

Bending stiff charged polymers: The electrostatic persistence length

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Abstract – Many charged polymers, including nucleic acids, are locally stiff. Their bending rigidity—quantified by the persistence length—depends crucially on Coulombic features, such as the ionic strength of the solution which offers a convenient experimental route for tuning the rigidity. While the classic Odijk-Skolnick-Fixman treatment fails for realistic parameter values, we derive a simple analytical formula for the electrostatic persistence length. It is shown to be in remarkable agreement with numerically obtained Poisson-Boltzmann theory results, thereby fully accounting for non-linearities, among which counter-ion condensation effects. Specified to double-stranded DNA, our work reveals that the widely used bare persistence length of 500 Å is overestimated by some 20%.

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Since the elucidation of DNA structure in the 1950s, it became increasingly clear that the mechanical behavior of a wealth of charged polymers (polyelectrolytes) is essential for their interactions with proteins, the operation of molecular motors and more generally, their biological function including gene regulation and cytokinesis [1,2]. Fostered in particular by scattering methods and the more recent advent of single-molecule techniques, the experimental study of polyelectrolyte rigidity has consequently been an active field of research in the last 30 years, see, *e.g.*, [3–24] and references therein. It is however arguably one of the most controversial domains of polymer physics [25–33].

Although their mechanical properties may depend on local structure, polyelectrolytes can satisfactorily be envisioned as coarse-grained “worm-like” chains in a variety of situations, with a continuous rather than discrete charge distribution [5,8,11,12,17,34]. Their flexibility is then quantified by a single quantity, the persistence length L_{tot} , which measures the distance over which the chain local orientation decorrelates [35]. For double-stranded DNA (ds-DNA) in physiological conditions, $L_{\text{tot}} \simeq 500$ Å, which significantly exceeds the typical thickness of the corresponding worm, having radius $a \simeq 10$ Å [5,12,36]. Unlike single-stranded DNA where both lengths are comparable, ds-DNA is thus a *locally* rigid object. A key question

then lies in the persistence length dependence on external control parameters, such as the electrolyte content of the solution (the so-called ionic strength).

A major breakthrough is due to Odijk [37] and independently to Skolnick and Fixman [38], who realized that for sufficiently rigid polymers, the persistence length L_{tot} accounts for the bending rigidity of the polyelectrolyte through the sum of the intrinsic persistence length L_0 of the uncharged polymer, and the electrostatic persistence length L_{el} : $L_{\text{tot}} = L_0 + L_{\text{el}}$. The presence of charges on the backbone stiffens the chain ($L_{\text{tot}} > L_0$), at least within the mean-field picture adopted by Odijk, Skolnick and Fixman (OSF). This translates into the celebrated relation $L_{\text{el}} = L_{\text{OSF}} = \lambda^2 \ell_B \kappa^{-2} / 4$ where λ is the line charge of the chain in units of the electron charge e , κ^{-1} is the Debye length, and ℓ_B is the Bjerrum length¹. It is important to stress that in addition to mean-field, the OSF result was derived under two stringent conditions: a) low charge limit (low λ or more precisely $\lambda \ll 1/\ell_B$, where a linearized approach, the so-called Debye-Hückel approximation, holds) and b) line charge limit (viewing locally the polymer as a cylinder of radius a , this means

¹ ℓ_B corresponds to the distance where the electrostatic repulsion between two electrons equals the thermal energy kT , which yields 7.1 Å in water at room temperature.

enforcing the limit $a \rightarrow 0$ or more precisely, $a \ll 1/\kappa$. It is a sobering thought that conditions a) and b) are often both violated in practice, and almost never met simultaneously: κa is typically of order 1 for DNA in physiological buffer while $\lambda \ell_B$ exceeds unity for single-stranded and *a fortiori* double-stranded DNA, as well as for a large gamut of synthetic polymers. It is generally believed that the non-small $\lambda \ell_B$ can be remedied accounting for counter-ion condensation *à la* Manning-Oosawa [39,40]², with the *ad hoc* replacement $\lambda \rightarrow 1/(q\ell_B)$ [30,41,42] for sufficiently charged chains; OSF formula, with this prescription, is the mainstay and reference law for an impressively large body of literature. This approach is to a large extent inadequate, and it is thus surprising that the limitations a) and b) above have received little attention since early works in the 1980s [42,43]³: L_{OSF} may underestimate the mean-field electrostatic persistence length by an order of magnitude or more. The consequences of the interpretation of experimental measures, and on a more theoretical level, on the scaling behavior of L_{el} , are far reaching. Deriving a “dressed” or “renormalized” OSF formula, *i.e.*, an analytically simple to use and accurate expression for the electrostatic persistence length of rigid polyelectrolytes, and discussing its physical consequences, is therefore particularly desirable. It is the main goal of the present study.

