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Challenging scaling laws of flexible polyelectrolyte solutions with effective renormalization concepts

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Abstract

Recasting a many-particle problem in a field-theoretic formalism is nowadays a well-established theoretical tool used by scientists across a wide spectrum of research areas, ranging from polymer physics to molecular electronic structure theory. It has shown to provide useful results in many complex situations, where the physics of the system involves many degrees of freedom and a multitude of different length scales, generally rendering its numerical treatment on a detailed level computationally intractable. To reduce the computational burden, field-theoretic methodologies usually take advantage of the mean-field approximation. This approximation technique is known to give reliable information about the system in the high concentration regime, where the interactions are highly screened. However, it is well established that the ranges of physical interest in most biological and technological applications lie in the intermediate to low concentration regimes, where fluctuations beyond the mean-field level of approximation become important and dominate the overall physical behavior. In this work we introduce a new self-consistent field theory for flexible polyelectrolyte chains, in which the monomers interact via a pair potential of screened Coulomb type, and derive suitable thermodynamic expressions for all concentration regimes. Our approach combines the renormalization concepts of tadpole renormalization, which has recently been successfully employed in calculations of prototypical neutral polymer and polyelectrolyte solutions, with the Hartree renormalization procedure. By comparing our approach to experimental measurements as well as alternative theoretical approaches, we demonstrate that it provides useful osmotic pressure results for polyelectrolyte systems composed of sodium poly(styrenesulfonate) without and with added salt over the whole range of monomer concentrations.

Keywords: Flexible polyelectrolyte solutions; Self-consistent field theory; Fluctuations

1. Introduction

Charged macromolecules are well known to play a vital role in nature and technology [1]. Of special importance among them are a special type of macromolecules called polyelectrolytes (PEs). They consist of long polymeric chains, possessing a multitude of ionizable groups along their backbone that may dissociate in a polar solvent by producing charged species [2]. Among the most prominent examples are the nucleic acids DNA and RNA, which are highly charged biopolyelectrolytes controlling the development and functioning of living cells. In addition to their central role played in biological systems, PEs find widespread use as solubilizing agents, phase separation agents, and rheological property modifiers in daily life and technological applications [3]. However, despite of their importance, PE systems still remain only poorly understood [4,5]. This relates to the fact that their chemistry and physics is influenced by many controlling parameters, such as molecular weight, salt concentration, pH of the solution, etc. Another important characteristic of PE systems is the coexistence of long-range Coulomb and short-range

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excluded volume interactions. The presence of long-range interactions generally renders their simulation particularly difficult because of the need for computationally expensive techniques, like the Ewald summation [6]. Moreover, their often highly polymeric nature introduces additional complexity by severely slowing down their equilibration [7].

Since the pioneering works of Edwards [8] and de Gennes [9], it has been well acknowledged that concepts originally introduced in quantum field theory (QFT) [10], like e.g. functional integrals or renormalization group theory, have substantially contributed to major breakthroughs in the field of polymer science [7,11,12]. For instance, the groundbreaking idea of Edwards to use functional integral methods to investigate the physics of polymers and complex fluids has led in the last few years to a rapid development of analytical calculation and computer simulation tools, suitable for describing structure and properties of a wide variety of important polymer systems, including polymer melts, blends, and block copolymers [11–21]. A standard approximation strategy for functional integral approaches is the mean-field (MF) approximation, which consists in replacing the many-body interaction term in the action by a term where all bodies of the system interact with an average effective field. This approach reduces any multi-body problem into an effective one-body problem by assuming that the partition function integral of the model is dominated by a single field configuration. A major benefit of solving problems with the MF approximation, or its numerical implementation commonly referred to as the self-consistent field theory (SCFT), is that it often provides some useful insights into the properties and behavior of complex many-body systems at relatively low computational cost. Successful applications of this approximation strategy can be found for various systems of polymers and complex fluids, like e.g. strongly segregated block copolymers of high molecular weight, highly concentrated neutral polymer solutions or highly concentrated block PE solutions [7,11–13]. There are, however, a multitude of cases for which SCFT provides inaccurate or even qualitatively incorrect results [7]. These comprise neutral polymer or polyelectrolyte solutions in dilute and semidilute concentration regimes, block copolymers near their order–disorder transition, polymer blends near their phase transitions, etc. In such situations the partition function integral defining the field-theoretic model is not entirely dominated by a single MF configuration and field configurations far from the saddle point can make important contributions, which require the use of more sophisticated calculation techniques beyond the MF level of approximation. One possibility to face the problem is to calculate higher-order corrections to the 0th-order MF approximation. Tsonchev et al. developed a MF strategy including leading-order (one-loop) fluctuation corrections, to gain new insights into the physics of confined PE solutions [22]. However, in situations where the MF approximation is bad many computationally demanding higher-order corrections to the integral are necessary to get the desired accuracy. Another possibility is to use Monte Carlo (MC) algorithms and to sample the full partition function integral in field-theoretic formulation. However, in a recent work Baeurle demonstrated that MC sampling in conjunction with the original field-theoretic representation is impracticable due to the so-called *numerical sign problem* [23]. The difficulty is related to the complex and oscillatory nature of the resulting distribution function, which causes a bad statistical convergence of the functional integral averages of the desired thermodynamic and structural quantities. In such cases special analytical and numerical techniques are necessary to accelerate their statistical convergence [23–27]. To make the methodology amenable for computation, Baeurle proposed to shift the contour of integration of the partition function integral through the homogeneous MF solution using Cauchy's integral theorem, which was previously successfully employed by Baer et al. in field-theoretic electronic structure calculations [28]. Baeurle demonstrated that this technique provides a significant acceleration of the statistical convergence of the functional integral averages in the MC sampling procedure [23,29]. An alternative theoretical tool to cope with strong fluctuation problems occurring in field theories has been provided in the late 1940s by the concept of renormalization, which has originally been devised to calculate functional integrals arising in QFTs [10,30]. In QFTs a standard approximation strategy is to expand the functional integrals in a power series in the coupling constant using perturbation theory. Unfortunately, generally most of the expansion terms turn out to be infinite, thereby rendering such calculations impracticable [30]. A way to remove the infinities from QFTs is to make use of the concept of renormalization [31]. It mainly consists in replacing the bare values of the coupling parameters, like e.g. electric charges or masses, by renormalized coupling parameters and requiring that the physical quantities do not change under this transformation, thereby leading to finite terms in the perturbation expansion. A simple physical picture of the procedure of renormalization can be drawn from the example of a classical electrical charge, Q, inserted into a polarizable medium, such as electrolytes. At a distance r from the charge due to polarization of the medium, its Coulomb field will effectively depend on a function $Q(r)$, i.e. the effective (renormalized) charge, instead of the bare electrical charge, Q [30]. At the beginning of the 1970s, Wilson further pioneered the power of renormalization concepts by developing the formalism of renormalization group (RG) theory, to investigate critical phenomena of statistical systems [32]. The RG theory makes use of a series of RG transformations, each of which consists of a coarse-graining step followed by a change of scale [7,33,34]. In case of statistical–mechanical problems the steps are implemented by successively eliminating and rescaling the degrees of freedom in the partition sum or integral that defines the model under consideration. De Gennes used this strategy to establish an analogy between the behavior of the zero-component classical vector model of ferromagnetism near the phase transition and a self-avoiding random walk of a polymer chain of infinite length on a lattice, to calculate the polymer excluded volume exponents [9]. Adapting this concept to field-theoretic functional integrals implies to study in a systematic way how a field theory model changes while eliminating and rescaling a certain number of degrees of freedom from the partition function integral [7,33]. An alternative approach is known as the *Hartree approximation* or *self-consistent one-loop approximation* [35,36]. It takes advantage of Gaussian fluctuation corrections to the 0th-order MF contribution, to renormalize the model parameters and extract in a self-consistent way the dominant length scale of the concentration fluctuations in critical concentration regimes [7]. In a more recent work Efimov and Nogovitsin showed that an alternative renormalization technique originating from QFT, based on the concept of *tadpole renormalization*, can be a very effective approach for computing functional integrals arising in statistical mechanics of classical many-particle systems [37,38]. They demonstrated that the main contributions to classical partition function integrals are provided by low-order tadpole-type Feynman diagrams, which account for divergent contributions due to particle self-interaction. The renormalization procedure performed in this approach effects on the self-interaction contribution of a charge (like e.g. an electron or an ion), resulting from the static polarization induced in the vacuum due to the presence of that charge [39]. As evidenced by Efimov and Ganbold in an earlier work [40,41], the procedure of tadpole renormalization can effectively be employed to remove the related divergences from the action of the original field-theoretic representation of the partition function, which leads to an alternative functional integral representation called the *Gaussian equivalent representation* (GER). They showed that the procedure provides functional integrals with significantly ameliorated convergence properties for analytical perturbation calculations. In subsequent works Baeurle applied [23–26,29] the concept of tadpole renormalization in conjunction with advanced Monte Carlo (MC) techniques in the grand canonical ensemble, and demonstrated that this approach efficiently accelerates the statistical convergence of the desired ensemble averages. Very recently, Baeurle et al. developed effective low-cost approximation methods based on the tadpole renormalization procedure, which have shown to deliver useful results for prototypical polymer and PE solutions [14,15,42].

In this work we develop a new field-theoretic methodology, which combines the concept of tadpole renormalization with the Hartree renormalization procedure, for solving statistical–mechanical problems of PE solutions over the entire range of monomer concentrations. We demonstrate the effectiveness of our approach on the example of a system of flexible PE chains, where the monomers interact via a Derjaguin–Landau–Verwey–Overbeek (DLVO) type of pair potential. We test the reliability of our method with regard to alternative theoretical approaches as well as experimental data, obtained from osmotic pressure measurements of sodium poly(styrene-sulfonate) (NaPSS) PE solutions without and with added salt in various concentration regimes.

Our paper is organized in the following way. In Section 2 we review the basic derivation of the field theory for flexible polymer chains, followed by the derivation of the GER formalism in conjunction with the Hartree renormalization procedure. Then, in Section 3 we show applications of the method on the example of NaPSS PE solutions, and demonstrate that the Hartree renormalized 0th-order GER methodology is an effective low-cost approximation strategy for evaluating thermodynamic information of systems composed of flexible PE chains over the whole range of monomer concentrations. Finally, we end our paper with a brief summary and conclusions.

