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Supplementary Information: On Short-ranged Pair-Potentials for Long-range Electrostatics

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Cutoff-effects

In this section we will evaluate effects due to primarily R_c^*, but also l and P. In Table. 1 we see that no potential recover the reference energy, albeit the standard deviation (*i.e.* a measure of the heat capacity) for q_0 is similar. The energy for $R_c^* \in \{4,5\}$ are maximized for some intermediate value of P, whereas for $R_c^* = 6$ at least q_0 gives the same energy (within the standard deviation) for all tested $P \geq 4$. By assuming that the maximized energy corresponds to the most accurate parameterization of P, which also can be expected by observing the mean squared dipole moments using q_0, we conclude that the closed interval for valid P values using $R_c^* \in \{4,5\}$ becomes half-open as the cut-off increases to $R_c^* = 6$. We also acknowledge that q_0 are far more accurate than q_2 with regard to the mean squared dipole moments. The mean squared dipole moments can trivially be converted to static dielectric constants by the procedure in Sec. S3.

In Fig. S1 we present the radial distribution functions for the tested parameters and note that q_2 is fairly independent of P and R_c^*. At first glance q_2 does seem to give accurate results though by inspecting the ratio to the reference we see a large difference, primarily compared to q_0 but also other pair-potentials[1]. For the q_0 results we see that a single higher-order cancellation substantially reduce the difference to the reference whereas even higher-order cancellation does not notably decrease it further. By moving on to the angular correlations in Fig. S2 we can confirm many of our previous observations, although we now notice that a cancellation of two higher-order moments seem to give most accurate results compared to the reference (note the negative values of $\langle \hat{\mu}(0) \cdot \hat{\mu}(r^*) \rangle$ for q_0 using $R_c^* \in \{5,6\}$ and $P = 4$). For larger cancellation it is clear to see that the results eventually (*i.e.* $P = \infty$) gives among the most erroneous angular-correlations.

We conclude this examination by recommending using $l = 0$ and $P = 4$ for the short cut-off $R_c^* = 4$, and for larger cut-offs such as $R_c^* \in \{5,6\}$ then $l = 0$ and $P = 5$. For $l = 2$ we do not give any recommendations since the potential itself seems erroneous.

Self-energy

Long-ranged interactions other than ion-ion, ion-dipole, dipole-dipole, and ion-quadrupole, does absolutely converge and thus no special summation technique is needed. Therefore the issue of the self-energy for such cases is not relevant and will not be discussed. For ion-dipole-interactions there is no need to specifically evaluate the self-energy since the ion and dipole self-energies are explicitly included in the ion-ion- or dipole-dipole-energies which we will later address. Similar arguments holds for the self-energy of the ion-quadrupole-interaction. The derivation of the self-energy follows the derivation of the Coulomb q-potential[2] and culminates into Eq. S1 for any valid k, l, or P.

$$E_{\text{Self}} = -\frac{k_c}{R_c^{k+l+1}} \sum_{j=1}^{N} \mathbf{v}_j^{\mathrm{T}} : \mathbf{v}_j \tag{S1}$$

Yet there are some discrepancies from the Coulomb q-potential since angular dependencies are present in higher order interactions, and hence we address this now. Following the Coulomb q-potential derivation[2], the order $k+l$ self-energy is shown in Eq. S2 (see Eq. B7 in reference).

$$E_{\text{Self}} = k_c \sum_{j=1}^{N} \frac{\mathbf{v}_j^{\mathrm{T}} \tilde{\mathbf{T}}_{k,l}(\Omega) \mathbf{v}_j}{R_c^{k+l+1}} \sum_{p=1}^{P} \frac{\left(-(-1)^{p-1} \frac{q^{(p-1)p/2}}{\prod_{i=1}^{p-1}(1-q^{p-i}) \prod_{i=1}^{P-p}(1-q^i)} \right)}{q^{-(p-1)(k+l+1)}} \tag{S2}$$

Here the normalized tensor $\tilde{\mathbf{T}}_{k,l}(\Omega)$ is related to $\nabla^k \mathbf{T}_l(\mathbf{r})$ as

$$\nabla^k \mathbf{T}_l(\mathbf{r}) = \frac{\tilde{\mathbf{T}}_{k,l}(\Omega)}{|\mathbf{r}|^{k+l+1}} \tag{S3}$$

