Supporting Information

Unifying Weak and Strong Charge Correlations within the Random Phase Approximation: Polyampholytes of Various Sequences

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I Description of the Polyampholyte Collapse: Comparison between the Generalized RPA and the Standard RPA

To perform a systematic comparison of the generalized RPA (GRPA) to the standard RPA, we consider the collapse of PAs of different sequences. Swelling ratios of PAs α and polymer volume fractions within the globules η are calculated using different functional forms of the correlation free energy and are shown in Figure S1. Figures S1a, b, and c correspond to alternating, ideally random, and diblock PAs. Solid curves are calculated using the GRPA correlation free energies given by eqs. 21-24, as described in Section IV of the manuscript; they coincide with those shown in Figure 3 in the manuscript's main text. Dashed curves for alternating, random, and diblock PAs are calculated using the simplest forms for the RPA correlation free energies given by eqs. 29, 27, and 30, respectively.

Random Polyampholytes. For random PAs (Figure S1b), the standard RPA underestimates globule dimensions and overestimates its density in the regime of strong charge correlations. This result is consistent with the theoretical estimates. Combining the correlation free energy found within the standard RPA and given by eq. 27, $F_{rand} \simeq -(uf\phi)^{3/2}$, with the free energy of three-body repulsions, $F_{vol} \simeq \phi^3$, one obtains eq. 32 predicting the density of the globule of random PA. At the scaling level of accuracy, this result reads

$$\phi_{rand}^{RPA} \simeq uf \tag{S1}$$

Within the GRPA, the strong correlation asymptotic for the Coulomb free energy is given by eq. 34 and reads $F_{rand}^{GRPA} \simeq -u\,(f\phi)^{4/3}$. This results in the following scaling law for the PA globule density

$$\phi_{rand}^{GRPA} \simeq u^{3/5} f^{4/5} \tag{S2}$$

We note that this result is valid for any PA sequence. Comparing eqs. S1 and S2 one can conclude that the standard RPA overestimates the density of the globule because, at