2. Theory

2.1. Field theory for flexible polymer chains

The standard continuum model of flexible polymers, introduced by Edwards [8], treats a solution composed of n linear monodisperse homopolymers as a system of coarse-grained polymers, in which the statistical mechanics of the chains is described by the continuous Gaussian thread model [7] and the solvent is taken into account implicitly. The Gaussian thread model can be considered as the continuum limit of the discrete Gaussian chain model, in which the polymers are described as continuous, linearly elastic filaments. The canonical partition function of such a system, kept at an inverse temperature $\beta = 1/k_B T$ and confined in a volume V, can be expressed as

$$Z(n,V,\beta)=\frac{1}{n!\left(\lambda_T^3\right)^{nN}}\prod_{j=1}^{n}\int\mathcal{D}\mathbf{r}_j\exp(-\beta\Phi_0[\mathbf{r}]-\beta\overline{\Phi}[\mathbf{r}]), \qquad (1)$$

where $\overline{\Phi}[\mathbf{r}]$ is the potential of mean force given by

$$\begin{aligned}\overline{\Phi}[\mathbf{r}]&\approx\frac{N^2}{2}\sum_{j\neq k}^{n}\int_0^1 \mathrm{d}s\int_0^1 \mathrm{d}s'\,\overline{\Phi}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)\\&=\frac{N^2}{2}\sum_{j=1}^{n}\sum_{k=1}^{n}\int_0^1 \mathrm{d}s\int_0^1 \mathrm{d}s'\,\overline{\Phi}\left(\left|\mathbf{r}_j(s)-\mathbf{r}_k(s')\right|\right)-\frac{1}{2}nN\overline{\Phi}(0), \qquad (2)\end{aligned}$$

representing the solvent-mediated non-bonded interactions among the segments, while $\Phi_0[\mathbf{r}]$ represents the harmonic stretching energy of the chains. The latter energy contribution can be formulated as

$$\Phi_0[\mathbf{r}]=\frac{3k_BT}{2Nb^2}\sum_{l=1}^{n}\int_0^1 \mathrm{d}s\left|\frac{\mathrm{d}\mathbf{r}_l(s)}{\mathrm{d}s}\right|^2, \qquad (3)$$

where b is the statistical segment length and N the polymerization index. To derive the basic field-theoretical representation of the canonical partition function, we next introduce the segment density operator of the polymer system

$$\hat{\rho}(\mathbf{r})=N\sum_{j=1}^{n}\int_0^1 \mathrm{d}s\,\delta\left(\mathbf{r}-\mathbf{r}_j(s)\right). \qquad (4)$$

Using this definition, we can rewrite Eq. (2) as

$$\overline{\Phi}[\mathbf{r}]=\frac{1}{2}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\hat{\rho}(\mathbf{r})\overline{\Phi}(|\mathbf{r}-\mathbf{r}'|)\hat{\rho}(\mathbf{r}')-\frac{1}{2}nN\overline{\Phi}(0). \qquad (5)$$

Next, we transform the model into a field theory by making use of the definition of the delta functional

$$\int \mathcal{D}\rho\,\delta\left[\rho-\widehat{\rho}\right]F[\rho]=F\left[\widehat{\rho}\right], \tag{6}$$

where $F[\widehat{\rho}]$ is a functional and $\delta[\rho-\widehat{\rho}]$ is the delta functional given by

$$\delta\left[\rho-\widehat{\rho}\right]=\int \mathcal{D}w\,\mathrm{e}^{\,i\int \mathrm{d}\mathbf{r}\,w(\mathbf{r})\left[\rho(\mathbf{r})-\widehat{\rho}(\mathbf{r})\right]}, \tag{7}$$

with $w(\mathbf{r})=\sum_{\mathbf{G}}w(\mathbf{G})\exp[i\mathbf{G}\mathbf{r}]$ representing the auxiliary field function. We note in this context that expanding the field function in a Fourier series implies that periodic boundary conditions are applied in all directions and that the $\mathbf{G}$ vectors designate the reciprocal lattice vectors of the supercell. Using the Eqs. (5)–(7), we can recast the canonical partition function in Eq. (1) in field-theoretic representation, which results in

$$\begin{aligned}Z(n,V,\beta)=Z_0\int \mathcal{D}w\exp\Bigg[-\frac{1}{2\beta V^2}\\ \times\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'w(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\Bigg]\mathcal{Q}^n[iw],\end{aligned} \tag{8}$$

where

$$Z_0=\frac{1}{n!}\left(\frac{\exp(\beta/2N\overline{\Phi}(0))Z'}{\lambda^{3N}(T)}\right)^n \tag{9}$$

can be interpreted as the partition function for an ideal gas of non-interacting polymers and

$$Z'=\int \mathcal{D}\mathbf{R}\exp[-\beta U_0(\mathbf{R})] \tag{10}$$

is the path integral of a free polymer in a zero field with elastic energy

$$U_0[\mathbf{R}]=\frac{k_{\mathrm{B}}T}{4R_{g0}^2}\int_0^1 \mathrm{d}s\left|\frac{\mathrm{d}\mathbf{R}(s)}{\mathrm{d}s}\right|^2. \tag{11}$$

It is worth considering that in the latter equation the unperturbed radius of gyration of a chain $R_{g0}=\sqrt{Nb^2/(2d)}$, where the space dimension $d=3$. Moreover, in Eq. (8) the partition function of a single polymer, subjected to the field $w(\mathbf{R})$, is given by

$$Q[iw]=\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}. \tag{12}$$

To derive the grand canonical partition function, we use its standard thermodynamic relation to the canonical partition function [43],

$$\Xi(\mu,V,\beta)=\sum_{n=0}^{\infty}\mathrm{e}^{\beta\mu n}Z(n,V,\beta), \tag{13}$$

where $Z(n,V,\beta)$ is given by Eq. (8). After performing the sum, this provides the field-theoretic representation of the grand canonical partition function,

$$\Xi(\xi,V,\beta)=\gamma_{\overline{\Phi}}\int \mathcal{D}w\exp[-S[w]], \tag{14}$$

where

$$S[w]=\frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')-\xi Q[iw] \tag{15}$$

is the grand canonical action with $Q[iw]$ defined by Eq. (12) and the constant

$$\gamma_{\overline{\Phi}}=\frac{1}{\sqrt{2}}\prod_{\mathbf{G}}\left(\frac{1}{\pi\beta\overline{\Phi}(\mathbf{G})}\right)^{1/2}. \tag{16}$$

Moreover, the parameter related to the chemical potential is given by

$$\xi=\frac{\exp(\beta\mu+\beta/2N\overline{\Phi}(0))Z'}{\lambda^{3N}(T)}, \tag{17}$$

where Z' is provided by Eq. (10).

2.2. Gaussian equivalent representation and its 0th-order approximation

To derive the GER of the grand canonical partition function, let us consider the partition function integral in Eq. (14) and perform the following shift of the integration contour by invoking Cauchy's integral theorem [29]

$$w(\mathbf{r})\rightarrow w(\mathbf{r})+i\psi^{\mathrm{GER}}(\mathbf{r}), \tag{18}$$

where $\psi^{\mathrm{GER}}(\mathbf{r})$ represents the shifting function of the partition function integral. We then get

$$\begin{aligned}\Xi(\xi,V,\beta)=\gamma_{\overline{\Phi}}\exp\Bigg[\frac{1}{2\beta V^2}\\ \times\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')\psi^{\mathrm{GER}}(\mathbf{r}')\Bigg]\\ \times\int \mathcal{D}w\exp\Bigg[-\frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'w(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\\ -\frac{i}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\\ +\xi Q\left[i\left(w+i\psi^{\mathrm{GER}}\right)\right]\Bigg],\end{aligned} \tag{19}$$

where $Q[i(w+i\psi^{\mathrm{GER}})]$ is defined via Eq. (12). To derive the GER, we employ the procedure of Efimov and Ganbold [40] and introduce the Gaussian measure $\mathcal{D}\mu_{\overline{\Phi}}[w]$ related to the potential of mean force $\overline{\Phi}$,

$$\mathcal{D}\mu_{\overline{\Phi}}[w] = \gamma_{\overline{\Phi}}\mathcal{D}w\exp\left[-\frac{1}{2\beta V^2}\times\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\right], \tag{20}$$

as well as the normal product with regard to this measure via the relations

$$:\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_{\overline{\Phi}} = \exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]\times\exp\left(\frac{1}{2}\beta N\overline{\Phi}(0)\right),$$
$$w(\mathbf{R}(s))w(\mathbf{R}'(s')) = :w(\mathbf{R}(s))w(\mathbf{R}'(s')):_{\overline{\Phi}} + \beta\overline{\Phi}(\mathbf{R}(s)-\mathbf{R}'(s')). \tag{21}$$

This implies that

$$\int \mathcal{D}\mu_{\overline{\Phi}}[w] :\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_{\overline{\Phi}} = 1. \tag{22}$$

Inserting the Eqs. (20) and (21) into Eq. (19), we obtain

$$\Xi(\xi,V,\beta) = \exp\left[\frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')\psi^{\mathrm{GER}}(\mathbf{r}')\right]\times\int \mathcal{D}\mu_{\overline{\Phi}}[w]\exp\left[-\frac{i}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\times\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}') + z\mathcal{Q}\left[i\left(w+i\psi^{\mathrm{GER}}\right)\right]\right], \tag{23}$$

where

$$\mathcal{Q}\left[i\left(w+i\psi^{\mathrm{GER}}\right)\right] = \frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{GER}(\mathbf{R}(s))\right] :\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_{\overline{\Phi}}}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]} \tag{24}$$

and the polymer activity $z = \xi\exp(-\beta/2N\overline{\Phi}(0))$. The basic idea of the method of GER is to concentrate the main contribution to the partition function integral in a Gaussian measure related to a modified potential $D(\mathbf{r})$ by employing the concept of tadpole renormalization [40]. By considering Eq. (20), the new Gaussian measure can be formulated as

$$\mathcal{D}\mu_D[\sigma] = \gamma_D\mathcal{D}w\exp\left[-\frac{1}{2\beta V^2}\times\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})D^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\right], \tag{25}$$

where the normalization constant γ_D is obtained just be replacing $\Phi(\mathbf{G})$ with $D(\mathbf{G})$ in Eq. (16). Moreover, the normal product according to this measure is defined similar to Eq. (21), which implies that

$$:\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_D = A^{-1}:\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_{\overline{\Phi}} \tag{26}$$

with $A = \exp(1/2\beta N(\overline{\Phi}(0) - D(0)))$. Introducing the Eqs. (25) and (26) into Eq. (23), we obtain for the grand canonical partition function

$$\Xi(\xi,V,\beta) = \frac{\gamma_{\overline{\Phi}}}{\gamma_D}\exp\left[\frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')\times\psi^{\mathrm{GER}}(\mathbf{r}')\right]\times\int \mathcal{D}\mu_D[w]\exp[W_{\mathrm{int}}], \tag{27}$$

with

$$W_{\mathrm{int}} = -\frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})\left(\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}') - D^{-1}(\mathbf{r}-\mathbf{r}')\right)w(\mathbf{r}') - \frac{i}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}') + zA\mathcal{Q}\left[i\left(w+i\psi^{\mathrm{GER}}\right)\right] \tag{28}$$

and

$$\mathcal{Q}\left[i\left(w+i\psi^{\mathrm{GER}}\right)\right] = \frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right] :\exp\left[-iN\int_0^1 \mathrm{d}s\,w(\mathbf{R}(s))\right]:_D}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}, \tag{29}$$

while

$$\frac{\gamma_D}{\gamma_{\overline{\Phi}}}=\prod_{\mathbf{G}}\left(\frac{\overline{\Phi}(\mathbf{G})}{D(\mathbf{G})}\right)^{1/2}. \tag{30}$$