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	$R_c^* = 4$				$R_c^* = 5$				$R_c^* = 6$			
	E^*_{Tot}		$\langle M^{*2} \rangle$		E^*_{Tot}		$\langle M^{*2} \rangle$		E^*_{Tot}		$\langle M^{*2} \rangle$	
P \ l	0	2	0	2	0	2	0	2	0	2	0	2
1	—	-6.226	—	3	—	-6.278	—	3	—	-6.304	—	3
2	—	-6.192	—	3	—	-6.257	—	3	—	-6.291	—	3
3	-6.573	-6.185	10	3	-6.550	-6.253	10	3	-6.541	-6.288	10	3
4	-6.509	-6.183	130	3	-6.465	-6.253	140	3	-6.438	-6.289	130	3
5	-6.509	-6.184	130	3	-6.465	-6.254	130	3	-6.438	-6.290	130	3
6	-6.512	-6.185	130	3	-6.465	-6.255	140	3	-6.438	-6.291	130	3
7	-6.514	-6.186	140	3	-6.465	-6.256	140	3	-6.438	-6.292	130	3
8	-6.516	—	140	—	-6.466	—	130	—	-6.438	—	130	3
9	-6.519	—	150	—	-6.466	—	140	—	-6.438	—	140	3
∞	-6.531	-6.188	160	3	-6.469	-6.258	140	3	-6.439	-6.294	140	3
Ref.	-6.383		130		-6.383		130		-6.383		130	

Table 1 Table for total particle energies, E^* (standard deviation $\sim 10^{-4}$), mean squared dipole moment of the simulation box $\langle M^{*2} \rangle$ (standard deviations $\sim 10^1$ for q_0 and $\sim 10^{-1}$ for q_2). We want to acknowledge that all values related to mean squared dipole moments are scaled by 10^{-3}.

where Ω index the angular dependence. By reshuffling the terms in Eq. S2 we then get Eq. S4.

$$E_{\text{Self}} = -k_c \sum_{j=1}^{N} \frac{\mathbf{v}_j^{\text{T}} \tilde{\mathbf{T}}_{k,l}(\Omega) \mathbf{v}_j}{R_c^{k+l+1}} \sum_{p=1}^{P} (-1)^{p-1} \frac{q^{(p-1)p/2} q^{(p-1)(k+l+1)}}{\prod_{i=1}^{p-1}(1-q^{p-i}) \prod_{i=1}^{P-p}(1-q^i)} \tag{S4}$$

We now let $q \to 0$ to get the self-energy, which comes from the following argument: Though we can not mirror the particle in the origin (since division by $q = 0$ is not possible) we choose to mirror an identical particle infinitesimally close ($q \to 0$) to the same. The right denominator in Eq. S4 is a polynomial with only non-negative powers. Thus if $q \to 0$ only the constant term 1 will be none-vanishing. In the same limit the numerator will be zero for every $p > 1$ and thus the entire far right sum will equal one. The final expression for the far right sum in the limit $q \to 0$ is thus 1 (as $p = 1$ gives the only non-vanishing term in the sum) as is shown in Eq. S5, and independent of P.

$$E_{\text{Self}} = -\frac{k_c}{R_c^{k+l+1}} \sum_{j=1}^{N} \mathbf{v}_j^{\text{T}} \tilde{\mathbf{T}}_{k,l}(\Omega) \mathbf{v}_j \tag{S5}$$

Finally we will approach the question of angular-dependence. For $k + l = 0$ there is no angular dependence and therefore $\tilde{\mathbf{T}}_{0,0}(\Omega) = 1$. The only other case we have to cover is $k + l = 2$, see earlier discussion in this section. Instead of using point image moments we will now use a uniform distribution in line with a previous work for dipoles[1] (see Appendix A in reference). The final result for the $k + l = \{0, 2\}$ self-energies is thus the previously presented Eq. S1.

Dielectric constant

By following an established scheme to retrieve an expression for the dielectric constant ε_r of the system[3] we get

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \left[1 - \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \tilde{T}(0) \right]^{-1} = \frac{1}{3\varepsilon_0} \frac{\langle M^2 \rangle}{3V k_B T} \tag{S6}$$

where ε_0 is the vacuum permittivity, $\langle M^2 \rangle$ is the fluctuation of the total dipole moment squared in the system, V the volume of the simulating cell, k_B the Boltzmann constant, and T the temperature. By then using Eq. 7 in the main text we, similar to an earlier work[2], get that $\tilde{T}(0) = 1$ for $l = 0$ whereas $\tilde{T}(0) = 0$ for $l = 2$ (see appendix in reference). Note that the dielectric constant obtained by using $\tilde{T}(0) = 1$ is the same as for the Ewald summation method with conducting boundary conditions, and $\tilde{T}(0) = 0$ gives an expression for the dielectric constant which represent high dielectric medium poorly[4].