We shall work at the mean-field level of Poisson-Boltzmann (PB) theory, that is trustworthy for monovalent electrolytes ($q = 1$), since ionic correlations effects are then small [44–46]. In doing so, we should recover the OSF results for small charges and thin chains, but more importantly, we will obtain a persistence length of relevance for the situations encountered in practice. At variance with a number of works that operate at Debye-Hückel (DH) level [4,22,27–29,47–51], our approach is thus non-linear. This is an essential prerequisite for describing most natural or synthetic polyelectrolytes. Indeed, introducing the dimensionless charge $\xi = q\lambda\ell_B$, a linearized treatment is, as a rule of thumb, justified for $\xi \ll 1$ while $\xi > 1$ for a wealth of synthetic and natural chains (RNA, DNA...). Aiming at analytical progress, we coarse-grain unnecessary atomistic details, to envision our polymer as a uniformly charged cylinder, a worm-like chain furthermore assumed to be weakly bent (with a large radius of curvature R). From the expression of F , the bending free energy per unit length for this single macromolecule in an electrolyte sea, the persistence length follows from $F = L_{\text{el}}/(2R^2)$. The calculation is performed within the PB framework where the dimensionless electric potential Ψ obeys Poisson’s equation $\nabla^2\Psi = \kappa^2 \sinh\Psi$ (we consider a 1:1 electrolyte, with $q = 1$ -valent co- and counter-ions).

²The idea is that locally cylindrical polyions create a logarithmic electrostatic potential that may be strong enough to bind oppositely charged microions (q -valent counterions), so that the rod takes the effective line charge $e/(q\ell_B)$ whenever $\lambda > 1/(q\ell_B)$.

³These studies involve numerical resolutions and remained rather difficult to transpose to practical situations.

To this end, we follow ref. [42] and expand Ψ in inverse powers of the curvature:

$$\Psi = \Psi^{(0)} + \frac{1}{\kappa R}\Psi^{(1)} + \frac{1}{(\kappa R)^2}\Psi^{(2)}. \quad (1)$$

The zeroth-order potential is the solution for the straight cylinder problem, an already non-trivial analytical problem [52–56]:

$$\frac{1}{\tilde{r}}\partial_{\tilde{r}}\left(\tilde{r}\partial_{\tilde{r}}\Psi^{(0)}\right) = \sinh\Psi^{(0)}, \quad (2)$$

where $\tilde{r} = \kappa r$. The next order obeys

$$\frac{1}{\tilde{r}}\partial_{\tilde{r}}\left(\tilde{r}\partial_{\tilde{r}}\Psi^{(1)}\right) - \frac{1}{\tilde{r}^2}\Psi^{(1)} = \Psi^{(1)}\cosh\Psi^{(0)} \quad (3)$$

and the equation for $\Psi^{(2)}$ requires the knowledge of $\Psi^{(0)}$ and $\Psi^{(1)}$:

$$\frac{1}{\tilde{r}}\partial_{\tilde{r}}\left(\tilde{r}\partial_{\tilde{r}}\Psi^{(2)}\right) + \frac{1}{2}\left(\partial_{\tilde{r}}\Psi^{(1)} + \frac{\Psi^{(1)}}{\tilde{r}} - \tilde{r}\partial_{\tilde{r}}\Psi^{(0)}\right) = \Psi^{(2)}\cosh\Psi^{(0)} + \frac{(\Psi^{(1)})^2}{4}\sinh\Psi^{(0)}. \quad (4)$$

While all Ψ ’s vanish for $r \rightarrow \infty$, the bare poly-ion charge sets the boundary conditions at contact ($\tilde{r} = \tilde{a} \equiv \kappa a$) where the derivatives of $\Psi^{(0)}$, $\Psi^{(1)}$ and $\Psi^{(2)}$ take the respective values $-2\xi/\tilde{a}$, 2ξ and $-\xi\tilde{a}$. The present formulation allows for numerical resolution of the coupled equations (2), (3) and (4), from which a classic charging process yields the free energy F , and thus the persistence length:

$$L_{\text{el}} = \frac{2}{\ell_B\kappa^2}\int_0^\xi\Psi^{(2)}(\tilde{a})d\xi. \quad (5)$$

The numerical data presented below have been obtained following these steps, that also prove useful to proceed analytically, as we now discuss.