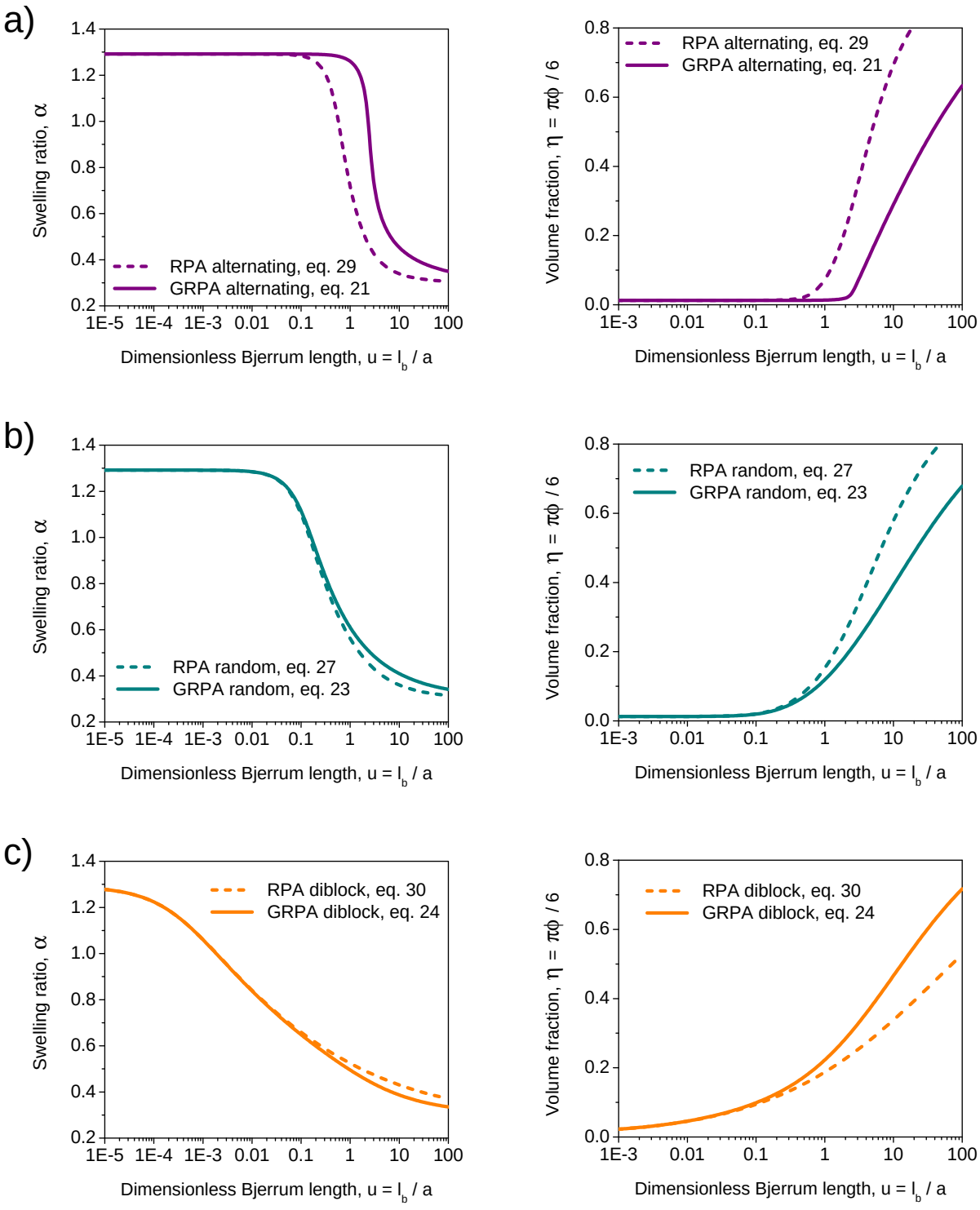

Figure S1: Comparison between the result of the standard random phase approximation (RPA, dashed curves) and generalized random phase approximation (GRPA, solid curves) for the swelling ratios α (left column) and volume fractions η within the PA globules (right column). Three rows correspond to the different sequences: a) alternating; b) ideally random; c) diblock PAs. Each PA has length $N = 10^3$, and all monomers are ionic, $f = 1$.

increasing u, ϕ_{rand}^{RPA} increases faster than ϕ_{rand}^{GRPA}.

Diblock Polyampholytes. For diblock PAs, standard RPA disregarding both q-integration cutoff and charge discreteness yields eq. 30, $R_{db}^{RPA} \simeq (uf^2\phi)^{3/4}$. Figure S1c shows that it underestimates globule density and overestimates chain dimensions as compared to the correct GRPA. This difference between the methods is in agreement with the analytical results. Standard RPA leads to eq. 33 that can be written as

$$\phi_{db}^{RPA} \simeq u^{1/3} f^{2/3} \tag{S3}$$

while the prediction of the GRPA reads

$$\phi_{db}^{GRPA} \simeq u^{3/5} f^{4/5} \tag{S4}$$

The latter increases with u faster, which is consistent with the higher position of the solid GRPA curve as compared to the dashed RPA curve in Figure S1c (right column).

We should also note that using the standard RPA neglecting only the finite number of fluctuation wave-modes but taking into consideration charge discreteness results in eq. 28. At high densities and hence $s \gg 1$, eq. 28 reduces to the Debye-Hückel result for disjointed charges, which is given eq. 27. The latter coincides with the standard RPA result for ideally random PAs. Therefore, in the form of eq. 28, the RPA for diblock PAs would overestimate globule density and underestimate its size in the region of strong charge correlations.

Alternating Polyampholytes. For alternating PAs, the asymptotic low-density result is given by eq. 29, $F_{alt}^{RPA} \simeq -u^2 f^{3/2} \phi^2$. Using this form of the RPA free energy strongly overestimates the globule density and underestimates globule dimensions, as seen in Figure S1a. This difference between the RPA and GRPA is consistent with the analytical estimates. Within the standard RPA, one arrives at eq. 31, which can be written as

$$\phi_{alt}^{RPA} \simeq u^2 f^{3/2} \tag{S5}$$

The prediction of the GRPA suggests higher values of the globule density in the regime of strong correlations:

$$\phi_{alt}^{GRPA} \simeq u^{3/5} f^{4/5} \tag{S6}$$

In contrast to the case of diblock PA, taking into consideration point-like type of charges for alternating PA (which leads to eq. 26) would not change the above comparison. Eq. 26 reproduces Debye-Hückel correlation free energy, eq. 27, when globule density is sufficiently high, $s \gg 1$. Therefore, using standard RPA in the form of eq. 26 for high u values would also overestimate PA density and underestimate chain swelling ratio as compared to the most rigorous method, GRPA. However, the deviation from the GRPA results in this case is noticeably lower.