Notes and references

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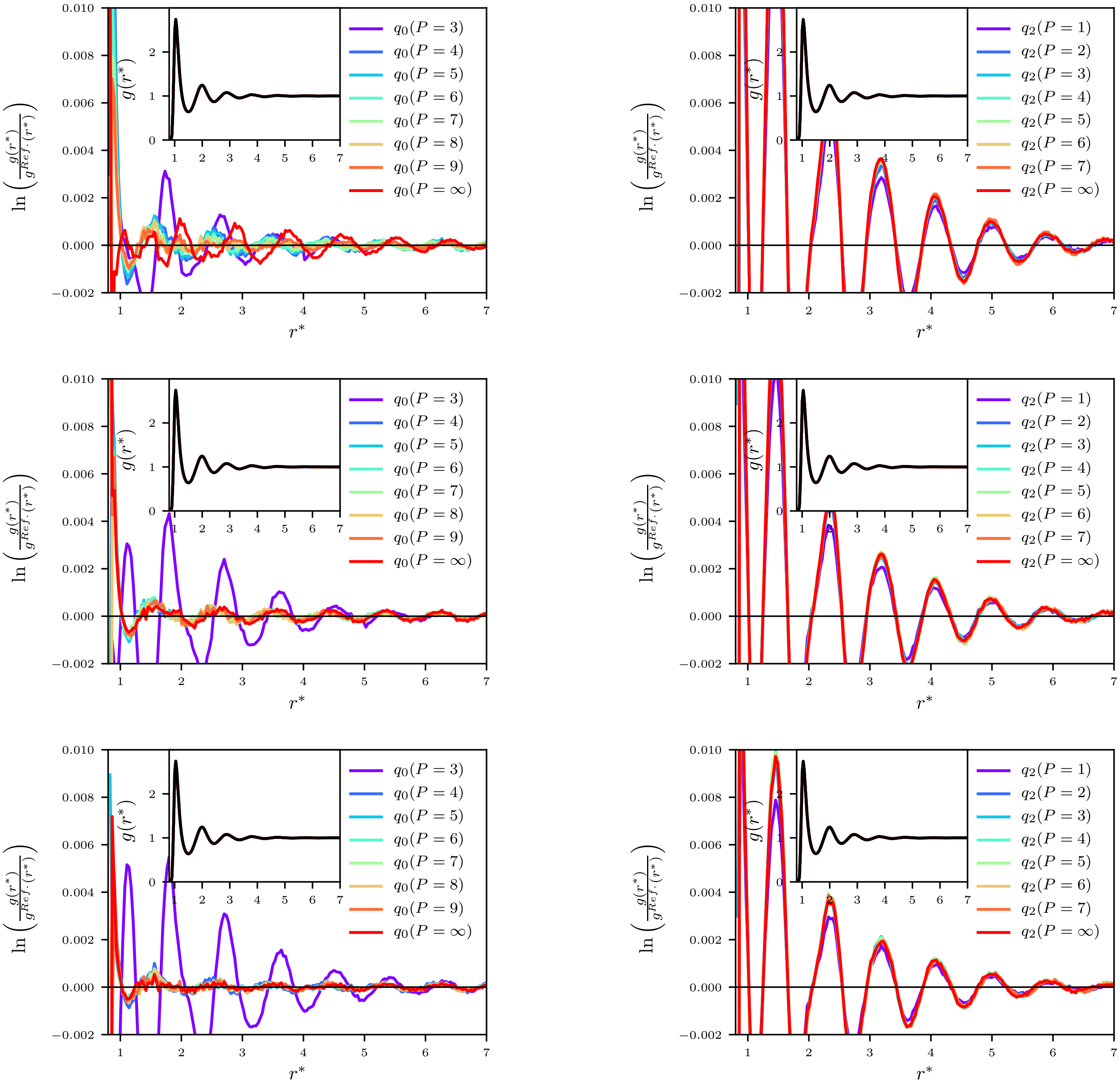

Fig. S1 The logarithm of the ratio between pair-potential and reference radial distribution functions using q_0 (left)/q_2 (right) and R_c^* equal to 4 (top) / 5 (middle) / 6 (bottom). The insets show the radial distribution functions. Black lines are Ewald results.