Afterwards, we expand in Eq. (29) the exponential term within the double dots in a Taylor series up to second order and take into account the properties of the normal product given in the Eqs. (21). We then obtain for the exponential term

$$:\exp\left[-iN\int_0^1 \mathrm{d}s\, w(\mathbf{R}(s))\right]:_D = 1 - iN\int_0^1 w(\mathbf{R}(s))\,\mathrm{d}s - \frac{N^2}{2}\int_0^1\int_0^1 :w(\mathbf{R}(s))w(\mathbf{R}(s')):_D\ \mathrm{d}s\,\mathrm{d}s' + :\exp_2\left[-iN\int_0^1 \mathrm{d}s\, w(\mathbf{R}(s))\right]:_D, \tag{31}$$

where the latter contribution contains all expansion terms beyond second order. Inserting the previous expression into Eq. (29) and making use of the second relation of the Eqs. (21), we can rewrite Eq. (28) as

$$\begin{aligned}
W_{\text{int}} = {} & zA\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{\text{GER}}(\mathbf{R}(s))\right] :\exp_2\left[-iN\int_0^1 \mathrm{d}s\, w(\mathbf{R}(s))\right]:_D}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]} \\
& + \left\{ zA\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{\text{GER}}(\mathbf{R}(s))\right]}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]} - \frac{1}{2V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\left(\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}') - D^{-1}(\mathbf{r}-\mathbf{r}')\right)D(\mathbf{r}-\mathbf{r}')\right\} \\
& - \left\{ zAiN\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{\text{GER}}(\mathbf{R}(s))\right]\int_0^1 w(\mathbf{R}(s))\,\mathrm{d}s}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]} + \frac{i}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\text{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')\right\} \\
& - :\left\{ zA\frac{N^2}{2}\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}] + N\int_0^1 \mathrm{d}s\,\psi^{\text{GER}}(\mathbf{R}(s))\right]\int_0^1\int_0^1 w(\mathbf{R}(s))w(\mathbf{R}(s'))\,\mathrm{d}s\,\mathrm{d}s'}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]} \right. \\
& \left. + \frac{1}{2\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})\left(\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}') - D^{-1}(\mathbf{r}-\mathbf{r}')\right)w(\mathbf{r}')\right\}:_D .
\end{aligned} \tag{32}$$

In order to concentrate the main contribution to the partition function integral in the Gaussian measure $\mathcal{D}\mu_D[w]$, the linear and quadratic terms in the field $w(\mathbf{r})$ in Eq. (32) should vanish. These requirements lead to the so-called GER equations in the following form:

$$zAN\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1 w(\mathbf{R}(s))\,\mathrm{d}s}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}+\frac{1}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')w(\mathbf{r}')=0,$$

$$zAN^2\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1\int_0^1 w(\mathbf{R}(s))w(\mathbf{R}(s'))\,\mathrm{d}s\,\mathrm{d}s'}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}$$

$$+\frac{1}{\beta V^2}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,w(\mathbf{r})\left(\overline{\Phi}^{-1}\left(\mathbf{r}-\mathbf{r}'\right)-D^{-1}\left(\mathbf{r}-\mathbf{r}'\right)\right)w(\mathbf{r}')=0, \tag{33}$$

which can easily be reformulated as

$$\psi^{\mathrm{GER}}(\mathbf{r})=-zAN\beta\times\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1 \overline{\Phi}(\mathbf{R}(s)-\mathbf{r})\,\mathrm{d}s}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]},$$

$$D(\mathbf{r}-\mathbf{r}')=\overline{\Phi}(\mathbf{r}-\mathbf{r}')-zAN^2\beta\times\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1\int_0^1 D(\mathbf{R}(s)-\mathbf{r})\overline{\Phi}(\mathbf{r}'-\mathbf{R}(s'))\,\mathrm{d}s\,\mathrm{d}s'}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}. \tag{34}$$

In Fourier representation the previous equations give

$$\psi^{\mathrm{GER}}(\mathbf{G})=-zAN\beta\overline{\Phi}(\mathbf{G})\times\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1 \exp[i\mathbf{G}\mathbf{R}(s)]\,\mathrm{d}s}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]},$$

$$D(\mathbf{G})=\overline{\Phi}(\mathbf{G})-zAN^2\beta\overline{\Phi}(-\mathbf{G})D(\mathbf{G})\times\frac{\int \mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1 \mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]\int_0^1\int_0^1 \exp[i\mathbf{G}(\mathbf{R}(s)-\mathbf{R}(s'))]\,\mathrm{d}s\,\mathrm{d}s'}{\int \mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}. \tag{35}$$

As a result, we obtain a new exact field representation of the grand canonical partition function, namely its Gaussian equivalent representation GER,

$$\Xi(\xi,V,\beta)=\mathrm{e}^{-\beta\Omega^0_{\mathrm{GER}}}\int D\mu_D[w]\exp\left[zA\frac{\displaystyle\int\mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1\mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]:\exp_2\left[-iN\int_0^1\mathrm{d}s\,w(\mathbf{R}(s))\right]:_D}{\displaystyle\int\mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]}\right],\tag{36}$$

with the 0th-order GER approximation (GER0) of the grand canonical free energy

$$\begin{aligned}\Omega^0_{\mathrm{GER}}={}&\frac{1}{\beta}\ln\frac{\gamma_D}{\gamma_{\overline{\Phi}}}-\frac{1}{2\beta^2V^2}\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\psi^{\mathrm{GER}}(\mathbf{r})\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')\psi^{\mathrm{GER}}(\mathbf{r}')\\&+\frac{1}{2\beta V^2}\int\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\left(\overline{\Phi}^{-1}(\mathbf{r}-\mathbf{r}')-D^{-1}(\mathbf{r}-\mathbf{r}')\right)D(\mathbf{r}-\mathbf{r}')\\&-\frac{zA}{\beta}\frac{\displaystyle\int\mathcal{D}\mathbf{R}\exp\left[-\beta U_0[\mathbf{R}]+N\int_0^1\mathrm{d}s\,\psi^{\mathrm{GER}}(\mathbf{R}(s))\right]}{\displaystyle\int\mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]},\end{aligned}\tag{37}$$

where the ratio $\gamma_D/\gamma_{\overline{\Phi}}$ is given by Eq. (30). It is worth noting at this stage that the GER provides an optimized representation of the partition function integral by increasing the influence of the quadratic term in the action with respect to the oscillatory interaction functional. As a consequence, the GER possesses better approximation characteristics [14,15,42] and statistical convergence properties [23,29], than the original field-theoretic representation defined in Eq. (14). In the following we further assume that the shifting function is homogeneous and translation invariant, i.e.

$$\psi^{\mathrm{GER}}(\mathbf{r})=\psi^{\mathrm{GER}}(\mathbf{G}=0)=\text{const.},\ \ D(\mathbf{r},\mathbf{r}')=D(\mathbf{r}-\mathbf{r}').\tag{38}$$

Inserting the Eqs. (38) into the Eqs. (35), we can rewrite the GER equations as

$$\begin{aligned}\psi^{\mathrm{GER}}(\mathbf{G}=0)={}&-\beta N\overline{\Phi}(\mathbf{G}=0)\xi\exp[-\beta/2ND(0)]\\&\times\exp\left[N\psi^{\mathrm{GER}}(\mathbf{G}=0)\right],\end{aligned}$$

$$\begin{aligned}D(\mathbf{G})={}&\overline{\Phi}(\mathbf{G})-zAN^2\beta\overline{\Phi}(-\mathbf{G})D(\mathbf{G})\exp\left[N\psi^{\mathrm{GER}}(\mathbf{G}=0)\right]\\&\times\frac{\displaystyle\int\mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]\int_0^1\int_0^1\exp[i\mathbf{G}(\mathbf{R}(s)-\mathbf{R}(s'))]\,\mathrm{d}s\,\mathrm{d}s'}{\displaystyle\int\mathcal{D}\mathbf{R}\exp[-\beta U_0[\mathbf{R}]]},\end{aligned}\tag{39}$$

with $D(0)=\sum_{\mathbf{G}}D(\mathbf{G})$ and $A=\exp(1/2\beta N(\overline{\Phi}(0)-D(0)))$. Moreover, inserting the Eqs. (38) into Eq. (37), we obtain for the GER0 approximation of the grand canonical free energy

$$\begin{aligned}\Omega^0_{\mathrm{GER}}(\xi,V,\beta,N)={}&\frac{1}{2\beta}\sum_{\mathbf{G}}\ln\left(\frac{\overline{\Phi}(\mathbf{G})}{D(\mathbf{G})}\right)-\frac{\psi^{\mathrm{GER2}}(\mathbf{G}=0)}{2\beta^2\overline{\Phi}(\mathbf{G}=0)}\\&+\frac{N\psi^{\mathrm{GER}}(\mathbf{G}=0)}{2\beta\overline{\Phi}(\mathbf{G}=0)}D(0)\\&-\frac{\xi}{\beta}\exp\left[N\psi^{\mathrm{GER}}(\mathbf{G}=0)\right]\exp\left[-\frac{\beta}{2}ND(0)\right],\end{aligned}\tag{40}$$

where the GER potential $D(\mathbf{G})$ and the shifting function $\psi^{\mathrm{GER}}(\mathbf{G}=0)$ are given by the Eqs. (39), while the chemical potential related parameter is provided by Eq. (17). Finally, the GER0 approximation of the grand canonical partition function can be obtained via

$$\Xi^0_{\mathrm{GER}}=\exp[-\beta\Omega^0_{\mathrm{GER}}],\tag{41}$$

where Ω^0_{GER} is given by Eq. (40).

