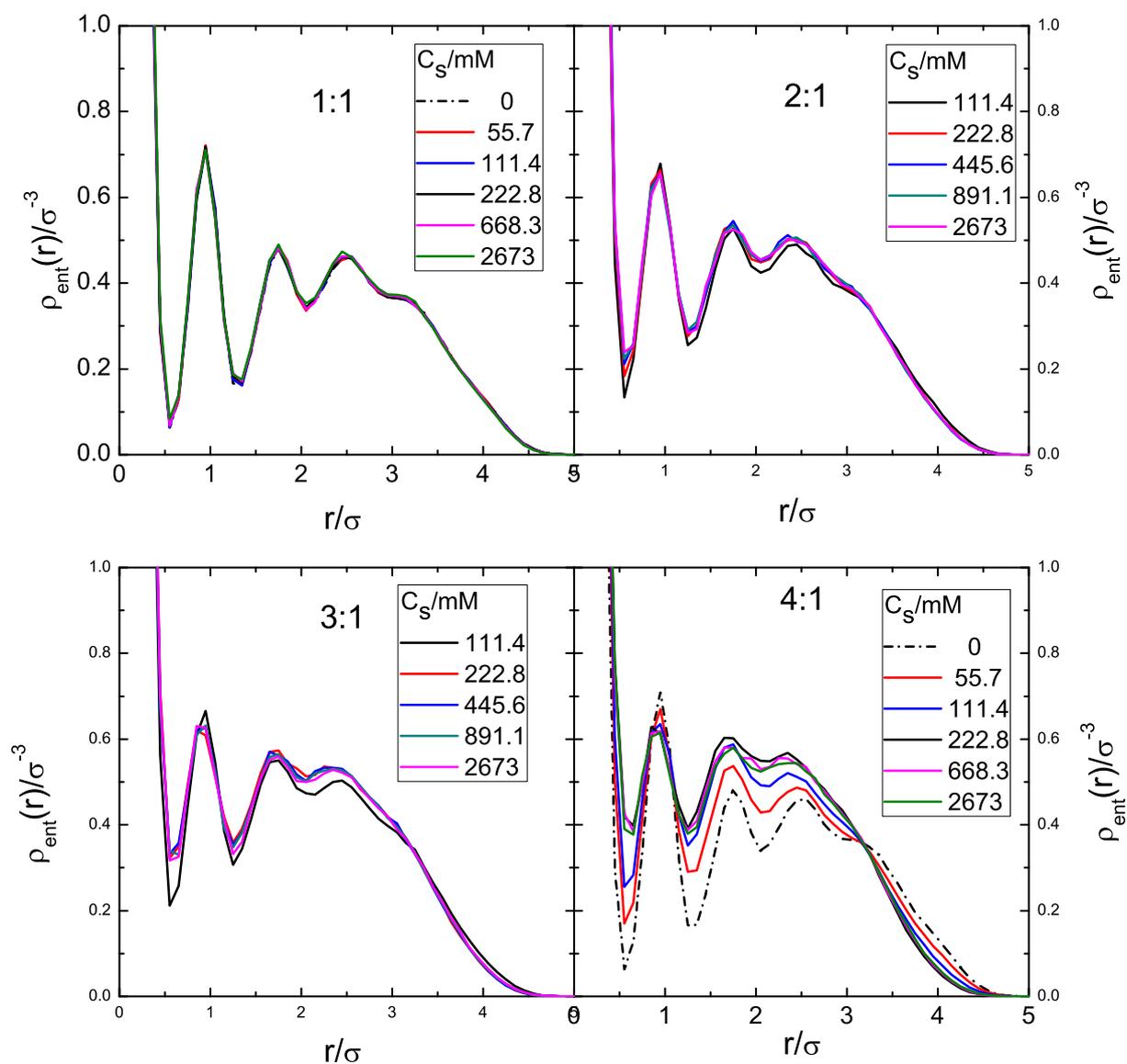


Fig. S 3: Radial density profiles of the whole dendrimer monomers, $\rho_{\text{ent}}(r)$, as a function of the distance r from the center-of-mass of the dendrimer at indicated salt concentration and valence.