Linearizing eqs. (2), (3) and (4) yields a (DH) description that should hold for small ξ (*i.e.* neglecting counterion condensation), but valid for arbitrary κa . In other words, deficiency a) above remains while b) is taken care of. After tedious calculations, the formula for the contact potential $\Psi^{(2)}(\tilde{a})$ can be written explicitly; it turns out immaterial for our purposes, since a particularly simple linear approximation yields an accuracy better than 10% for all κa ’s:

$$\Psi_{DH}^{(2)}(\tilde{a}) \simeq \xi\left(\frac{1}{4} + \kappa a\right), \quad (6)$$

as shown in the inset of fig. 1. Such a relation is exact for $\kappa a \rightarrow 0$ and $\kappa a \rightarrow \infty$. At this linear level of description, the consequence in terms of stiffness is straightforward: eq. (5) leads to the Debye-Hückel (DH) expression $L_{\text{el}}^{DH} = \xi^2(1 + 4\kappa a)/(4\ell_B\kappa^2)$. For $\kappa a \ll 1$, the OSF expression is recovered but the correcting factor $1 + 4\kappa a$ is in general non-negligible: for instance, considering ds-DNA, having $a \simeq 10\text{Å}$, κa is close to unity in physiological conditions. OSF leads here to a fivefold underestimation.

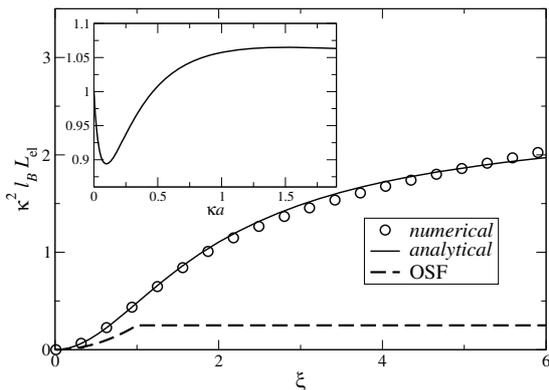


Fig. 1: Electrostatic persistence length *vs.* bare charge $\xi = \lambda \ell_B$ for $\kappa a = 0.4$. Comparison of numerical Poisson-Boltzmann results, solving the non-linear coupled equations (2), (3) and (4), to the analytical surmise, eq. (7). The OSF law (bottom) is shown by the dashed line. The inset shows the rescaled contact potential $\xi^{-1} \Psi_{DH}^{(2)}(\tilde{a})/(\tilde{a} + 1/4)$ at linearized (DH) level, remaining close to 1 for all κa 's.

The remaining task is to account for non-linearities that also enhance the Coulombic rigidity compared to OSF expectations. This requires the analytical resolution of eqs. (2), (3) and (4), an intractable task. To circumvent that difficulty, we formulate a surmise that will be gauged later against numerics:

