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Editors' Suggestion

Origin of Anomalously Large Depletion Zones in Like-Charged Colloid-Polyelectrolyte Mixtures

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Depletion zones in polyelectrolyte solutions in contact with like-charged flat surfaces are investigated. Using a coupled self-consistent field and Debye-Hückel approach, an explicit expression for the thickness δ of the depletion layer is derived. It is found that $\delta \sim \delta_{\mathrm{n}} + c\kappa^{-1}$, where δ_{n} is the depletion thickness at a neutral surface, c is a function of the electrostatic characteristics of the system, and κ^{-1} is the Debye length. It is argued that the theory still holds beyond the mean-field approximation, which is confirmed by quantitative agreement between our theoretical results and experiments.

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Introduction.—The depletion interaction [1,2] plays a crucial role to explain key aspects of the dynamics, colloidal interactions, and resulting phase behavior in materials and living systems involving colloidal mixtures. This depletion concept allows for the quantification of properties in model colloid-polymer mixtures [3] and provides a qualitative description of several phenomena in practical applications [4].

Considerable progress has been made in understanding depletion phenomena in uncharged colloid-polymer mixtures over the past few decades, thanks to extensive scientific efforts [5–9]. The current challenge lies in comprehending interactions in mixtures where the direct interactions between colloids and/or depletants are more realistic than pure hard-core interactions [10]. This involves considering factors such as charges in colloid-polyelectrolyte mixtures, an area that remains less understood from both experimental and theoretical perspectives [11].

Mixtures of polyelectrolytes and like-charged colloidal particles in an aqueous salt solution are ubiquitous in both industrial applications [12,13] and biological systems [14,15]. A typical example is the high concentration of various charged macromolecules and proteins in living cells, leading to macromolecular crowding phenomena [15]. Because of the electrostatic repulsion between the polyelectrolyte monomers and the colloidal surface, a depletion zone void of polyelectrolytes and with typical size δ is formed around the colloidal particles. The size of the depletion zone has significant impact on colloidal interactions [4,16], dynamics [17–19], and phase behavior [9,20] of such mixtures. Depletion forces significantly affect protein stability within cells, with electrostatic interactions playing a crucial role [21].

The lack of a theoretical description of electrostatically driven depletion, next to its complexity, is possibly due to the absence of experimental measurements of δ. However, in recent years, various measurements of δ of a polyelectrolyte solution next to a flat like-charged surface have been performed [19,22,23], allowing for a direct comparison with theory. In these experiments, anomalously large depletion zones with a size up to 25 times those of neutral systems were found [22], owing to the repulsive electrostatic interactions of the polyelectrolytes with the surface.

Thus, in this Letter, we develop a theory to describe electrostatically driven depletion and derive an explicit expression for the thickness of the depletion layer adjacent to a like-charged flat surface. We find that δ logarithmically depends on the surface potential and linearly varies with the Debye length κ^{-1}. The scaling behavior of our theory is consistent with previous theoretical work [24] and is in quantitative agreement with both experiments and exact mean-field calculations.

Theory.—We model the polyelectrolytes with a total charge eZ_{p}, where e is the elementary charge, as continuous chains with degree of polymerization N, Kuhn length l, and an average charge per monomer of $f = Z_{\mathrm{p}}/N$. The polyelectrolytes are in solution at a bulk concentration of $c_{\mathrm{b}} = n_{\mathrm{p}}N$, where n_{p} is the number density of polyelectrolytes, and are mixed with a 1:1 salt consisting of point particles at number density c_{s}. The solution is in contact with a flat surface with surface charge density $e\sigma$. Apart from electrostatics, the polyelectrolytes have no specific interactions with the pointlike salt ions. In the limit of infinitely long polyelectrolyte chains, the local density of polyelectrolytes is given by $\rho(x) = c(x)/c_{\mathrm{b}} = g(x)^2$, where $g(x)$ satisfies a second-order differential equation [25,26],

$$\frac{\partial^2 g}{\partial x^2} = \frac{6}{l^2} u(x) g(x), \tag{1}$$

which may be derived using either field theoretical methods [27] or phenomenologically [25]. Equation (1) is the ground-state approximation to the well-known Edwards equation [6,28,29]. The quantity $u(x)$ in Eq. (1) is the local potential, relative to the bulk solution in units of $k_B T$, which in a mean-field approximation is given by [27]