2.3. Monomer interaction model

To describe the inter-monomer interactions, we make use of the Derjaguin–Landau–Verwey–Overbeek (DLVO) potential [44,45], whose electrostatic part arises as an approximate solution to the Poisson–Boltzmann equation. By neglecting its long-range attractive contribution, we can write it as [44–46]

$$\overline{\Phi}(r)=\frac{z_{\mathrm{M}}^2A(\kappa,a)}{\beta}\left(\frac{\lambda_{\mathrm{B}}}{r}\right)\exp(-\kappa r),\tag{42}$$

with $r=|\mathbf{r}|$ as the distance between the monomer centers and $\lambda_{\mathrm{B}}=e^2/(\epsilon k_{\mathrm{B}}T)$ as the Bjerrum length, where e and ϵ denote, respectively, the elementary charge and the dielectric constant of the suspending medium. Moreover, we take into account that z_{M} is the monomer charge number and

$$A(\kappa,a)=\left(\frac{\exp(\kappa a/2)}{1+\kappa a/2}\right)^2\tag{43}$$

the geometrical factor, where a is the radius of the sphere representing the excluded volume of a monomer. The screening parameter κ governs the range of interactions and is given by

$$\kappa = \sqrt{4\pi\lambda_{\mathrm{B}} I} \tag{44}$$

with the total ionic strength

$$I = \sum_i z_i^2 \langle \rho_i \rangle, \tag{45}$$

where the sum runs over all microionic species involved in the system. In case of a PE system with one type of counterions with density ρ_{m} and salt ions with the density ρ_{s} the ionic strength can be written as

$$I = z_{\mathrm{m}}^2 \langle \rho_{\mathrm{m}} \rangle + z_{\mathrm{s}}^2 \langle \rho_{\mathrm{s}} \rangle = z_{\mathrm{m}}^2 N \langle \rho \rangle + z_{\mathrm{s}}^2 \langle \rho_{\mathrm{s}} \rangle, \tag{46}$$

where $N\langle\rho\rangle$ is the density of counterions with charge number z_{m} and $\langle\rho_s\rangle$ is the density of salt ions with charge number z_{s}^2. Note that, since the potential in Eq. (42) is singular at the origin, we regularize it by the replacement $\overline{\Phi}(r) \to \overline{\Phi}(r+\epsilon)$ with ϵ as a vanishingly small parameter, which is taken into account implicitly [13]. The Fourier transform of the interaction potential is given by

$$\tilde{\overline{\Phi}}(\mathbf{G}) = \int_V \overline{\Phi}(\mathbf{r}) \exp[-i\mathbf{G}\mathbf{r}]\, \mathrm{d}\mathbf{r} = A(\kappa, A)\, \tilde{\overline{\Phi}}_{a=0}(\mathbf{G}), \tag{47}$$

where

$$\tilde{\overline{\Phi}}_{a=0}(\mathbf{G}) = \frac{4\pi z_{\mathrm{M}}^2 \lambda_{\mathrm{B}}}{\beta\left(|\mathbf{G}|^2 + \kappa^2\right)}, \tag{48}$$

with $\tilde{\overline{\Phi}}(\mathbf{G}) = \overline{\Phi}(\mathbf{G})V$. It is worth noting that, at small to moderate PE concentrations, the geometrical factor $A(\kappa, a)$ is independent of κ and a, providing

$$A(\kappa, a) \approx 1. \tag{49}$$

In contrast at larger concentrations it gives approximately

$$A(\kappa, a) \approx \left(\frac{1 + \kappa a/2 + 1/2(\kappa a/2)^2}{1 + \kappa a/2} \right)^2 = \left(1 + \frac{1}{2}\left[\frac{(\kappa a/2)^2}{1 + \kappa a/2} \right] \right)^2 \tag{50}$$

with $\kappa a/2 \gg 1$, so that

$$A(\kappa, a) \approx \left(1 + \frac{1}{4}\kappa a \right)^2 \approx \frac{\kappa^2 a^2}{16}. \tag{51}$$

Therefore, for large κ, $\overline{\Phi}(\mathbf{r})$ provides a pair potential of delta-function type [47].

2.4. Thermodynamic quantities within the GER0 approach

The thermodynamic and structural quantities within the GER0 approach can be derived in two ways, i.e. via the free energy route (F-route) and the radial distribution function route (g(r)-route). In the F-route the standard thermodynamic relations [43] are used in conjunction with the GER0 approximation of the grand canonical free energy in Eq. (40) or equivalently the grand canonical partition function in Eq. (41), while in the g(r)-route the standard thermodynamic expressions defined via the radial distribution function are employed [15]. For example, to derive the average density of polymer chains within the F-route, we make use of the following formula:

$$\langle \rho \rangle = \frac{\xi}{V} \frac{1}{\Xi(\xi, V, \beta)} \left(\frac{\partial \Xi(\xi, V, \beta)}{\partial \xi} \right)_{V,\beta}. \tag{52}$$

Inserting the GER0 approximation of the partition function, given in Eq. (41), into Eq. (52), we get

$$\begin{aligned} \langle \rho \rangle_{\mathrm{GER}}^0 &= -\frac{\psi^{\mathrm{GER}}(\mathbf{G}=0)}{NV\beta\overline{\Phi}(\mathbf{G}=0)} \\ &= \frac{\xi}{V} \exp\left[N\psi^{\mathrm{GER}}(\mathbf{G}=0)\right] \exp\left[-\frac{\beta}{2} N D(0)\right]. \end{aligned} \tag{53}$$

Next, inserting the previous expression into Eq. (40), we can reformulate the GER0 approximation of the grand canonical free energy as

$$\begin{aligned} \Omega_{\mathrm{GER}}^0 = &- \frac{1}{2} N^2 V^2 \langle \rho \rangle_{\mathrm{GER}}^{0\;2} \overline{\Phi}(\mathbf{G}=0) - \frac{V \langle \rho \rangle_{\mathrm{GER}}^0}{\beta} \\ &+ \frac{1}{2\beta} \sum_{\mathbf{G}} \ln\left[1 + \beta N^2 V \langle \rho \rangle_{\mathrm{GER}}^0 \overline{\Phi}(\mathbf{G})\right] \\ &- \frac{1}{2} N^2 V \langle \rho \rangle_{\mathrm{GER}}^0 \sum_{\mathbf{G}} \frac{\overline{\Phi}(\mathbf{G})}{\left[1 + \beta N^2 V \langle \rho \rangle_{\mathrm{GER}}^0 \overline{\Phi}(\mathbf{G})\right]}. \end{aligned} \tag{54}$$

The osmotic pressure can now easily be derived via the standard thermodynamic relation $\prod_{\mathrm{GER}}^0 = -\Omega_{\mathrm{GER}}^0/V$ by inserting into it Eq. (54), which leads to

$$\begin{aligned} \frac{\Pi_{\mathrm{GER}}^0}{RT} = &\frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2} B \mathcal{C}_{\mathrm{m}}^2 \upsilon(\mathbf{G}=0) \\ &- \frac{1}{2N_{\mathrm{A}}V} \sum_{\mathbf{G}} \ln[1 + \mathcal{B} N \mathcal{C}_{\mathrm{m}} \upsilon(\mathbf{G})] \\ &+ \frac{1}{2N_{\mathrm{A}}V} \sum_{\mathbf{G}} \frac{\mathcal{B} N \mathcal{C}_{\mathrm{m}} \upsilon(\mathbf{G})}{[1 + \mathcal{B} N \mathcal{C}_{\mathrm{m}} \upsilon(\mathbf{G})]}, \end{aligned} \tag{55}$$

where $\mathcal{B} = \tilde{\overline{\Phi}}_{a=0}(\mathbf{G}=0) N_{\mathrm{A}} \beta$ with N_{A} as the Avogadro constant and $\upsilon(\mathbf{G}) = \overline{\Phi}(\mathbf{G})/\overline{\Phi}_{a=0}(\mathbf{G}=0)$. Moreover, we have defined the monomolar concentration as $\mathcal{C}_{\mathrm{m}} = N N_{\mathrm{A}}^{-1} \langle \rho \rangle$ with the average polymer density given by Eq. (53). Next, let us suppose that in the thermodynamic limit, we can perform the replacement $\sum_{\mathbf{G}} \to \left[V/(2\pi)^3\right] \int \mathrm{d}\mathbf{G}$ and rewrite the osmotic pressure as a sum of a MF contribution and a fluctuation term F, which yields

$$\frac{\Pi^0_{\mathrm{GER}}}{RT} = \frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2}A(\kappa,a)B\mathcal{C}^2_{\mathrm{m}} - \mathcal{F}, \tag{56}$$

where

$$\mathcal{F} = \frac{1}{2}\frac{1}{(2\pi)^3 N_{\mathrm{A}}}\int \mathrm{d}\mathbf{G}\left\{\ln[1+\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})] - \frac{\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})}{[1+\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})]}\right\}. \tag{57}$$

Next, we analytically integrate the fluctuation integral (see Appendix A) and obtain

$$\mathcal{F} = \frac{\kappa^3}{24\pi N_{\mathrm{A}}}\left\{2+\sqrt{1+A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}}}\,(A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}}-2)\right\}. \tag{58}$$

In the regime where $A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}}$ is large, the fluctuation term can be simplified to $\mathcal{F} \approx \kappa^3(A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}})^{3/2}/(24\pi N_{\mathrm{A}})$, and we finally get for the osmotic pressure

$$\frac{\Pi^0_{\mathrm{GER}}}{RT} \approx \frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2}A(\kappa,a)B\mathcal{C}^2_{\mathrm{m}} - \frac{\kappa^3}{24\pi N_{\mathrm{A}}}(A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}})^{3/2}. \tag{59}$$

