Thermodynamic properties of ring polyelectrolytes in the binding mean spherical approximation

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ABSTRACT

A simple model for charged ring polyelectrolyte is proposed, to describe their thermodynamic properties. Starting from an analytical expressions previously obtained for charged chains within the binding mean spherical approximation, we present a method to determine suitable modifications in order to describe charged rings. It is shown that the electrostatic excess thermodynamic properties can still be computed from relatively simple formulas which involve a screening parameter Γ^B.

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1. Introduction

We are pleased and honored to contribute to the Festschrift dedicated to the 70th birthday of Vojko Vlachy, a well-known expert in the modeling of the structural and thermodynamic properties of polyelectrolytes. The description of the thermodynamic properties of polymers has made great progress with the various models developed by Wertheim [1,2]. In these models, it was assumed that the polymers can be described as a set of spherical sub-units linked together to form chains, rings, star polymers, etc. A thermodynamic perturbation theory (TPT) was developed in order to calculate the free energy of polymers from the reference free energy of its dissociated constituents. From these free energies other thermodynamic quantities such as the pressure can be deduced by differentiation. This approach enabled one to develop analytical models of polymer properties. The statistical associating fluid theory (SAFT) is based on this approach [3,4]. Thus, if neutral polymers are assumed to be composed of hard spheres, the reference free energy is that of a system of hard spheres for which accurate expressions are available.

Moreover, integral equations have also been developed to describe polymer chains from the interactions between their subunits. This complementary approach allows one to derive thermodynamic quantities such as the pressure, but also permits to describe the structure in terms of the radial distribution function between the various elementary constituents of these polymers. This approach is particularly useful when the subunits constituent of the polymer interact through a long-range potential. In this case the fact that these subunits are linked together has a profound influence on these interactions, which significantly changes the structure and thermodynamics of these systems. In particular, the integral equations were used to describe the properties of polyelectrolytes made up of charged hard spheres in chain assemblies [5–9]. Important contributions to the development and application of this approach have been made by V. Vlachy et al., particularly for spherical [10,11] and flexible polyelectrolytes in explicit solvent [12]. To solve these integral equations analytically, the mean spherical approximation (MSA) was used as a closure relationship [13–16]. For these charged hard sphere chains, explicit expressions were established for the electrostatic contributions to the various thermodynamic properties [8,9]. The pressure computed using these expressions was compared to those derived from simulation. These pressure can describe those deduced from simulation for weakly charged polyelectrolytes [17].

Integral equations can also be applied to the description of polymers with other structures than simple chain: branched polymers or star polymers. However these equations are not suitable to describe ring polymers. For uncharged rings, modifications of the thermodynamic perturbation theory have been developed [18–22]. By contrast, for charged rings, there is currently no suitable expression for the electrostatic contributions to the various thermodynamic properties usually calculated using integral equations. In this article we present a method to obtain such expressions from suitable modifications of the expressions established previously for charged chains.

We present in the next section how to obtain these expressions. In the following section these expressions are applied to calculate the osmotic pressure for charged rings in solution. A comparison is made with a similar calculation made for charged chains. Finally, prospects of this work are presented.

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2. Theory

The development of expressions for the electrostatic contributions to the various thermodynamic quantities (internal energy, Helmholtz energy, pressure) is carried out from expressions previously obtained in the case of polyelectrolytes represented as chains of charged hard spheres. These previous expressions were obtained from Wertheim Ornstein-Zernike (WOZ) integral equations solved using the MSA approximation as a closure relationship. We first present the model and the expressions. Then, changes to these terms are presented in order to describe polyelectrolyte rings.

2.1. The model of fixed length polyelectrolyte

We consider a system with an arbitrary number of components m, with number density ρ_i, charge ez_i, (e is the elementary charge) and hard core diameter σ_i in a solvent viewed as a continuum of relative permittivity ϵ_r. We consider that the particles $1, 2, \cdots n$ with $z_1 = z_2 = \cdots = z_n$ and $\sigma_1 = \sigma_2 = \cdots = \sigma_n$ are the constituents of the polyelectrolyte chain. There is also counterions c of charge z_c, diameter σ_c and number density ρ_c such that the system is electroneutral. Possibly the system also contains coions of arbitrary sizes and charges. The set of particles with indices $1, 2, \cdots n$ are participating in the bonding to form the polyelectrolyte chains, while those with $n + 1, \cdots m$ are not. The temperature of the system is T, Boltzmann's constant is k_B and we use $\beta = 1/k_B T$ throughout. Each hard sphere of the set of particles $2, \cdots n - 1$ has two sticky points, A and B, randomly positioned on its surface. In contrast, spheres 1 and n have only one sticky point and the counterions and coions have no sticky points. The pair potential for this model is given by

$$u_{ij}(12) = u_{ij}^{HS}(r) + u_{ij}^{el}(r) + \sum_{K,L} U_{ij}^{KL}(12) \tag{1}$$

where 1 and 2 stand for the spatial and orientational coordinates of two ions, i and j are the indexes for the ionic species, $u_{ij}^{HS}(r)$ is the hard-sphere potential, $u_{ij}^{el}(r)$ is the Coulomb potential, and $U_{ij}^{KL}(12)$ is the short-ranged site-site potential responsible for association. Hereafter K and L take the values A and B and denote the type of site. The short-ranged site-site potential $U_{ij}^{KL}(r)$ between sites K and L on ions i and j are defined in terms of the Mayer function, $f_{ij}^{KL}(r)$, as

$$f_{ij}^{KL}(r) = \exp[-\beta U_{ij}^{KL}(r)] - 1 = \mathcal{B}_{ij}^{KL} \delta(r - \sigma_{ij}^-) \tag{2}$$

where $\mathcal{B}_{ij}^{KL}$ is an element of the matrix of the sticky interactions. The Coulomb potential, $u_{ij}^{el}(r)$, is given by

$$u_{ij}^{el}(r) = \frac{e^2 z_i z_j}{\varepsilon r} \tag{3}$$

with $\varepsilon = 4\pi\epsilon_0 \epsilon_r$ and ϵ_0 the permittivity of vacuum.