$$u(x) = v c_b \left[g(x)^2 - 1\right] + f\Psi(x), \tag{2}$$

where v is the excluded volume between monomers and $\Psi(x) = \psi(x)e/(k_B T)$ is the normalized local electrostatic potential. The local electrostatic potential is a solution to the Poisson-Boltzmann equation,

$$\frac{\partial^2 \Psi}{\partial x^2} = \kappa_s^2 \sinh\Psi(x) + 4\pi l_B f c_b [e^{\Psi(x)} - g(x)^2], \tag{3}$$

where $\kappa_s^2 = 8\pi l_B c_s$, with l_B being the Bjerrum length. In general, the coupled set of Eqs. (1)–(3) has to be solved numerically with suitable boundary conditions, which for the electrostatic depletion problem at hand are $g(\infty) = 1$, $g(0) = 0$, $\Psi(\infty) = 0$, and $\Psi'(0) = -4\pi l_B \sigma$ (constant surface charge), where the prime denotes differentiation with respect to x. With the obtained density profile, the depletion thickness is subsequently calculated as $\delta = \int_0^\infty [1 - g(x)^2] \mathrm{d}x$.

We now derive an approximate analytical expression for δ. Assuming $\Psi(x) \ll 1$, we first take the Debye-Hückel approximation and linearize Eq. (3),

$$\frac{\partial^2 \Psi}{\partial x^2} = \kappa^2 \Psi(x) - 4\pi l_B f c_b [g(x)^2 - 1], \tag{4}$$

where $\kappa^2 = 4\pi l_B (f c_b + 2c_s)$. We now split the density profile of the polyelectrolyte monomers into two hypothetical regions as depicted in Fig. 1: an electrostatic depletion zone, where electrostatic repulsion between the monomers and surface is dominant [the second term of Eq. (2) dominates] and an excluded volume depletion zone [where the first term of Eq. (2) dominates].

We make the *a priori* assumption that within the electrostatic depletion zone $g(x) \ll 1$ and is virtually stationary due to the electrostatic repulsion between the monomer segments and the surface. Beyond the electrostatic depletion zone $\Psi(x) \approx 0$. One may then use a separation of length-scale approximation and solve Eq. (4) with a stationary $g(x)$ to obtain

$$\Psi(x) \simeq \frac{4\pi l_B \sigma}{\kappa} e^{-\kappa x} + \frac{4\pi l_B f c_b}{\kappa^2} \left[g(x)^2 - 1\right], \tag{5}$$

which is expected to be accurate within the electrostatic depletion zone, but inaccurate in the excluded volume zone. Insertion of Eq. (5) into Eqs. (1) and (2) yields

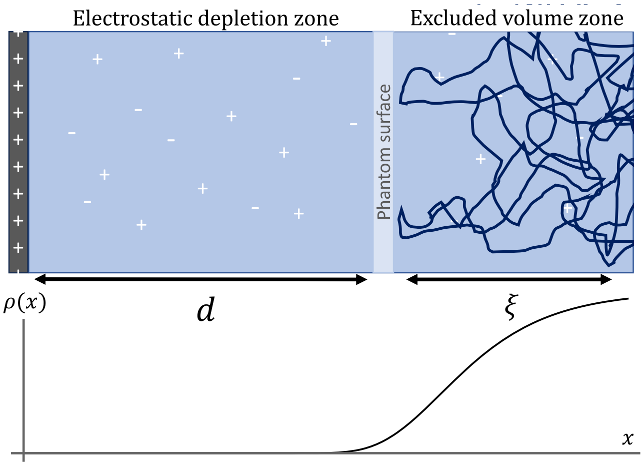

FIG. 1. Schematic picture of the subdivision of the interfacial region in two separate zones: an electrostatic depletion zone with characteristic thickness d and an excluded volume zone with characteristic thickness ξ. At $x = d$ there is a phantom neutral surface.

$$\frac{\partial^2 g}{\partial x^2} = \frac{2}{\xi^2} \left[g(x)^3 - g(x)\right] + \frac{24\pi l_B f \sigma}{\kappa l^2} e^{-\kappa x} g(x), \tag{6}$$

where we defined the mean-field correlation length as $\xi^2 = l^2/[3(v + 4\pi l_B f^2/\kappa^2) c_b]$, with $4\pi l_B f^2/\kappa^2$ an effective electrostatic excluded volume. One may classify the first term on the right-hand side of Eq. (6) as the excluded volume contribution and the second term as a contribution due to the repulsive interaction between a monomer and the surface.