We note that the deviation between the GRPA and the standard RPA is the highest for alternating PAs. At low u values, Coulomb attractions between the opposite charges are the weakest for alternating charge statistics. For this reason, when the GRPA improvements are introduced, curves shift the most for alternating PAs.

Finally, the low amplitude of the PA collapse is another reason for deviations between the curves at relatively high α values. The ratio between the α values in the ideal-coil and globular states is very moderate, $\alpha_{coil}/\alpha_{glob} \approx 1.3/0.35 \approx 3$, which is close to the theoretically expected ratio $\alpha_{coil}/\alpha_{glob} \simeq N^{1/2}/N^{1/3} \simeq N^{1/6} = 1000^{1/6} \approx 3.2$. Interestingly, the limiting scaling law for alternating PAs still remains reasonable because the RPA an GRPA curves for α are almost parallel in the regime of weak globule, as seen in Figure S1a.

II Discussion on the Integration Cutoff due to Hard-Core Repulsions, $\widetilde{q_0} = 1/a$

The integration cutoff

$$q_0 = (9\pi^2 f\phi)^{1/3} a^{-1} \tag{S7}$$

which was used in the manuscript, is based on general physical considerations. It is universal and applicable to any condensed phase of PEs or PAs, with monomers interacting via arbitrary non-Coulomb repulsive potentials.

However, within the liquid state theory approaches, monomers are often considered as hard spheres, and real smooth repulsive potentials are often substituted by hard core repulsions. The earlier work by Ermoshkin and Olvera de la Cruz[1] has used cutoff given by

$$\widetilde{q_0} = 1/a \tag{S8}$$

to account for these hard-core repulsions. It is interesting to consider how the results of our RPA calculations change if the employed integration cutoff due to a finite number of the fluctuation wavemodes, $q_0 = (9\pi^2 f\phi)^{1/3} a^{-1}$, is substituted by the hard-core repulsions cutoff, $\widetilde{q_0} = 1/a$. In this case, the RPA correlation energies for alternating, ideally random, and diblock PAs (eqs. 21, 23, and 24 of the main text, respectively) remain unchanged

$$F_{RPA}^{alt} = \frac{1}{12\pi^2 \left(r_D/a\right)^3} \left[\widetilde{t_0}^3 \ln\left(1 + \frac{1}{\widetilde{t_0}^2 + s^{-2}}\right) - \widetilde{t_0} + s^{-1}\left(3 + 2s^{-2}\right) \arctan\left(s\widetilde{t_0}\right) - 2\left(1 + s^{-2}\right)^{3/2} \arctan\left(\frac{\widetilde{t_0}}{\sqrt{1 + s^{-2}}}\right) \right] \tag{S9}$$

$$F_{RPA}^{rand} = \frac{1}{12\pi^2 \left(r_D/a\right)^3} \left[\widetilde{t_0}^3 \ln\left(1 + \frac{1}{\widetilde{t_0}^2}\right) - \widetilde{t_0} - 2\arctan\left(\widetilde{t_0}\right) \right] \tag{S10}$$

$$F_{RPA}^{db}=\frac{1}{12\pi^2\left(r_D/a\right)^3}\left[\widetilde{t_0}^3\ln\left(1+\frac{1}{\widetilde{t_0}^2}+\frac{1}{s^2\widetilde{t_0}^4}\right)-\widetilde{t_0}+\frac{3}{s^2\widetilde{t_0}}\right.$$
$$\left.-\frac{\left(1-\varkappa\right)^{3/2}}{\sqrt{2}}\arctan\left(\frac{\sqrt{2}\,\widetilde{t_0}}{\sqrt{1-\varkappa}}\right)-\frac{\left(1+\varkappa\right)^{3/2}}{\sqrt{2}}\arctan\left(\frac{\sqrt{2}\,\widetilde{t_0}}{\sqrt{1+\varkappa}}\right)\right] \quad \text{(S11)}$$