$$L_{el} = \frac{\xi_{eff}^2}{4\ell_B\kappa^2} (1 + 4\kappa a), \quad (7)$$

where ξ_{eff} is the effective charge of the rod. The concept of effective charges is widespread in colloidal science, but it is sometimes elusive. Here, it has the clear-cut meaning of describing the far-field of the straight charged cylinder [56,57], *i.e.*, $\Psi^{(0)} \sim 2\xi_{eff}K_0(\tilde{r})/[\tilde{a}K_1(\tilde{a})]$ for $\tilde{r} \gg 1$, where K_0 and K_1 denote the 0th and 1st order modified Bessel functions of the second kind. By construction, ξ_{eff} and ξ coincide for weakly charged polymers, while the fact that $\xi_{eff} < \xi$ and possibly $\xi_{eff} \ll \xi$ for large ξ gives a quantitative meaning to the notion of counterion condensation. Implicit in (7) is the idea that large-scale features of the electrostatic interactions dominate for the Coulombic rigidity: when bending a straight chain so that it finally has curvature R , two charges that lie a distance s apart along the backbone become closer by $\Delta s \simeq -s^3/(24R^2)$, a rapidly increasing function of s . In a pairwise (DH) picture for a thin chain, the free-energy cost F (and thus L_{el}^{DH}) is the weighted integral of Δs times the energy variation $\partial_s(e^{-\kappa s}/s)$. In calculating that integral, we recover OSF, with the interesting information that large distances mostly do contribute. This backs up the substitution $\xi \rightarrow \xi_{eff}$ to account for non-linearities, beyond DH, a conclusion also reached in [16]. Similar propositions have been put forward, see, *e.g.*, the variational treatment of refs. [13,24]. We can finally invoke progress in theoretical understanding of effective charges made in the last 15 years, that provide usable expressions. Here, thick and

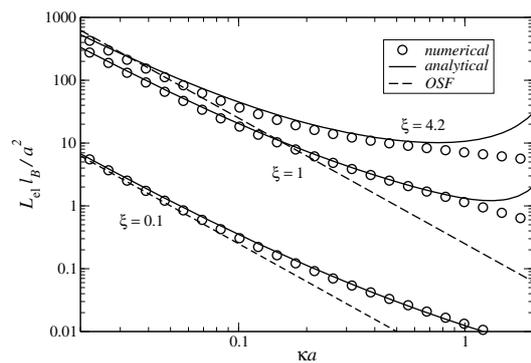


Fig. 2: Persistence length as a function of salt content, for three charges (including $\xi = 4.2$ for double-stranded DNA). OSF (dashed line) does not discriminate between $\xi = 1$ and $\xi > 1$. The analytical curve is for eq. (7).

thin polymers have to be distinguished, meaning that for small and large κa , different expressions should be used. Specifically, for $\kappa a < 1/2$ we took [56,57]

$$\xi_{eff} = 2\kappa a K_1(\kappa a) \frac{1}{\pi} \cosh(\pi\mu) \quad \text{with} \\ \mu = \frac{-\pi/2}{\log(\kappa a) + \gamma - \log 8 - (\xi - 1)^{-1}}, \quad (8)$$

valid, for $\xi > 1$ (see footnote ⁴) and where $\gamma \simeq 0.5772$ is the Euler constant. For $\kappa a > 1/2$, use was made of eqs. (4) and (5) of ref. [58]:

$$\xi_{eff} = 2 \kappa a t_\lambda + \frac{1}{2} \left(5 - \frac{t_\lambda^4 + 3}{t_\lambda^2 + 1} \right) t_\lambda, \quad (9)$$

where $t_\lambda = T(\xi/(\kappa a + 1/2))$ and the function T is defined as $T(x) = (\sqrt{1+x^2} - 1)/x$.

We are now in a position to test analytical against numerical results. First of all, at a particular salt content, fig. 1 shows that eq. (7) is remarkably accurate, for all charges. On the other hand, OSF fails even at small charges, due to the omission of the steric factor $1 + 4\kappa a$, and with a growing disagreement as the charge increases. Of course, enforcing both $\xi \ll 1$ and $\kappa a \ll 1$, OSF is recovered, as can be seen in fig. 2. This figure also illustrates the quality of the analytical prediction for $\kappa a < 1$, in particular for moderately to strongly charged polymers ($\xi > 1$), for which OSF prediction should not be employed. For $\kappa a > 1$ the quality of our prediction deteriorates.

Arguably, the most iconic stiff polyelectrolyte is ds-DNA, the mechanical properties of which have been the subject of a flood of publications. To account for experimental measures, its persistence length is almost invariably fitted assuming OSF, *i.e.*, with the formula $L_0 + L_{OSF}$ where L_0 is unknown. This yields the bare length $L_0 \simeq 500 \text{ \AA}$, a value that is widely taken for granted [6,36,59].

⁴More general expressions can be found in [56,57]; we focus here on the most relevant $\xi > 1$ regime, beyond the so-called Manning threshold.