Within the electrostatic depletion zone $g(x) \ll 1$, such that $g(x)^3 - g(x) < 0$, while the electrostatic repulsion is positive and dominant, and thus $g''(x) > 0$. There exists, however, an inflection point $g''(x) = 0$ where the repulsive electrostatic contribution to Eq. (6) is exactly canceled by the excluded volume contribution. It is easy to verify that at this point Eq. (2) $u(x) = 0$. We define this point $x = d$ as the edge of the electrostatic depletion zone; for $x > d$ the depletion is no longer dominated by electrostatics. Using the condition $g''(d) = 0$, we solve Eq. (6) for d to obtain

$$d \simeq \kappa^{-1} \ln\left(\frac{12\pi l_B f \xi^2 \sigma}{\kappa l^2 (1 - g(d)^2)}\right). \tag{7}$$

The limit $f = 0$ implies d should vanish, which we use to determine $g(d)^2 \approx [1 + 12\pi f \xi^2 l_B \sigma/(\kappa l^2)]^{-1}$ to yield

$$d = \kappa^{-1} \ln\left(\frac{12\pi l_B f \xi^2 \sigma}{\kappa l^2} + 1\right). \tag{8}$$

For $f = 0$, $g(d)^2 = 1$, which seems contradictory, as $d = 0$ and $g(0) = 0$ in this case. However, Eqs. (4) and (6) are strictly valid *only* in the electrostatic depletion zone; therefore, Eq. (8) is also strictly valid only for nonzero f, as the electrostatic depletion zone is undefined for $f = 0$. This can be better understood by realizing that solving Eq. (6) with $g''(x) \approx 0$ yields $g(x)^2 = \rho(x) = 1 - 3f(\xi^2/l^2)\Psi_0 e^{-\kappa x}$, where $\Psi_0 = 4\pi l_B \sigma/\kappa$. This can be regarded as a first order expansion in $\Psi(x) = \Psi_0 e^{-\kappa x}$. The polyelectrolyte density is then $\rho(x) \simeq e^{-f_{\mathrm{eff}}\Psi(x)}$, where $f_{\mathrm{eff}} = 3f\xi^2/l^2$ is an effective charge. Thus, within the electrostatic depletion zone the polyelectrolyte roughly behaves as a hypothetical macroion with charge f_{eff}. For $f = 0$, $\rho = 1$, while $d = 0$, as within this electrostatic depletion zone the concentration would be equal to the bulk concentration.

Outside the electrostatic depletion zone, the solution approximately behaves as if it were adjacent to a neutral wall, as the excluded volume contribution then is dominant. Setting $\sigma = 0$ in Eq. (6) and solving gives $\delta_{\mathrm{n}} = \xi$ [6]. The total depletion thickness is then roughly given by the sum of the depletion thickness ξ of a polyelectrolyte solution in contact with a neutral wall, and the size d of the electrostatic depletion zone $\delta \simeq \xi + d$,

$$\delta \simeq \xi + \kappa^{-1} \ln\left(\frac{12f\xi^2\pi l_B\sigma}{\kappa l^2} + 1\right). \tag{9}$$

Note that the concept of a phantom neutral surface is analogous to defining an effective hard-sphere diameter in the thermodynamic perturbation theory of charged systems, as discussed by Barker and Henderson [30]. Equation (9) has a similar form to the depletion thickness around a small spherical protein with radius a in a semidilute polyelectrolyte solution, as derived using a Wentzel-Kramers-Brillouin approximation by Odijk: $\delta \simeq a + c\kappa^{-1}$, where c depends logarithmically on the charge of the protein particle [24]. Note that Eq. (9) is derived using a point-ion mean-field approximation, which ignores ion-ion correlations and excluded volume interactions between ions and is strictly only valid for low ion concentrations [31]. It is known that for macroions near same-sign surfaces, finite-sized microions cause the size of the depletion zone to shrink [32]. This effect can primarily be attributed to excluded volume interactions and a higher *effective* concentration of species in the solution. We anticipate that at high salt concentrations a similar trend is observed in polyelectrolytes at same-sign surfaces.