Here the parameter $\widetilde{t_0}$ is defined as

$$\widetilde{t_0}=r_D\widetilde{q_0}=\left(4\pi u f\phi\right)^{-1/2} \quad \text{(S12)}$$

We note that $\widetilde{t_0}$ differs from t_0, which is given by eq. 22 of the main text. *At that, the crossover between weak and strong charge correlations is still given by* $t_0\simeq 1$*, but not by* $\widetilde{t_0}\simeq 1$. One can only argue that high and low values of $\widetilde{t_0}$ correspond to low and high densities of the system, respectively.

In the limit of low densities, $\widetilde{t_0}\gg 1$, the RPA with the hard-core cutoff reproduces the results of the standard RPA given by eqs. 29, 27, and 30 of the manuscript. At high densities, $\widetilde{t_0}\ll 1$, the RPA correlation correction is sequence-independent:

$$F_{RPA}^{alt}=F_{RPA}^{rand}=F_{RPA}^{db}=\frac{-3\widetilde{t_0}}{12\pi^2\left(r_D/a\right)^3}=-\frac{1}{\pi}uf\phi \quad \text{(S13)}$$

This result provides the linear in ϕ scaling, which coincides with the predictions of the MSA and ion pairing models. Indeed, according to eq. 36-37 of the manuscript, the MSA prediction for high densities (strong correlations) reads $F_{MSA}(x\to\infty)=-l_b\phi/\sigma=-u\phi$, where we assumed $\sigma=a$ and $f=1$. Thus, the predictions of the MSA and the RPA with the hard-core repulsions cutoff, $\widetilde{q_0}=1/a$, differ by the factor of π. (Generally speaking, the numerical prefactor in the cutoff value can be adjusted to provide the exact coincidence with the MSA, $\widetilde{q}=1/a\to\widetilde{q_0}=\pi/a$.) In this case, the resulting scaling for the PA globule density would read $\phi_{SC}^{MSA}\simeq u^{1/2}f^{1/2}$. This estimate is close to the strong correlations scaling $\phi_{SC}^{GRPA}\simeq u^{3/4}f^{4/5}$, which is obtained within the GRPA with q_0 cutoff or within the Wigner liquid model, than the predictions of the standard RPA given by eqs. S1, S3, and S5. We also

note that $\phi_{SC}^{MSA} \sim u^{1/2} < \phi_{SC}^{GRPA} \sim u^{3/5}$ at high Bjerrum length u because the monomers are less compressible for the MSA-like cutoff, $\widetilde{q_0}$, than for the GRPA cutoff, q_0. *The result given by eq. S13 differs from the Wigner liquid scaling and is not supported by our simulations.*

It is also interesting to consider how the rigorous applicability of the generalized RPA, that is, the convergence of the perturbation series of the corrections to the free energy, is affected by introducing the hard-core cutoff, $\widetilde{q_0}$. To this end, one should perform the analysis of section III.5 and calculate the next order correction to the free energy, $F^{(3)}$, see eqs. 40-41 of the main text. For $\widetilde{t_0} \gg 1$ and ideally random PAs

$$F_{rand}^{(3)} \simeq a^6 \int_0^{\widetilde{q_0}} \left[\Gamma^{(3)}(q_1,q_2,q_3)\right]^2 G(q_1)G(q_2)G(q_3)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)d^3q_1 d^3q_2 d^3q_3 \simeq \frac{a^6}{f\phi r_D^6} \quad \text{(S14)}$$

and the ratio between the second and the third order corrections, which is of order the perturbation theory parameter (PTP),[2] reads

$$PTP = \frac{F_{rand}^{(3)}}{F_{RPA}^{rand}} \simeq \frac{a^6/f\phi r_D^6}{a^3/r_D^3} \simeq \frac{l_b}{r_D} \simeq \left(\frac{d}{r_D}\right)^3 \simeq \left(\frac{l_b}{d}\right)^{3/2} \ll 1 \quad \text{(S15)}$$

Therefore, the requirement of the RPA consistency reads $d \ll r_D$ and coincides with the requirement of weak correlations. (The same RPA's applicability condition was obtained in the manuscript for the cutoff due to the finite number of the density fluctuations, q_0.) However, inequality S15 being the weak correlations requirement is now not ensured by $\widetilde{t_0} \gg 1$ (while it would be ensured by $t_0 \gg 1$ for q_0 cutoff).