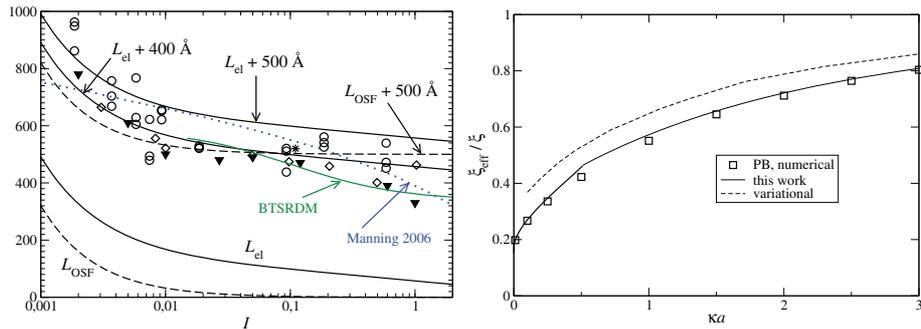


Fig. 3: (Colour online) Left: comparison to experimental and numerical data for ds-DNA: total persistence length in Å as a function of ionic strength I (salt concentration) in mol L⁻¹. The latter is defined by $\kappa^2 = 8\pi\ell_B I$ so that $(\kappa a)^2 \simeq 11I$ (with I again in mol L⁻¹ and $a = 10 \text{ Å}$). The diamonds are from [60] and the circles show the results from [6] (three for each ionic strength corresponding to different methods of calculation). The * is for the measure reported in [12] ($L_{tot} = 520 \pm 20 \text{ Å}$ in near-physiological conditions). The down triangles show the simulation data of [61]. The bottom part of the graph displays the sole electrostatic contribution from the present work (continuous line, obtained numerically) and from OSF (dashed line). The bare contribution L_0 is subsequently added, with $L_0 = 400 \text{ Å}$ or $L_0 = 500 \text{ Å}$ as indicated. For comparison, the prediction of ref. [15] is indicated by the thick dotted line. Right: amplitude of charge renormalization effect *vs.* salt for $\xi = 4.2$. The effective charge extracted from the numerical solution of PB equation (2) is compared to the analytical prediction of eqs. (8) and (9). The result of the variational treatment following refs. [13] and [24] is also shown (dashed line), together with the fit reproducing the 2060 bp experimental data of ref. [24] (“BTSRDM” curve).

However, L_{OSF} underestimates the electrostatic length (see the two bottom curves of fig. 3), a deficiency that needs to be compensated by an overestimation of L_0 . The OSF-based value $L_0 \simeq 500 \text{ Å}$ should thus be reconsidered. Figure 3 shows that $L_0 + L_{el}$ with $L_0 = 400 \text{ Å}$ provides an equally good fit, if not better, than $L_{OSF} + 500 \text{ Å}$. On the other hand, $L_{el} + 500 \text{ Å}$ yields a poor agreement with the experimental data. The latter are quite scattered, so that no attempt was made at providing a more accurate estimation of L_0 . We conclude at this point that a consistent treatment of Coulombic effects at Poisson-Boltzmann level leads to a ds-DNA bare persistence length that is some 20% smaller than reported in the literature. It is worth emphasizing here that a distinct in spirit approach was proposed by Manning in [15], accounting for the internal tension on DNA caused by phosphate-phosphate repulsion. As a consequence, the persistence length of the uncharged backbone enters multiplicatively into the formula for L_{el} , and not additively as here. These results also are seen in fig. 3 to be in fair agreement with experimental data. We will see however that the formula of ref. [15] fails to reproduce the data of fig. 4. Finally, we show for completeness in fig. 3, right, how our effective charge compares to the variational treatment of [13,24].

The spread of experimental points in fig. 3 evidences the fact that inferring persistence length from force-extension curves or other measures is an indirect and delicate task [24,62]. For nucleic acids, the bare length L_0 is furthermore unknown (charges cannot be “switched off”), and we have seen that fitting this quantity within an improper framework may conceal theoretical glitch. It is thus of particular interest to consider systems where the charge can be tuned, and even made to vanish, a limit where L_{tot} and L_0 coincide. This is the case of the doped