Equation (9) was derived using the infinite chain-length assumption $N \to \infty$, such that the relevant length scale is the (bulk) correlation length ξ. However, for neutral systems, Fleer *et al.* [7] showed that finite chain-length corrections can be taken into account by formally replacing ξ with the relevant length scale $\delta_{\mathrm{n}}^{-2} = \delta_0^{-2} + \xi^{-2}$, where in a mean-field approximation $\delta_0^2 = 2Nl^2/(3\pi)$. In the dilute limit $\delta_{\mathrm{n}} = \delta_0$, while in the semidilute and concentrated regime $\delta_{\mathrm{n}} = \xi$. In uncharged polymer solutions, δ_{n} can be regarded as the N-dependent generalized correlation length [7]. The formal replacement $\xi \to \delta_{\mathrm{n}}$ yielded quantitative agreement with both experimental work and exact mean-field computations [7,33].

A simple phenomenological argument can be made for the replacement $\xi \to \delta_{\mathrm{n}}$: Consider Eq. (6) for a neutral system $f = 0$ of polymers with infinite chain length. The solution of which is given by $g(x) = \tanh(x/\xi)$, such that $\rho(x) = \tanh(x/\xi)^2$ and $\delta = \int_0^\infty [1 - \rho(x)]\mathrm{d}x = \xi$, in agreement with the work of De Gennes [6]. Contrastingly, for finite chain length in the dilute regime, $\rho(x) \simeq \tanh(x/\delta_0)^2$ [34]. Replacing $\xi \to \delta_{\mathrm{n}}$ in Eq. (6) exactly interpolates between these two limits (see Fig. 8 of Ref. [7]). It turns out that, in general, for polymers near a nonadsorbing neutral interface the density profile is given by $\rho(x) \simeq \tanh(x/\delta_{\mathrm{n}})^2$, as long as the exact expressions for the dilute limit δ_0 and semidilute regimes ξ are chosen [33].

Therefore, we propose that Eq. (9) is generally valid as long as the "exact" relevant length scale is introduced. Thus, we make the formal replacement $\xi \to \delta_{\mathrm{n}}$. This formal replacement yields our main result for finite N,

$$\delta \simeq \delta_{\mathrm{n}} + \kappa^{-1} \ln\left(\frac{12f\delta_{\mathrm{n}}^2\pi l_B\sigma}{\kappa l^2} + 1\right). \tag{10}$$

All equations derived so far are valid next to a flat wall. Extensions to the depletion thickness around a spherical or cylindrical particle are straightforward by performing the same derivation using either spherical or cylindrical coordinates in Eqs. (4) and (6).

Results.—We now compare Eqs. (9) and (10) with experimental results. Barraud *et al.* [22] measured the depletion thickness δ using a dynamic surface force apparatus, through the apparent slip of the solution. These authors used a salt-free hydrolyzed polyacrylamide solution with $N = 2.6 \times 10^5$ in contact with a same-sign surface consisting of platinum with a one-monomer thick layer of the hydrolyzed polyacrylamide. In this system, $|f| = 0.25$ and we assume no counterion condensation takes place [22], as the distance between charges on the backbone is larger than the Bjerrum length [35]. The surface charge density was measured to be $|\sigma| = 0.192\ \mathrm{nm}^{-2}$. Because of the large size of the polyelectrolytes, the relevant length scale is ξ. To account for correlations in the monomer density, we go beyond our mean-field theory and estimate ξ using the variational theory of Muthukumar [36]. The measured concentration polyelectrolyte range $c \gg c^*$, where c^* is the overlap concentration such that the system is in the highly entangled regime [22], for which $\xi \simeq (24\pi c_b l_B f^2/l^2)^{-1/4}$ [Eq. (1.14) of Ref. [36]].