In case of neutral polymer solutions in the regime of large monomolar concentrations $\mathcal{C}_{\mathrm{m}}$, the fluctuation term $\mathcal{F}$ in the previous expression is small compared to the MF contribution $1/2\,A(\kappa,a)B\mathcal{C}^2_{\mathrm{m}}$. This defines the so-called concentrated regime of neutral polymer solutions, whose importance and relation to PE solutions will be discussed in the forthcoming sections. Moreover, it is worth noting that, in contrast to the Gaussian fluctuation correction procedure to the MF approximation or random phase approximation (RPA) [7], the GER0 procedure provides the osmotic pressure formula in Eq. (59) to lowest order. Higher-order corrections can easily be derived using the correction procedure described by Eq. (19) in Ref. [37]. When $\mathcal{C}_{\mathrm{m}} \to \infty$ at fixed B, N, $A(\kappa,a)$ and κ, the MF term,

$$\frac{\Pi^0_{\mathrm{MF}}}{RT} \approx \frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2}A(\kappa,a)\mathcal{B}\mathcal{C}^2_{\mathrm{m}}, \tag{60}$$

provides the dominant contribution to the osmotic pressure, and the fluctuation term is asymptotically negligible. This can be explained by the fact that with increasing concentration the inter-monomer interactions effectively screen each other and the MF contribution becomes dominant with respect to the fluctuations, reflecting the correlated motion of the monomers. Analogously as in the case of neutral polymer solutions [7], we can reexpress the fluctuation term in Eq. (59) by introducing a correlation length

$$\zeta = (\kappa^2 A(\kappa,a)\mathcal{B}N\mathcal{C}_{\mathrm{m}})^{-1/2}. \tag{61}$$

It can easily be demonstrated that ζ represents the dominant length scale in a concentrated PE solution over which the segment density fluctuations are correlated [7]. With the previous definition, the osmotic pressure can alternatively be written as

$$\frac{\Pi^0_{\mathrm{GER}}}{RT} \approx \frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2}A(\kappa,a)\mathcal{B}\mathcal{C}^2_{\mathrm{m}} - \frac{1}{24\pi N_{\mathrm{A}}\zeta^3}. \tag{62}$$

According to de Gennes [48], regions (blobs) of characteristic volume ζ^3 fluctuate independently because segment density fluctuations are only correlated over a length scale of order ζ. By equipartition, each such region has an energy of order of the thermal energy $k_{\mathrm{B}}T$, which implies that the fluctuation contribution to the osmotic pressure in the concentrated regime should scale as $k_{\mathrm{B}}T/\zeta^3$.

2.5. Hartree renormalization

As already mentioned previously, the standard GER0 approximation of the osmotic pressure, given in Eq. (59), is only accurate at higher PE concentrations, which usually does not correspond to the range of physical interest of most biological and technological applications. At lower PE concentrations, this simple approximation procedure does not provide physically useful results, since the osmotic pressure can become negative. To solve the problem, we make use of a renormalization procedure widely employed in field theory, which is commonly referred to as the Hartree approximation [35,36]. We will use this procedure in conjunction with the GER0 theory, to derive viable expressions for the osmotic pressure in lower concentration regimes. In essence it consists in allowing the correlation length in the expression (62) of the osmotic pressure to be determined self-consistently as a part of the calculation. To implement this renormalization procedure, we simply reformulate the osmotic pressure formula in Eq. (56) as

$$\frac{\Pi^0_{\mathrm{GER}}}{RT} \approx \frac{\mathcal{C}_{\mathrm{m}}}{N} + \frac{1}{2}A(\kappa,a)\mathcal{B}_{\mathrm{r}}\mathcal{C}^2_{\mathrm{m}}, \tag{63}$$

where

$$\mathcal{B}_{\mathrm{r}} = \mathcal{B} - \frac{1}{2\pi^2 N_{\mathrm{A}} A(\kappa,a)\mathcal{C}^2_{\mathrm{m}}}\int_0^\infty \mathrm{d}G\,G^2\left\{\ln[1+\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})] - \frac{\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})}{[1+\mathcal{B}N\mathcal{C}_{\mathrm{m}}\upsilon(\mathbf{G})]}\right\}. \tag{64}$$

The Hartree renormalization is now realized by replacing $\mathcal{B}$ with $\mathcal{B}_{\mathrm{r}}$ inside the fluctuation integral of Eq. (64), which amounts to the assumption that the dominant length scale for segment density fluctuations is given by the renormalized correlation length

$$\zeta_{\mathrm{r}} = (\kappa^2 A(\kappa,a)\mathcal{B}_{\mathrm{r}}N\mathcal{C}_{\mathrm{m}})^{-1/2}. \tag{65}$$

By evaluating the integral in Eq. (64) with this replacement through using the same procedure as in Appendix A and considering that $A(\kappa,a)\mathcal{B}N\mathcal{C}_\mathrm{m}$ is large, we obtain

$$\mathcal{B}_\mathrm{r} = \mathcal{B} - \frac{1}{12\pi N_\mathrm{A}} A^{1/2}(\kappa,a)\mathcal{B}_\mathrm{r}^{3/2} N^{3/2}\mathcal{C}_\mathrm{m}^{-1/2}\kappa^3. \tag{66}$$

Next, we define $x = \mathcal{B}_\mathrm{r}^{1/2}$ and can easily see that this equation is a cubic equation in $\mathcal{B}_\mathrm{r}^{1/2}$ that can be solved analytically. For large N and $\mathcal{B}$ the cubic equation in Eq. (66) provides the real root as (see Appendix B)

$$\mathcal{B}_\mathrm{r} \approx (12\pi N_\mathrm{A})^{2/3} A^{-1/3}(\kappa,a)\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{1/3}\kappa^{-2}. \tag{67}$$

Substitution of this result into Eq. (65) produces the renormalized correlation length

$$\zeta_\mathrm{r} \approx (12\pi N_\mathrm{A})^{-1/3}\left(A^{2/3}(\kappa,a)\mathcal{B}^{2/3}\mathcal{C}_\mathrm{m}^{4/3}\right)^{-1/2}. \tag{68}$$

Analogously, substituting Eq. (67) into Eq. (63) yields the osmotic pressure as

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{\mathcal{C}_\mathrm{m}}{N} + \frac{(12\pi N_\mathrm{A})^{2/3}}{2} A^{2/3}(\kappa,a)\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{7/3}\kappa^{-2}. \tag{69}$$

It can easily be deduced from Eq. (69) that in the dilute regime of PE solutions, where $\mathcal{C}_\mathrm{m} \to 0$, the ideal gas term is dominant, which consequently leads to

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{\mathcal{C}_\mathrm{m}}{N}. \tag{70}$$

In contrast, at higher PE concentration the interaction term is dominant over the ideal gas term and the osmotic pressure results in

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{(12\pi N_\mathrm{A})^{2/3}}{2} A^{2/3}(\kappa,a)\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{7/3}\kappa^{-2}, \tag{71}$$

where $\kappa^2 = 4\pi\lambda_\mathrm{B} I$ with $I = z_\mathrm{m}^2 N_\mathrm{A}\mathcal{C}_\mathrm{m} + z_\mathrm{s}^2 N_\mathrm{A}\mathcal{C}_\mathrm{s}$ and $\mathcal{C}_\mathrm{s} = N_\mathrm{A}^{-1}\langle\rho_\mathrm{s}\rangle$. To derive an expression for the osmotic pressure of a system of PEs without salt in the semidilute regime, we take into account that $\mathcal{C}_\mathrm{s} = 0$ in the previous equations and, thus, get

$$\kappa^2 = 4\pi\lambda_\mathrm{B} z_\mathrm{m}^2 N_\mathrm{A}\mathcal{C}_\mathrm{m}. \tag{72}$$

Inserting this expression as well as $A(\kappa,a) \approx 1$ into Eq. (71), we get the osmotic pressure as

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{(12\pi)^{2/3}}{8\pi\lambda_\mathrm{B} z_\mathrm{m}^2 N_\mathrm{A}^{1/3}}\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{4/3}, \tag{73}$$

where $\mathcal{B} = z_\mathrm{M}^2/(z_\mathrm{m}^2\mathcal{C}_\mathrm{m})$. In this case $\mathcal{B}$ is a constant if we replace the charge number of the monomers z_M by a renormalized charge number $\bar{z}_\mathrm{M}$ and assume that, due to the interplay of chain self-contraction and counterion condensation, each monomer interact with increasing strength with the cloud of the surrounding monomers as the concentration of the monomers grows, which implies that $\bar{z}_\mathrm{M}^2 \sim N N_\mathrm{A}^{-1}\langle\rho(\mathbf{r})\rangle = \mathcal{C}_\mathrm{m}$. Next, by fitting Eq. (73) to the experimental measurement results of NaPSS PE solutions in the low concentration range, we deduce that the renormalized $\bar{z}_\mathrm{M}^2 \sim \mathcal{C}_\mathrm{m}^{11/16}$, which provides an additional scaling law with exponent 9/8 in the low concentration regime. For a more detailed discussion of the latter issues we refer to Section 3.2. Moreover, we conclude from Eq. (73) that in the semidilute regime the osmotic pressure is almost independent of the polymerization index, since it scales only as $N^{1/3}$, in agreement with experimental observations [4]. By contrast, in the concentrated regime of PEs without salt, we take into account that $A(\kappa,a) \approx \kappa^2 a^2/16$ (see Eq. (51)) and that $\kappa = \kappa_\mathrm{eff}$ is concentration independent due to a complete condensation of the counterions onto the polyions. Inserting both expressions into Eq. (71), we get the osmotic pressure as

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{(192\pi N_\mathrm{A})^{2/3}}{2}\frac{a^{4/3}\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{7/3}}{(\kappa_\mathrm{eff})^{2/3}}. \tag{74}$$

We will see in Section 3 that the scaling of the physical parameters in this case corresponds to the scaling of neutral polymer solutions. In a system of PEs with high concentrations of added salt $z_\mathrm{s}^2 N_\mathrm{A}\mathcal{C}_\mathrm{s} \gg z_\mathrm{m}^2 N_\mathrm{A}\mathcal{C}_\mathrm{m}$ and, thus, $\kappa^2 \approx 4\pi\lambda_\mathrm{B} z_\mathrm{s}^2 N_\mathrm{A}\mathcal{C}_\mathrm{s}$. Employing this expression as well as $A(\kappa,a) \approx 1$ to rewrite Eq. (71), we obtain the osmotic pressure in this latter case as

$$\frac{\Pi^0_\mathrm{GER}}{RT} \approx \frac{(12\pi)^{2/3}}{8\pi\lambda_\mathrm{B} z_\mathrm{s}^2 N_\mathrm{A}^{1/3}\mathcal{C}_\mathrm{s}}\mathcal{B}^{2/3} N^{-1}\mathcal{C}_\mathrm{m}^{7/3}. \tag{75}$$

Since the grand canonical free energy is directly connected to the osmotic pressure via $\Omega^0_\mathrm{GER} = -V\Pi^0_\mathrm{GER}$, we can also readily derive the corresponding expressions for the grand canonical free energy. Higher-order corrections to the Hartree renormalized 0th-order GER (HR-GER0) methodology can easily be obtained using the correction procedure described in Ref. [37] and will be presented in a subsequent work.