Radial density profiles of the whole dendrimer monomers (see Fig. S3) provide a direct manifestation of the filled core conformation of dendrimer in the four salt solutions with various salt ion concentrations. It can also be found that the result of backfolding of terminal monomers is tenable at all salt concentrations and valences studied. This can be disclosed by comparing the radial density profiles of the terminal dendrimer monomers (shown in Fig.

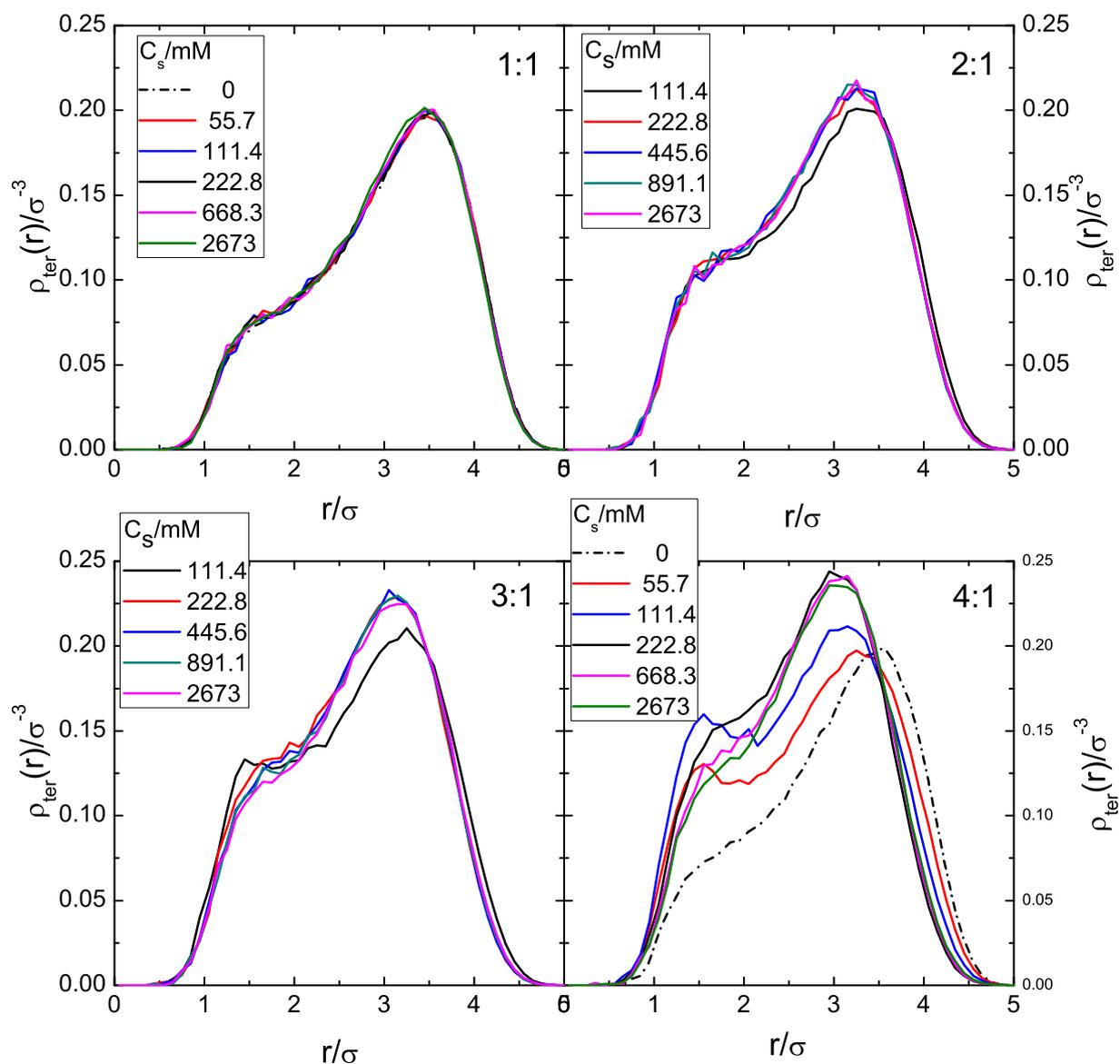


Fig. S 4: Radial density profiles of the terminal dendrimer monomers, $\rho_{\text{ter}}(r)$, as a function of the distance r from the center-of-mass of the dendrimer at indicated salt concentration and valence.

S4) with that of the whole dendrimer monomers.