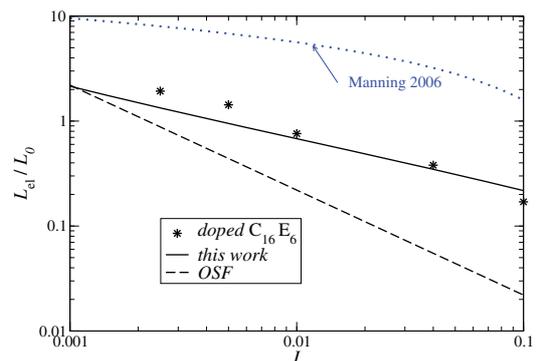


Fig. 4: (Colour online) Stiffness of worm-like non-ionic micelles (surfactant $C_{16}E_6$), doped with ionic surfactant to tune the resulting equilibrium polymer charge density [9,63]. The ionic strength I is in mol L⁻¹. Here, $\xi = 1.2$, $a = 30 \text{ Å}$. The bare persistence length L_0 can be measured independently: $L_0 = 150 \text{ Å}$.

giant micelles studied in [9,63]. The comparison in fig. 4 is thus fitting-parameter free. Unlike OSF, our approach fares well against the experiments. Using Manning’s formula [15] leads to an overestimation of $L_{tot} - L_0$ by a factor close to 5, see the thick dotted curve [64].

Before concluding, we briefly comment on the scaling properties of L_{el} , a question that has not been undisputed. Weakly charged chains (for which $\xi_{eff} \simeq \xi$ is fixed in eq. (7)) exhibit two regimes, $L_{el} \propto \kappa^{-2}$ for $\kappa a < 1/4$ and $L_{el} \propto \kappa^{-1}$ for $\kappa a > 1/4$. However, realistically charged polymers reveal a much weaker dependence on κ (see footnote ⁵), except under weak screening ($\kappa a \ll 1$), where

⁵A similar conclusion was reached in ref. [13].

the standard κ^{-2} form is recovered⁶. Indeed, the effective charge ξ_{eff} is an increasing function of salt density, to such an extent that the κ -dependence of L_{el} becomes small for DNA-like parameters, see the $\xi = 4.2$ curve in fig. 2. Upon increasing ξ further, the persistence curves become flatter and flatter in fig. 2 (not shown). It is worth emphasizing that the κ -dependence of ξ_{eff} is not algebraic, so that nonlinearities wipe out the power-law features present in the linear (DH) treatment. We also stress that at any rate, the OSF scaling in κ^{-2} should never be expected, irrespectively of the charge of the polymer, for $\kappa a > 0.1$ (see footnote ⁷).

Conclusion. – Flexibility is a key property of chain macromolecules. We have accounted for the Coulombic contribution to the rigidity of stiff polyelectrolytes by a simple formula, eq. (7). It remedies the shortcomings of the celebrated Odijk, Skolnick and Fixman law, limited to weak screening (thin rods) and weak charges. The resulting renormalized treatment is thus applicable to situations of experimental interest, as we have discussed. A byproduct of our analysis is that the bare ds-DNA persistence length of 500 Å has been systematically overestimated, and that a consistent value is quite smaller, $L_0 \simeq 400$ Å. We did not present any comparison with single-stranded DNA, since this chain is considerably more flexible than its double-stranded form. Yet, our description might be relevant for single-stranded DNA under sufficient tension [65]. Finally, our simple approach clearly bears its own limitations. While a relevant starting point, the homogeneous worm-like view, subsuming all elastic features in a single quantity, is quite crude. It does not account for heterogeneities (like sequence dependence for nucleic acids), the possible existence of non-smooth bending through flexible joints [66], the importance of end effects [67], the coupling between stretching and bending [47] or the fact that elasticity may be scale-dependent [4]. In addition, the Poisson-Boltzmann framework discards from the outset specificity effects. It also dispenses with ionic correlations, relevant for multivalent ions, and that may lead to a decrease of stiffness [6,49,68–70], somewhat reminiscent of like-charge colloidal attraction.

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⁶This is due to the fact that the effective charge ξ_{eff} goes to a constant when $\kappa a \rightarrow 0$. This property is geometry sensitive, and cannot be transposed to planar or spherical macroions.

⁷When plotted as a function of $I^{-1} \propto \kappa^{-2}$, experimental persistence lengths exhibit a *concave* shape, that is the signature of non-linear screening effects [24]. Our analytical predictions have this property.

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