Direct comparison between Eq. (9) and the experimental measurements is shown in Fig. 2. As all parameters of the theory are known, no adjustable fit parameters are used. Here we find reasonably close agreement between the analytical theory and the experimentally measured depletion thickness. The inset shows the ratio δ/ξ, which

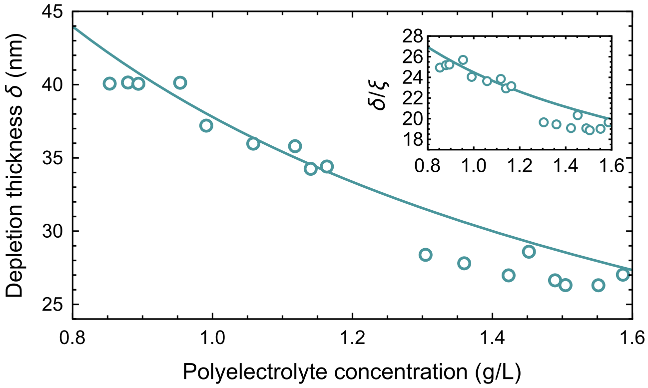

FIG. 2. The depletion thickness of a salt-free hydrolyzed polyacrylamide solution at a same-sign surface as a function of the polyelectrolyte concentration calculated using Eq. (9), with ξ calculated using Eq. (1.14) of Ref. [36] with $f = 0.25$ and $\sigma = 0.194\ \mathrm{nm}^{-1}$ [22]. The data points are obtained from Ref. [22].

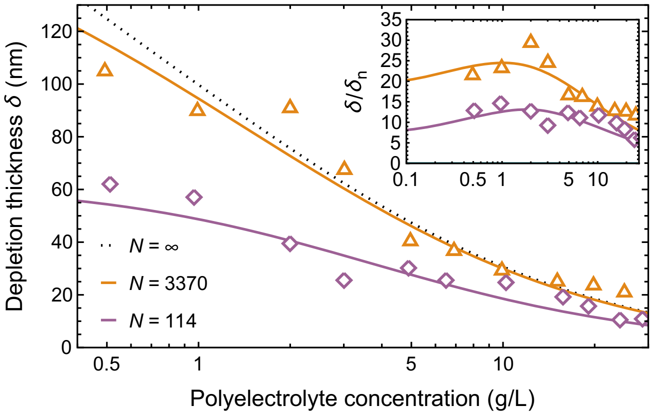

FIG. 3. The depletion thickness of a salt-free NaPSS solution at a silica surface as a function of the polyelectrolyte concentration calculated using Eq. (10), with ξ calculated using Eq. (1.12) of Ref. [36] with $|f| = 0.01$. The dotted curve is Eq. (9) for infinite chain length. The data points are obtained from Ref. [23]. Fitting the surface charge density yielded $|\sigma| \approx 0.03\ \mathrm{nm}^{-2}$.

reveals that the excluded volume contribution to δ is small compared to the electrostatic contribution. As expected, the depletion thickness decreases with increasing polyelectrolyte concentration, as both the surface charges and polyelectrolyte charges are increasingly screened by the counterions. Similar effects have been observed in solutions of macroions near same-sign surfaces [32].

Similarly, we may compare our theory with the recent reflectivity measurements by Gvaramia *et al.* [23]. These authors used salt-free sodium polystyrene sulphonate (NaPSS) solution with various degrees of polymerization in contact with a silica surface and obtained δ as a function of the polyelectrolyte bulk concentration. Unfortunately, no surface charge density was measured, thus we use this as a fit parameter. These authors found an extraordinarily low concentration of free sodium ions of 1% of the theoretical maximum, corresponding to an effective charge per monomer of $|f| = 0.01$. The pH of the solution was 4, such that the concentration of free sodium ions is comparable to that of the hydronium ions. In this case, Eq. (1.12) of Ref. [36], $\xi \simeq l/(24 c_\mathrm{b} \pi l_\mathrm{B} f^2/\kappa^2)^{1/2}$, is applicable. To test the validity of Eq. (10) we compare measurements for $N = 3370$ and $N = 114$ monomers per chain with the theoretical predictions in Fig. 3. Because of the finite and relatively small N, $1/\delta_0^2 \neq 0$, for which we use the mean field δ_0. For a universal fit value of $|\sigma| = 0.03\ \mathrm{nm}^{-2}$, semiquantitative agreement is found between the experimental data points and Eq. (10), which is well within the surface charge density range of silica [37].