As shown in Fig. S5, the profiles of negative charged particles for the four valences at both salt concentrations are similar to the $\rho_{\text{ter}}(r)$ within the domain of the dendrimer, implying that the local negative charge profile mainly results from the terminally charged monomers of dendrimer, the distribution of which is also impacted by concentrations and valences of

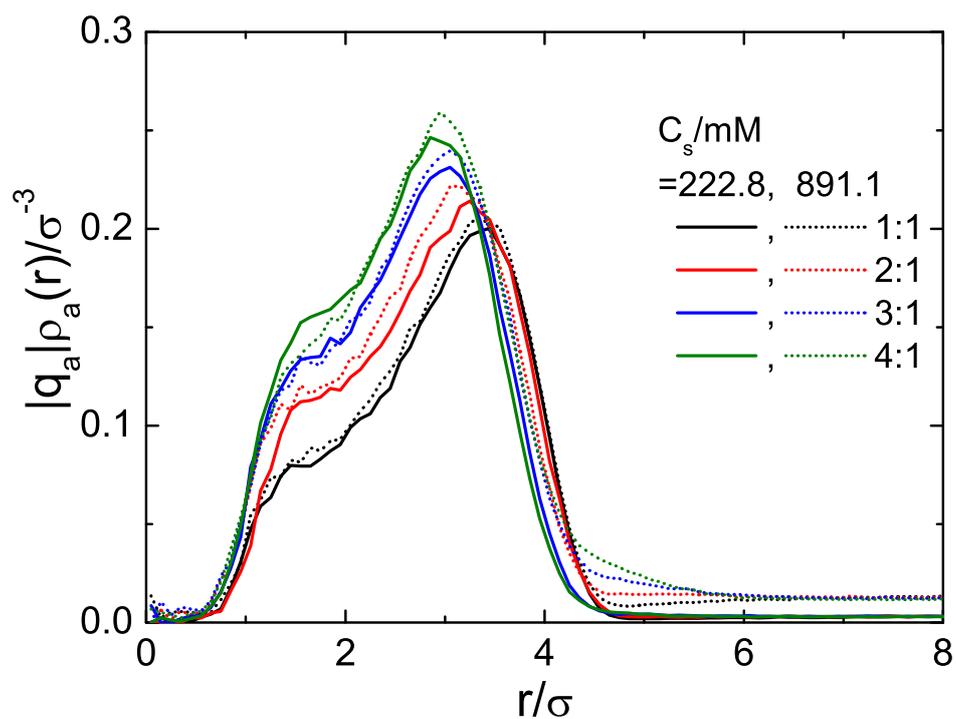


Fig. S 5: Charge density profiles of negative particles(including anions and negative charged terminal monomers) as a function of the distance r from the center-of-mass of the dendrimer with different salt concentrations and valences.

multivalent cations. At the high salt concentration, the heights of profiles display a slight increase at different r for different valences of salt solution. This means that the more anions are around the charged dendrimer, which can also be seen from the inset of Fig. 7, due to the entropy effect of extra anions and overcharging of dendrimer.