3. Results

In the following we assess the reliability of our HR-GER0 approach with respect to osmotic pressure experiments on solutions of sodium poly(styrene-sulfonate) NaPSS without and with added salt. Moreover, we also compare the usefulness of our method against various theoretical approaches, like scaling theory and computer simulation results.

3.1. Comparative scaling laws

Scaling theory has mainly been successful in elucidating the static and dynamic behaviors of neutral polymer and PE solutions with added salt. To derive scaling laws for PE solutions without salt, let us first analyze the case of neutral polymer solutions. In the dilute regime of neutral polymer solutions $\mathcal{C}_\mathrm{m} \ll \mathcal{C}_\mathrm{m}^*$, where $\mathcal{C}_\mathrm{m}^*$ is the so-called overlap concentration specifying the concentration at which the polymer coils pack to fill space with unit volume fraction [7]. In this regime the osmotic pressure can be expressed in form of a virial expansion. If truncated at quadratic order with regard to concentration, we get

$$\frac{\Pi}{RT} \approx \frac{\mathcal{C}_{\mathrm{m}}}{N} + A_2 \mathcal{C}_{\mathrm{m}}^2, \tag{76}$$

where $A_2 = 4\pi^{3/2}\rho(z)N_{\mathrm{A}}R_{\mathrm{F}}^3/N^2$ is the second virial coefficient with $\rho(z)$ as the penetration function, which is a constant in good solvents. The parameter R_{F} is the Flory radius of the polymers representing the radius of a single chain in the good solvent limit, which varies as $R_{\mathrm{F}} \sim N^{3/5}$. According to the scaling approach of des Cloizeaux [49], the osmotic pressure of neutral polymer solutions in the semidilute regime of concentrations, $\mathcal{C}_{\mathrm{m}} \gg \mathcal{C}_{\mathrm{m}}^*$, should obey the following relation

$$\frac{\Pi}{RT} \sim \mathcal{C}_{\mathrm{m}}^{9/4}, \tag{77}$$

and should be independent of the polymerization index N. Odijk [50] argued that the same relations should be valid for semidilute PE solutions in the presence of added salt, provided the influence of the electrostatic interactions between fixed charges on the macromolecular chains is taken into account. He considered a Debye–Hückel (DH) type of interaction potential between the fixed charges with a screening parameter

$$\kappa^2 = 8\pi\lambda_{\mathrm{B}} I, \tag{78}$$

where I is the ionic strength. Odijk gave the osmotic pressure of semidilute PE solutions in the presence of added salt as

$$\frac{\Pi}{RT} \sim \left(\frac{L_{\mathrm{t}}}{\kappa}\right)^{3/4} (A\mathcal{C}_{\mathrm{m}})^{9/4}, \tag{79}$$

where L_{t} is the total persistence length of the charged macromolecules. It has been demonstrated in the Refs. [4,50,51] that the latter quantity may be approximated by a sum of two terms, i.e. $L_{\mathrm{t}} = L_{\mathrm{p}} + L_{\mathrm{e}} = L_{\mathrm{p}} + 1/(4\kappa^2 A^2 f^2)$, where L_{p} is the intrinsic persistence length and L_{e} the electrostatic persistence length, while A represents the linear charge spacing along the chains and f accounts for the effective charge on the PE chains. According to counterion condensation theory [52], one has $f = 1$ if $A > \lambda_{\mathrm{B}}$ and $f = \lambda_{\mathrm{B}}/A$ if $A < \lambda_{\mathrm{B}}$. The scaling approach to PE solutions without added salt, developed by de Gennes et al. [53], distinguished three concentration regimes. At very low concentrations in the dilute regime, these authors considered that the PEs are on average widely separated and, if strongly charged, they should be fully stretched because of the ineffective screening between the polyions. Above a certain critical concentration in the semidilute regime of PE solutions, there is a considerable overlap between chains and a transient network is formed, whose characteristic mean distance (correlation length) between adjacent chains decreases with increasing concentration as $\mathcal{C}_{\mathrm{m}}^{-1/2}$. In this case the electrostatic energy per monomer is of order $k_{\mathrm{B}}T$. According to de Gennes et al., the osmotic pressure contributed from the polyions scales like the free energy per unit volume and is, thus, of order

$$\frac{\Pi}{RT} \sim \mathcal{C}_{\mathrm{m}}. \tag{80}$$

Odijk considered DH screening as being caused by uncondensed counterions only, which implicates that the screening parameter depends on $\mathcal{C}_{\mathrm{m}}$ according to

$$\kappa^2 = 4\pi A\mathcal{C}_{\mathrm{m}}. \tag{81}$$

To derive the osmotic pressure, the Eqs. (81) and (79) are combined to yield the scaling relation [51]

$$\frac{\Pi}{RT} \sim A^{3/8}\mathcal{C}_{\mathrm{m}}^{9/8}. \tag{82}$$

We point out that the scaling exponent in the latter relation is similar to the exponent in expression (80), obtained by de Gennes et al. [53].

3.2. Analysis and discussion

We start our investigations by comparing the results obtained with the theoretical approaches discussed previously to osmotic pressure measurements on NaPSS solutions in water without and with added salt for various molecular weights and a temperature of $T = 298$ K. In Fig. 1 we plot the results obtained for the osmotic pressure as a function of monomolar concentration in the semidilute concentration range, obtained with the HR-GER0 approach as well as the scaling theory from Odijk and de Gennes, in comparison to experimental data of NaPSS solutions at various molecular weights. We point out that the concentration unit monomol/l refers to the concentration of the monomers in solution. We observe that

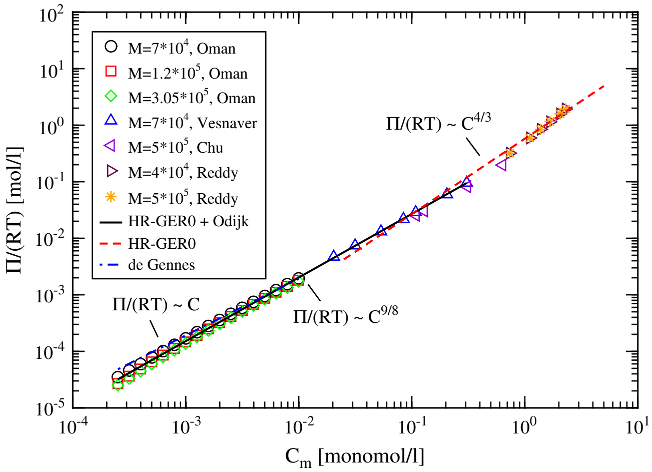

Fig. 1. Osmotic pressure of NaPSS solutions in the semidilute regime as a function of monomolar concentration without added salt at various molecular weights, obtained with the HR-GER0 approach as well as the Odijk and de Gennes scaling theories in comparison to experimental measurement results. Experimental data are taken from Oman [66], Vesnaver and Skerjanc [67], Chu and Marinsky [68], as well as Reddy and Marinsky [69].

at low concentrations the power law with an exponent of 9/8, obtained with the HR-GER0 as well as Odijk approach, fits the experimental data very well, while the scaling law of de Gennes with an exponent of 1 deviates increasingly in the low concentration regime from the experimental results with NaPSS of high molecular weight. Moreover, we recognize that with increasing concentration there is an accelerated increase of the osmotic pressure curve and that at a critical concentration of $C_m^{ICC} \approx 0.1$ monomol/l there is a smooth crossover between the power law with exponent 9/8 to a power law with exponent 4/3. We attribute this smooth crossover to the simultaneous action of the phenomena of screening of the monomer charges and self-contraction of the stretched PE chains, leading to a change of the PE shapes. The effect of electrostatic screening of the monomer charges is undertaken by the counterions, which form a diffuse double layer to neutralize the monomer charges of opposite sign [54,55]. The size of this double layer is roughly given by $1/\kappa$ with κ in the semidilute regime defined by Eq. (72), which implies that the size is inversely proportional to concentration. This dependency of the size of the counterion cloud on concentration can be explained by the fact that only a part of the counterions are condensed onto the sulfonate groups of the NaPSS chains, forming the so-called Stern layer [56]. The rest of the counterions contribute as highly mobile ions to the diffuse double layer surrounding each PE chain, and, therefore, they are responsible for the concentration dependence of the screening length κ in the semidilute regime. The size of this double layer is mainly determined by the competition between the thermal motion of the counterions, which tend to spread out or homogenize their distribution in order to increase their entropy, and the electrostatic interactions, which attract the counterions toward the monomer surfaces while repelling the monomers with charges of same sign [55]. As pointed out by Alexander et al. on the example of systems of charged colloids, the DH potential can be applied to a wide range of concentrations, if the bare macroion (monomer) charge is suitably renormalized [57,58]. The physical concept behind this approach relies on the assumption that counterions can tightly bind (condense) to the fixed surface charges of the macroions and contribute in this way to neutralize the bare macroion charges, leading to smaller effective macroion charges. The counterions will condense onto the charged macroions, until the charge densities adjacent to the macroions are reduced below a certain critical value [52]. This process is also known as the phenomenon of *counterion condensation* and has led in the late 1960s to the development of the counterion condensation theory for PE solutions by Manning [52]. However, in case of PE solutions this effect goes along with the phenomenon of contraction of the PE chains onto themselves as the concentration of the monomers grows, resulting in a rapid increase of the effective monomer charge and monomer interaction. We attribute the change of power law from exponent 9/8 to 4/3 at the critical concentration C^{ICC} to a crossover from outer-chain contraction (OCC) to inner-chain contraction (ICC), caused by changing bending properties along the PE chains due to non-uniform counterion condensation. As recently shown by Rubinstein et al. [59] using computer simulations of dilute PE solutions, the center parts of the chains experience strong stretching due to strong Coulomb repulsion of loosely attached counterions, which act as a supporting corset. In contrast, the counterions at the outer parts of the chains are attached more tightly, leading to a strong screening of the monomer interactions. As a consequence, at the chain ends the entropy of forming a kink is favored over the entropy of elongation due to Coulomb repulsion. This causes that the outer-chain segments are somewhat more flexible than the inner-chain segments and their probability to contract grows with increasing concentration. In their molecular dynamics (MD) simulations Stevens and Kremer [60] observed that the chains contract significantly due to counterion condensation before they overlap, forming PEs with horseshoe shape. They argued that the fraction of condensed counterions increases with polymer concentration, leading to the decrease of the effective charges on the chains and inducing in this way their contraction. As pointed out by Rubinstein et al. [59] as well as Stevens and Kremer [60], the two effects of non-uniform counterion condensation and counterion-mediated chain self-contraction were in the past always ignored in simple scaling theories and, thus, may question their validity. In our HR-GER0 approach these effects are taken into account by renormalizing the monomer charge number in a suitable way. This causes that, besides the length scale associated with the strength of the Coulomb interaction, additional length scales associated with both effects are introduced in our HR-GER0 approach. Next, in Fig. 2 we show the osmotic pressure as a function of monomolar concentration in the high concentration regime, in comparison to experimental measurement results from NaPSS solutions of various molecular weights. We recognize that with increasing concentration the experimental data agree increasingly well with the power laws with the exponents 7/3 and 9/4, obtained using the HR-GER0 approach and scaling theory of des Cloizeaux,