The ratio δ/δ_n (inset) shows that the excluded volume contribution to the depletion thickness δ is small compared to the electrostatic contribution over the whole concentration range. The electrostatic contribution reaches a maximum for both chain lengths, which is due to a subtle balance between increased electrostatic screening and decreasing δ_n. The maximum corresponds to the maximum increase in the size of the depletion zone, compared to the neutral case.

The dashed curve in Fig. 3 is Eq. (9) without the finite N correction, showing that, for small N, this correction is indeed necessary. It is of fundamental interest to compare Eq. (10) with exact numerical self-consistent field theory calculations of the depletion thickness. To this end, we employ Scheutjens-Fleer self-consistent lattice computations (SF-SCF) for charged systems [38–40], which is the lattice equivalent of the full Edwards equation [29] coupled to the Poisson-Boltzmann equation. The depletion thickness calculated using Eq. (10) (solid curves) and Eq. (9)

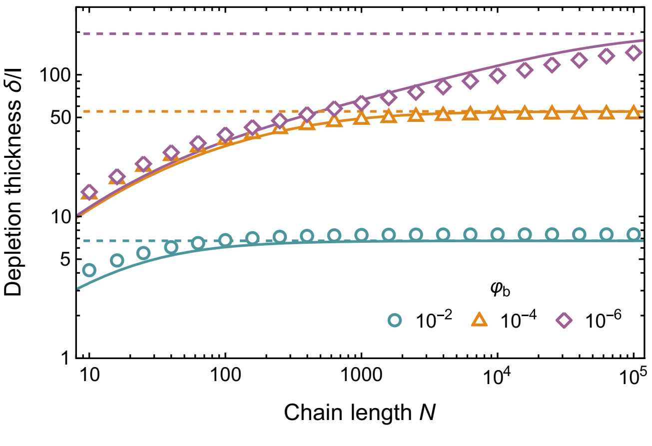

FIG. 4. The mean-field depletion thickness in a polyelectrolyte solution at a flat wall as a function of the polyelectrolyte chain length for various $\varphi_\mathrm{b} = c_\mathrm{b} l^3$. Parameters: $|f| = 0.1$, $v = l^3$, 10 mM salt, and $|\sigma| = 0.1\ \mathrm{nm}^{-2}$. The symbols are Scheutjens-Fleer self-consistent field computations, the solid curves are Eq. (10), and the dashed curves are Eq. (9).

(dashed curves) are compared with SF-SCF computations (symbols) as a function of N at three different $\varphi_b = c_b l^3$ and 10 mM salt in Fig. 4. We used $|f| = 0.1$ and $l = 0.3$ nm. Except for small $N < 50$, close agreement between the exact mean-field calculations and Eq. (10) is found. Small deviations between Eq. (10) and the SF-SCF computations highlight the approximate nature of our theory. Nevertheless, in general, for $\delta_0 \lesssim \xi$ the finite-N correction is important, $\delta_0 \sim R_g$, thus for systems below the overlap concentration.

Coming back to the discussion below Eq. (8), in the electrostatic depletion zone, the polyelectrolyte thus behaves as a macroion with effective charge $f_{\mathrm{eff}} = 3f\delta_n^2/l^2$, which in dilute conditions gives $f_{\mathrm{eff}} \sim fN = Z_p$ as expected, and $f_{\mathrm{eff}} = 3f\xi^2/l^2$ in the semidilute regime. Thus, $f_{\mathrm{eff}} \sim fN_{\mathrm{corr}}$, where N_{corr} is the number of correlated monomers, calculated as $N_{\mathrm{corr}} = \delta_n^2/l^2$.

Conclusions.—In summary, we have derived an analytical approximation for the size of the depletion zone δ in polyelectrolyte systems in contact with a same-sign surface. It was found that the interfacial region can be understood to be composed of two zones, an electrostatic depletion zone, where the polyelectrolyte roughly behaves as a macroion with an effective charge, and an excluded volume zone, where the polyelectrolyte behaves as it would be next to a neutral surface. The thickness of the depleted layer was found to scale as $\delta \sim \kappa^{-1} \ln \kappa^{-1}$. When one uses a correlation length beyond the mean-field approximation, our analytical theory was found to be in quantitative agreement with experimental measurements. However, more experiments and simulations are necessary to test the full applicability of the theoretical predictions.

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