Indeed, $\widetilde{t_0} \gg 1$ is equivalent to $r_D \gg a$, which is slightly weaker condition that the needed $r_D \gg d$. In other words, one can imagine the situation when charge correlations are already strong but the distance between the charges is still higher than the monomer size, $a < d < r_D$. To illustrate that, one can consider the crossover between weak and strong correlations, $uf^{1/2} \simeq 1$, when the Debye length and the distance between the neighboring charges are comparable and both noticeably exceed the monomer size, $r_D \simeq d \simeq af^{-1/2} \gg a$. A moderate increase in u would result in $r_D > d$, as expected in the strong correlations

regime, but $d > a$ would be still fulfilled if correlations are not very strong and system is not very dense. For instance, consider ideally random PAs and the value $u^* \simeq f^{-3/4}$ simultaneously providing strong correlations ($u^* f^{1/2} \simeq f^{-1/4} > 1$) and $\widetilde{t_0} \gg 1$ (to be checked a posteriori). At this value of the Bjerrum length, $\phi_{rand}^{RPA} \simeq uf$ because $\widetilde{t_0} \gg 1$ and the $\widetilde{q_0}$-integration cutoff is not essential, which leads to $r_D \simeq af^{-1/4}$ and $d \simeq af^{-5/12}$. Therefore, we have $d/r_D \simeq f^{-1/6} > 1$ and correlations are already strong, while the integration cutoff in fact remains negligible, $t_0 = r_D a^{-1} \simeq f^{-1/4} > 1$ and $r_D > a$. To summarize, at $u^* \simeq f^{-3/4}$, the inequality $a < d \simeq af^{-5/12} < r_D \simeq af^{-1/4}$ is fulfilled, and the third order correction exceeds the second order RPA term, which makes the RPA generalization with $\widetilde{q_0} = a^{-1}$ not rigorously consistent. *For this reason, we prefer using the cutoff due to a finite number of fluctuation wave modes, $q_0 = d^{-1}$, which provides the convergence of the perturbation theory and hence rigorous applicability of the GRPA.*

However, it should be noted that for fully charged PEs, $f = 1$, the q_0 and $\widetilde{q_0}$ cutoffs are virtually equivalent, and the inequality providing the perturbation theory convergence for weak charge correlations, $d < r_D$, is never strongly violated. In other words, the hard-core cutoff used in work 1 remains a very reasonable alternative to that used in our work. This conclusion is consistent with the results by Ermoshkin and Olvera de la Cruz, who considered fully charged PE and reported no substantial change in the binodals of the PE solution upon $\widetilde{q_0} \to q_0$ substitution.[1]

The above analysis demonstrates that, in the context of the RPA generalization to strong charge correlations for condensed PE and PA systems with arbitrary f values, the cutoff $q_0 \simeq d^{-1}$, which is introduced in the main text of the manuscript and takes into account the finite number of the fluctuation wavemodes, is not only more general and universal (i.e., independent of the pairwise potential) but also more rigorous and consistent as compared to the hard-core cutoff, $\widetilde{q_0} = a^{-1}$. We also note that the cutoff $\widetilde{q_0} = a^{-1}$ has been introduced in ref. 1 in order to account for the short-range hard-sphere repulsions rather than to consider strong charge correlations. To consider the latter, the authors have used the model of ion

pairing between the charges in polymer chains and counterions.

References

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(2) Borue, V. Yu.; Erukhimovich, I. Ya. A statistical theory of weakly charged polyelectrolytes: Fluctuations, equation of state and microphase separation. *Macromolecules* **1988**, 21, 3240–3249.