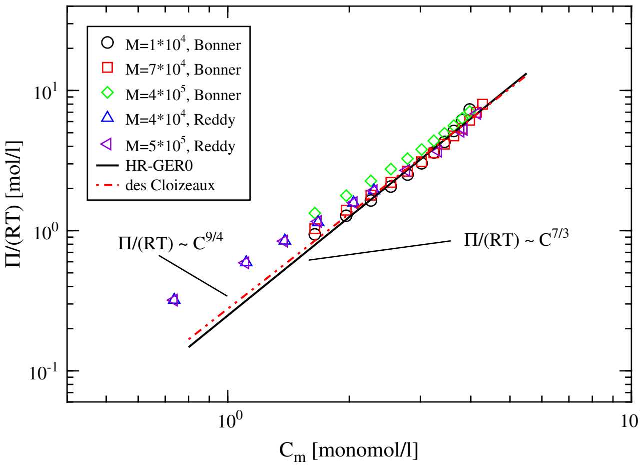

Fig. 2. Osmotic pressure of NaPSS solutions in the high concentration regime as a function of monomolar concentration without added salt at various molecular weights, obtained with the HR-GER0 approach and des Cloizeaux scaling theory in comparison to experimental measurement results. Experimental data are taken from Bonner and Overton [70] as well as Reddy and Marinsky [69].

respectively. A good match is achieved at concentrations starting from $C^{\mathrm{OVP}} \approx 2$ monomol/l, which we consider in the following to be the critical concentration of the crossover from the semidilute to concentrated regime of the NaPSS PE solutions. In the high concentration range the counterions can be assumed to be almost entirely condensed onto the charged surface of the monomers, thereby screening their interactions effectively. As a consequence, the inter-monomer interactions are short-ranged and the screening length becomes independent of concentration. Due to the effective and almost uniform screening of the counterions in this regime, the chains are entirely collapsed onto themselves and form polymer coils, as in case of neutral polymer solutions [7,61,62]. At the critical overlap (OVP) concentration C^{OVP}, the screened PE coils pack to fill the entire space with unit volume fraction and, thus, they can be assumed to overlap with each other. Next, in Fig. 3 we plot the osmotic pressure of dilute NaPSS solutions as a function of monomolar concentration at various molecular weights, obtained with our HR-GER0 approach and the scaling theory of Odijk in comparison to experimental measurement results. We recognize that in the low concentration range the experimental curves, resulting from solutions of NaPSS PEs of different molecular weights, show a considerable scatter. This is a manifestation of the molecular weight dependence of the osmotic pressure, reflecting the polymeric nature of the PE chains in the dilute concentration regime [4]. Moreover, we visualize in the graph the two curves derived for the semidilute regime, obeying a power law with exponent 9/8 and 4/3, respectively, as well as the ideal gas law (i.e. a power-law curve with exponent 1), obtained for a PE system with $N = 1$ in the dilute regime. We observe that the experimental curves with the NaPSS PEs of intermediate molecular weights of $M = 7 \times 10^4$ g/mol and $M = 3.05 \times 10^5$ g/mol obey the theoretically derived power law with exponent 9/8 very well. The experimental curve with higher molecular weight NaPSS, i.e. $M = 3.2 \times 10^5$ g/mol, deviates increasingly with decreasing concentration from the power law with exponent 9/8 and approaches the power law with exponent 4/3 at very low concentrations. In contrast, the experimental curve of the low-molecular weight NaPSS PEs with $M = 2 \times 10^4$ g/mol deviates from the curves of the intermediate molecular weight NaPSS PEs, while being more close to the power law with exponent 1 than the latter curves. In conclusion, we deduce from the graph that the HR-GER0 approach correctly reproduces the molecular weight dependence of NaPSS solutions in the dilute concentration regime and that the ideal gas law is recovered in the limit of short chain lengths. In this regime the strongly charged PEs remain extended and well separated due to the unscreened action of the long-range Coulombic interactions. As a result, the thermodynamic quantities of strongly charged dilute PE solutions are mainly dominated by single chain properties. In this context, it is also worth mentioning that the long-range nature of the inter-monomer interactions causes that the dilute concentration regime is only observed at very low concentrations and, thus, it is difficult to investigate it experimentally [60,63]. Next, in Fig. 4 we visualize the osmotic pressure as a function of monomolar concentration, obtained for solutions of NaPSS PEs of various molecular weights and at a concentration of added salt of $C_s = 0.01$ mol/l. We plot the power laws with exponent 7/3 and 9/4, obtained, respectively, with the HR-GER0 approach and the Odijk scaling theory in comparison to experimental measurement results. We deduce from the graph that at higher concentrations the results from both theories agree well with the experimental data. Finally, in Fig. 5 we show the osmotic pressure as a function of the monomolar concentration for solutions of NaPSS PEs at different molecular weights over the whole concentration range, obtained from the HR-GER0 approach as well as experimental measurements in comparison to the MD simulation results of Stevens and

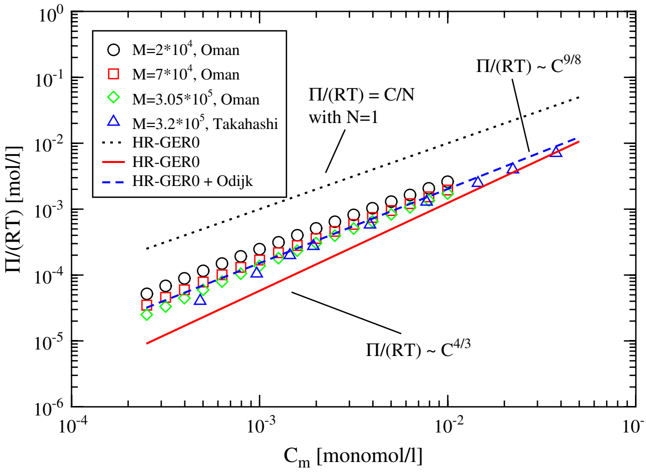

Fig. 3. Osmotic pressure of NaPSS solutions in the dilute concentration regime as a function of monomolar concentration without added salt at various molecular weights, obtained with the HR-GER0 approach as well as Odijk scaling theory in comparison to experimental measurement results. Experimental data are taken from Oman [66] and Takahashi et al. [71].

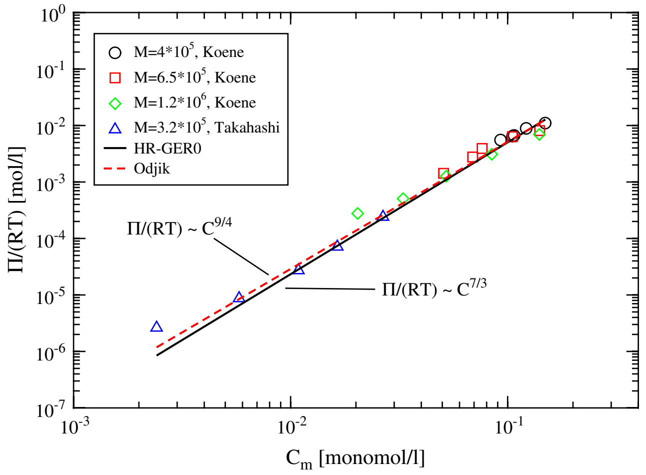

Fig. 4. Osmotic pressure of NaPSS solutions as a function of monomolar concentration with a concentration of added salt of $C_s = 0.01$ mol/l at various molecular weights, obtained with the GER0 approach and Odijk scaling theory in comparison to experimental measurement results. Experimental data are taken from Koene et al. [72] and Takahashi et al. [71].

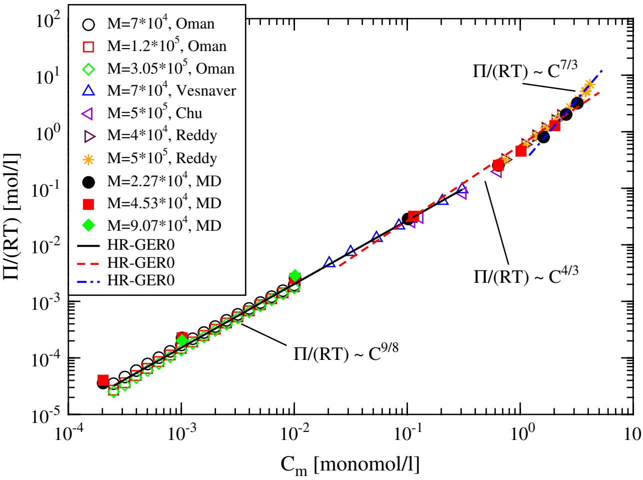

Fig. 5. Osmotic pressure of NaPSS solutions as a function of monomolar concentration over the entire concentration range without added salt and at various molecular weights, obtained with the HR-GER0 approach as well as using the MD method by Stevens and Kremer [57] in comparison to experimental measurement results. Experimental data are taken from Oman [66], Vesnaver and Skerjanc [67], Chu and Marinsky [68], as well as Reddy and Marinsky [69].