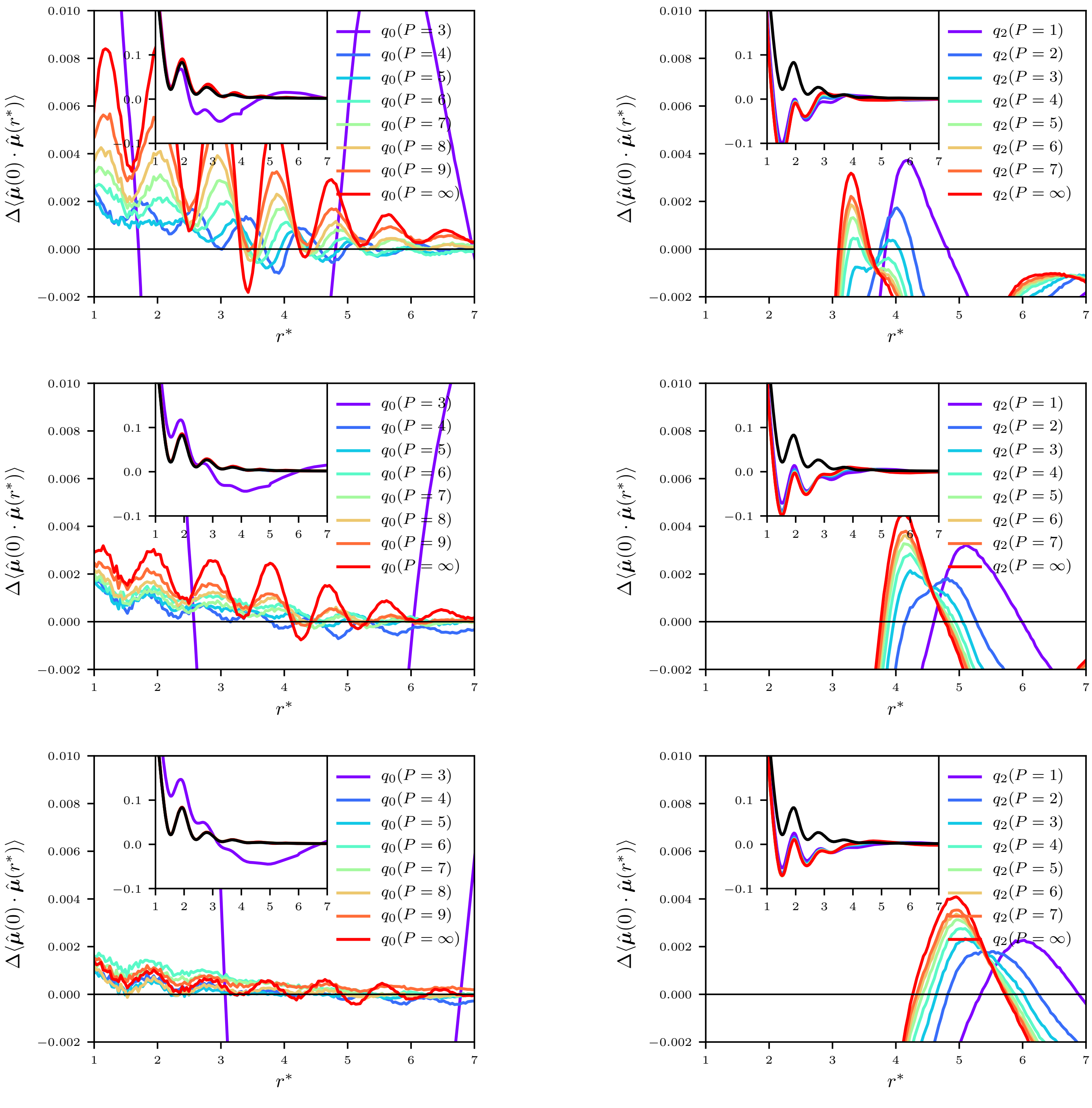

Fig. S2 Dipole-dipole correlation differences to the reference result using q_0 (left)/q_2 (right) and R_c^* equal to 4 (top) / 5 (middle) / 6 (bottom). The insets show the dipole-dipole correlation $\langle\hat{\mu}(0)\cdot\hat{\mu}(r^*)\rangle$. Black lines are Ewald results.