The thermodynamic properties of this model can be evaluated by using thermodynamic perturbation theories [23–27] or by using the WOZ integral equations [8,9,28-31]. In both case it has been shown, that the thermodynamic properties like the excess Helmholtz free energy ΔA, may be decomposed in three terms as

$$\Delta A = \Delta A^{HS} + \Delta A^{chain} + \Delta A^{el} \tag{4}$$

in which ΔA^{HS} is the contribution from uncharged dissociated hard spheres, which was computed using a classic expression [32]. ΔA^{chain} is a contribution arising from association between the subunits $1, 2, \cdots n$ of the chain regarded as being uncharged, and ΔA^{el} is the electrostatic contribution from charged associated hard spheres. The

relation giving the chain part of the free energy ΔA^{chain}, is identical to that obtained in TPT1 or SAFT approximations [1–4].

The electrostatic contribution from charged hard sphere chains and counterions ΔA^{el}, have been determined from the WOZ integral equations. By averaging the correlation functions over the orientations of each site, the orientation dependence of the site-site potentials can be eliminated to obtain the total orientation-averaged pair correlation function, $h_{ij}(r)$. As an outcome of the attractive potentials defined in Eq. (2), the functions $h_{ij}(r)$ have additional short range attractive contributions proportional to the orientation-averaged Mayer functions, $f_{ij}^{KL}(r)$. Initially, Wertheim developed his integral equations for particles with binding off-center sites with fixed positions. So the corresponding correlation functions are orientation dependent. As a simplification, the orientation-averaged total pair correlation functions $h_{ij}(r)$ can be coupled with the orientation-averaged direct correlation functions $c_{ij}(r)$ through a set of approximate orientation-averaged integral equations [1,2] called Wertheim-Ornstein-Zernike (WOZ) equations. This procedure has been proposed and used initially to describe flexible polymers [33,34]. WOZ equations couple total correlation functions $\mathbf{h}_{ij}(r)$ and direct correlation functions $\mathbf{c}_{ij}(r)$. For each pair of particles of species i and j, $\mathbf{h}_{ij}(r)$ and $\mathbf{c}_{ij}(r)$ are matrices, consisting of the partial correlation functions for the different bonding states. Partial correlations corresponding to species i and j simultaneously unbound (denoted with superscript 00) have a special role in the definition of the closure relations for the integral equations. In particular, a MSA-like closure relation has been used to solve these equations, namely for the direct correlation functions one set $c_{ij}^{00}(r) = u_{ij}^{el}(r)$ for $r > \sigma_{ij}$ [35,36]. The analytic solution of this Binding (or Associative) Mean Spherical Approximation (BiMSA) was obtained in the case of polyelectrolytes represented as charged hard sphere chains [5–9]. Explicit expressions were obtained for the thermodynamic properties in terms of a scaling parameter [8,9], Γ^B, similar to the Debye-Hückel κ screening parameter. The electrostatic contribution to the internal energy ΔE^{el} can be deduced from the solution of the WOZ equations. From the thermodynamic relation $\partial \beta A / \partial \beta = E$, the electrostatic contribution to the Helmholtz energy ΔA^{el}, can be deduced by thermodynamic integration. Then, the osmotic and mean activity coefficients can be calculated by differentiation of the Helmholtz energy ΔA^{el}. To simplify the presentation of the equations, we will now consider that all the sub-units forming the chain have the same diameter. The generalization to chains made of subunits of arbitrary size is straight forward but tedious. In previous work different closure relations have been studied. A chain approximation that takes 3 body hard core exclusion into account has been introduced [8]. It has been shown that this triplet exclusion chain approximation (TECA) satisfies explicitly the Debye Hückel limiting law for all lengths n, and also for all charge combinations. Now we will consider only the results obtained with this closure.

2.2. Thermodynamic properties of polyelectrolyte chains

Hereafter, we will consider the case of the charged chains constituted of the hard spheres $1, 2, \cdots n$ having the same diameter σ and with counterions and coions of arbitrary sizes and charges. In this case, the internal energy is given by [8]

$$\Delta E^{el} = \frac{e^2}{\varepsilon} \left[\sum_k \rho_k z_k M_k^0 + \rho_p \sum_{k=1}^{n-1} \sum_{i=1}^{n-k} \frac{z_k \mathcal{X}_{k+i}^0}{(i+1)\sigma} y^i + \rho_p \sum_{k=2}^{n} \sum_{i=1}^{k-1} \frac{z_k \mathcal{X}_{k-i}^0}{(i+1)\sigma} y^i \right] \tag{5}$$