Kremer [57]. The latter authors modeled the PE chains as freely-jointed bead-spring chains, where the charged monomers interacted via the DH pair potential, while the solvent was modeled by a dielectric background. The simulations were performed for systems of DH chains with chain lengths of $N = 32$ and $N = 64$ beads, as well as for low densities with a chain length of $N = 128$ beads, while the number of DH chains was either 8 or 16. We mapped the MD simulation results onto systems of NaPSS PEs in water according to the procedure proposed by Stevens and Kremer [57]. We see that, similar to the HR-GER0 results, the MD simulation results of Stevens and Kremer reproduce the experimental osmotic pressure curves well over the entire concentration range. However, it is worth noting that MD simulations with systems of moderate to high PE concentrations can only be achieved for PEs of short chain lengths. This severely limits the scope of application of the MD methodology, since systems of biological and technological interest generally consist of longer PE chains possessing prohibitively long equilibration times [7].

4. Summary and conclusions

In summary, we have demonstrated in this article on the example of a model of flexible PE chains, where the monomers interact via a DLVO-type of pair potential, that the Hartree renormalized GER0 approach is an efficient novel low-cost approximation method for calculating functional integrals of sophisticated polymer chain models beyond the MF level of approximation. In particular, we have demonstrated by comparing our theoretical approach to experimental measurements that it provides reliable results of the thermodynamic osmotic pressure over the whole range of monomer concentrations. To solve the multiple length scale problem arising in the semidilute regime, we derive an appropriate functional form of the quantity by suitably renormalizing the monomer charge number, which takes into account the interplay of *non-uniform counterion condensation* and *counterion-mediated chain self-contraction*. As a consequence, the correlation length of segment density fluctuations becomes concentration dependent and a crossover from outer-chain contraction OCC to inner-chain contraction ICC takes place with increasing monomolar concentration, leading to PE chains with horseshoe shape. In the concentrated regime we show that the osmotic pressure is dominated by excluded volume interactions and, therefore, the scaling behavior is similar to neutral polymer solutions, as demonstrated by computer simulation calculations [57,63]. Moreover, it is also worth pointing out that our Hartree renormalized GER0 theory possesses the advantage over traditional scaling theories that it is able to predict not only the slopes, but also the prefactors of the thermodynamic properties, as well as to provide a suitable framework for developing systematic higher-order scaling laws, as will be demonstrated in subsequent investigations. Finally, it is worth considering that our approach, in contrast to conventional simulation methods like e.g. MD, permits to deliver useful results for PE systems with long polymer chains in non-dilute concentration regimes, as needed in many applications of biological and technological interest. In conclusion, we believe that the Hartree renormalized GER0 approach can become an appealing alternative to conventional computer simulation tools and scaling approaches in cases, where the latter approaches fail to provide useful results. Our future efforts will therefore concentrate on applying the Hartree renormalized GER0 methodology, to derive scaling laws of sophisticated polymeric systems like the ones occurring in biomaterials [64] and complex foods [65]. A further work will deal with the study of PE solutions on a more fundamental level, taking into account the degrees of freedom of the counterions and salt ions explicitly and describing their interactions via the Coulomb potential.

Acknowledgements

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Appendix A. Analytical evaluation of the fluctuation integral

To perform the analytical integration of the fluctuation integral in Eq. (57), we transform it in polar coordinates and obtain

$$\mathcal{F} = \frac{1}{4\pi^2 N_{\mathrm{A}}} \int\limits_0^\infty \mathrm{d}G\ G^2 \left\{ \ln[1 + \mathcal{B}N\mathcal{C}_{\mathrm{m}} v(G)] - \frac{\mathcal{B}N\mathcal{C}_{\mathrm{m}} v(G)}{[1 + \mathcal{B}N\mathcal{C}_{\mathrm{m}} v(G)]} \right\}, \tag{83}$$

where $G = |\mathbf{G}|$. This expression can be rewritten as

$$\mathcal{F}=\frac{1}{4\pi^2}\int\limits_0^\infty \mathrm{d}(G^3/3)\left\{\ln[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]-\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}\right\}. \tag{84}$$

Next, we use the formula $\int u\,\mathrm{d}v = uv - \int v\,\mathrm{d}u$ to rewrite Eq. (84) and get

$$\begin{aligned}\mathcal{F}&=\frac{1}{4\pi^2N_\mathrm{A}}\left\{\frac{G^3}{3}\left[\ln[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]-\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}\right]\right\}_{G=0}^{G=\infty}\\&\quad-\frac{1}{4\pi^2N_\mathrm{A}}\int\limits_{G=0}^{G=\infty}\mathrm{d}\left[\ln[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]-\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}\right]\frac{G^3}{3}\\&=-\frac{1}{4\pi^2N_\mathrm{A}}\int\limits_{G=0}^{G=\infty}\mathrm{d}\left[\ln[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]-\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}\right]\frac{G^3}{3}\\&=-\frac{1}{4\pi^2N_\mathrm{A}}\int\limits_{G=0}^{G=\infty}\mathrm{d}G\left[\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}(\mathrm{d}\upsilon(G)/\mathrm{d}G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}-\frac{\mathcal{B}N\mathcal{C}_\mathrm{m}(\mathrm{d}\upsilon(G)/\mathrm{d}G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]}\right.\\&\quad\left.+\frac{\mathcal{B}^2N^2\mathcal{C}_\mathrm{m}^2\upsilon(G)(\mathrm{d}\upsilon(G)/\mathrm{d}G)}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]^2}\right]\frac{G^3}{3}\\&=-\frac{1}{12\pi^2N_\mathrm{A}}\int\limits_{G=0}^{G=\infty}\mathrm{d}G\left\{\frac{\mathcal{B}^2N^2\mathcal{C}_\mathrm{m}^2\upsilon(G)(\mathrm{d}\upsilon(G)/\mathrm{d}G)G^3}{[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\upsilon(G)]^2}\right\}.\end{aligned} \tag{85}$$

Next, inserting

$$\upsilon(G)=\frac{\kappa^2A(\kappa,a)}{G^2+\kappa^2} \tag{86}$$

and

$$\frac{\mathrm{d}\upsilon(G)}{\mathrm{d}G}=-\frac{\kappa^2A(\kappa,a)}{[G^2+\kappa^2]^2}2G \tag{87}$$

into Eq. (85), we obtain

$$\begin{aligned}\mathcal{F}&=-\frac{1}{12\pi^2N_\mathrm{A}}\int\limits_{G=0}^{G=\infty}\mathrm{d}G\left\{\frac{\mathcal{B}^2N^2\mathcal{C}_\mathrm{m}^2\left[\frac{\kappa^2A(\kappa,a)}{G^2+\kappa^2}\right]\left[-\frac{\kappa^2A(\kappa,a)}{[G^2+\kappa^2]^2}2G\right]G^3}{\left[1+\mathcal{B}N\mathcal{C}_\mathrm{m}\left[\frac{\kappa^2A(\kappa,a)}{G^2+\kappa^2}\right]\right]^2}\right\}\\&=\frac{1}{6\pi^2N_\mathrm{A}}\mathcal{B}^2N^2\mathcal{C}_\mathrm{m}^2\kappa^4A^2(\kappa,a)\\&\quad\times\int\limits_{G=0}^{G=\infty}\mathrm{d}G\left\{\frac{G^4}{[G^2+\kappa^2][G^2+(\kappa^2+\mathcal{B}N\mathcal{C}_\mathrm{m}\kappa^2A(\kappa,a))]^2}\right\}.\end{aligned} \tag{88}$$

To solve this integral, we use the following integral relation

$$\int\limits_0^\infty\frac{x^4}{(x^2+m)(x^2+n)^2}\mathrm{d}x=\frac{\pi}{4(m-n)^2}\left[2m^{3/2}+\sqrt{n}(n-3m)\right] \tag{89}$$

and get for the fluctuation integral

$$\mathcal{F}=\frac{\kappa^3}{24\pi N_\mathrm{A}}\left\{2+\sqrt{1+A(\kappa,a)\mathcal{B}N\mathcal{C}_\mathrm{m}}(A(\kappa,a)\mathcal{B}N\mathcal{C}_\mathrm{m}-2)\right\}. \tag{90}$$

Appendix B. Solving the cubic equation of the Hartree renormalized GER0 approach

In order to solve Eq. (66), we rewrite it in a cubic equation of the form

$$x^3+qx^2+rx+s=0 \tag{91}$$

by defining $x=\mathcal{B}_\mathrm{r}^{1/2}$ and

$$q=\frac{12\pi N_\mathrm{A}}{A^{1/2}(\kappa,a)N^{3/2}\mathcal{C}_\mathrm{m}^{-1/2}\kappa^3},\ r=0,\ s=-\mathcal{B}q. \tag{92}$$

Cubic equations possess three possible solutions, from which at least one is real. The real solution is given by

$$x_1=S+T-\frac{1}{3}q, \tag{93}$$

where

$$S=\left(R+\sqrt{Q^3+R^2}\right)^{1/3},\ T=\left(R-\sqrt{Q^3+R^2}\right)^{1/3}, \tag{94}$$

with

$$Q=\frac{1}{9}\left(3r-q^2\right),\ R=\frac{1}{54}\left(9qr-27s-2q^3\right). \tag{95}$$

Using the coefficients given in the Eqs. (92), we get for the previous expressions

$$Q=-\frac{1}{9}q^2,\ R=\frac{q}{54}\left(27\mathcal{B}-2q^2\right), \tag{96}$$

and

$$\begin{aligned}S&=\left(\frac{q}{54}(27\mathcal{B}-2q^2)+\sqrt{-\frac{1}{9^3}q^6+\frac{q^2}{54^2}(27\mathcal{B}-2q^2)^2}\right)^{1/3},\\T&=\left(\frac{q}{54}(27\mathcal{B}-2q^2)-\sqrt{-\frac{1}{9^3}q^6+\frac{q^2}{54^2}(27\mathcal{B}-2q^2)^2}\right)^{1/3}.\end{aligned} \tag{97}$$

Considering that $q\rightarrow0$ for $N\rightarrow\infty$, the previous equations provide

$$S=(q\mathcal{B})^{1/3},\ T=0. \tag{98}$$

Thus, for large $\mathcal{B}$, we obtain

$$x_1\approx S=(q\mathcal{B})^{1/3} \tag{99}$$

or

$$\mathcal{B}_\mathrm{r}=x_1^2\approx(q\mathcal{B})^{2/3}. \tag{100}$$

Next, inserting q of Eq. (92) in Eq. (100), we finally get

$$\mathcal{B}_{\mathrm{r}} \approx (12\pi N_{\mathrm{A}})^{2/3}\left(\frac{\mathcal{B}^{2/3}\mathcal{C}_{\mathrm{m}}^{1/3}}{A^{1/3}(\kappa,a)N\kappa^{2}}\right). \tag{101}$$

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