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Configurational Properties of Charged Hard Sphere Rings and Stars in a Solvent

Clive A. Croxton

Department of Mathematics, University of Newcastle, Newcastle, New South Wales, Australia 2308

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ABSTRACT: The effect of charge and solvent density on the configurational properties of perfectly flexible hard sphere rings and stars is investigated on the basis of the iterative convolution approximation. It is found that solvent density has a negligible effect upon the configurational properties, while charge effects are substantial.

Introduction

In a variety of previous publications the configurational properties and the scattering functions of rings and stars have been presented, incorporating in some cases the effects of self-avoidance in the case of systems comprised of hard sphere segments. Of direct relevance to the present study is the application of the iterative convolution (IC) technique to such hard sphere systems in which the various parametric features of the stars such as branch length and functionality (number of branches) were investigated, with similar investigation of rings. It is inappropriate to reiterate the IC technique here, and instead we direct the reader to the original publications[1,3] and its applications. However, we do take this opportunity to emphasize that the IC description enables us to incorporate explicitly the hard sphere and electrostatic features of the polymer and we may, therefore, regard those descriptions as being fully self-avoiding representations of the configurational properties of such rings and stars. Moreover, we have, in most cases, confirmed the legitimacy of the IC approach by means of complementary Monte Carlo studies, as well as comparisons with existing experimental data, where they are available. We should emphasize from the outset that the objective of the IC technique is to provide an analogous configurational description of the polymer to that of the statistical theory of liquids, which is by now well established. The set of working integral equations by means of which we calculate the total set of spatial probability functions $Z(r_{ij})$ developed between each pair of segments is

$$Z(ij) = H(ij)\prod_{i,j\neq k}^{N}\int Z(ik)\,Z(kj)\,\mathrm{d}\mathbf{k}$$

$$H(ij) = \exp -\Phi(r_{ij}/kT)$$

where the only input function is the pair potential $\Phi(r_{ij})$ or, in the presence of a solvent, the effective pair potential between polymer segments. $\prod$ represents the formation of a geometric mean of the integrals which arise throughout the body of the polymer. Beginning with an initial guess for the Z functions, the integrals are evaluated iteratively by fast Fourier transform techniques.

In this paper we extend the IC technique in two important respects. First, we investigate the effect of a hard sphere solvent on the configurational properties of the molecule. These results should, of course, complement the IC calculations previously reported and illustrate the effects of charge and solvent density. We direct the reader to these earlier papers on self-avoidance for the details of the technique and concentrate here upon the role of charge and solvent.[2]

Second, we introduce the effect of electrostatic charge between the star and ring segments. Unfortunately, an extensive literature search[6] failed to provide a body of experimental or Monte Carlo (MC) data with which to compare the present theoretical results. Primarily, the experimentally determined configurational properties of rings and stars were restricted to Θ solvents with no account of charge effects, and to this extent the calculations presented here await the execution of substantial Monte Carlo simulations (although some MC determinations confined to the face-centered cubic lattice have been reported[7]) or the appropriate experimental investigations. The execution of off-lattice Monte Carlo simulations with which to compare our IC predictions is unfortunately prohibitively slow due mainly to the complicating presence of the solvent, and we regard the present convolution calculations as being essentially predictive in nature, with our confidence based upon the substantial number of convolution calculations previously reported for which experimental data and Monte Carlo simulations were available and have essentially confirmed the IC results.

In all cases the isolated star is comprised of perfectly flexible identical hard sphere branches, all terminally attached to a central hard sphere vertex segment. On the basis of the IC technique we calculate the spatial probability distributions $Z(r_{ij}|N)$ developed between any pair of segments ij both within a given branch and between branches. Of course, since all branches are considered identical, the number of Z distributions that needs to be determined is relatively small. On the basis of these $Z(r_{ij}|N)$ for a given star we are able to determine the mean-square branch length, radius of gyration, scattering function, and star mobility, which is a sensitive function of star collapse, with similar assessments for rings.

Model

We first investigate the configurational properties of perfectly flexible hard sphere stars of various functionalities, $3 \leq f \leq 6$, in which each segment is charged. The hard sphere potential operating between any pair of segments or between segment and solvent is

$$\Phi(ij) = +\infty \qquad r_{ij} < 1.0$$
$$= 0 \qquad r_{ij} \geq 1.0$$

as in the previously reported analysis,[4] while the electrostatic interaction between any pair of star/ring segments

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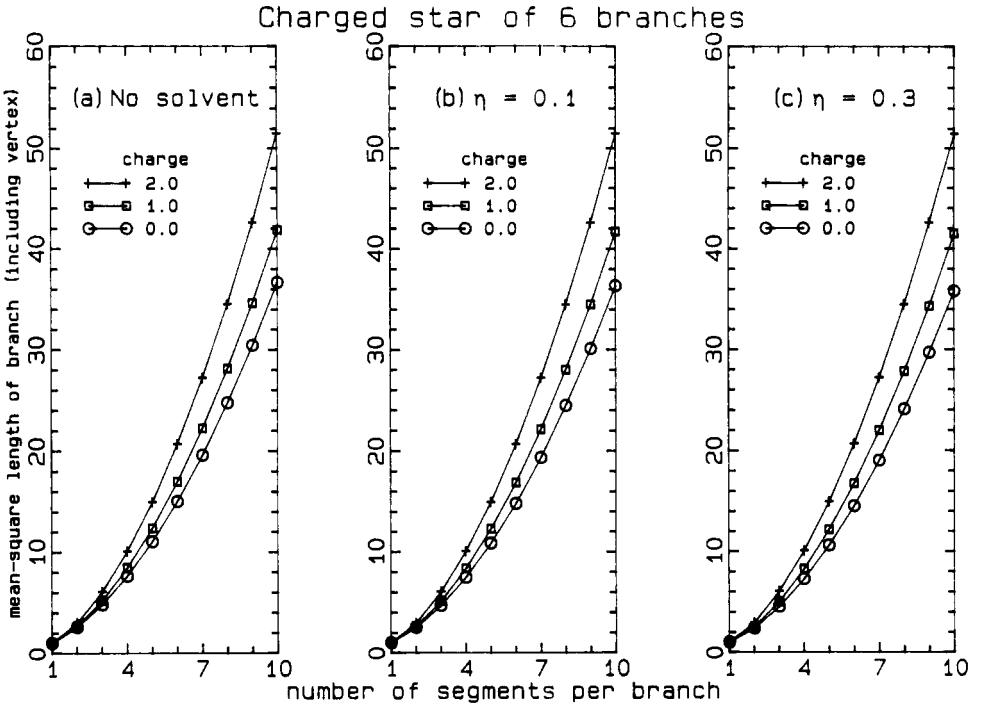

Figure 1. Mean-square length of branch for hard sphere stars of six branches. The effect of charge is seen to substantially determine the branch length. Parts a–c show the effects of solvent density, which is secondary to charge effects.

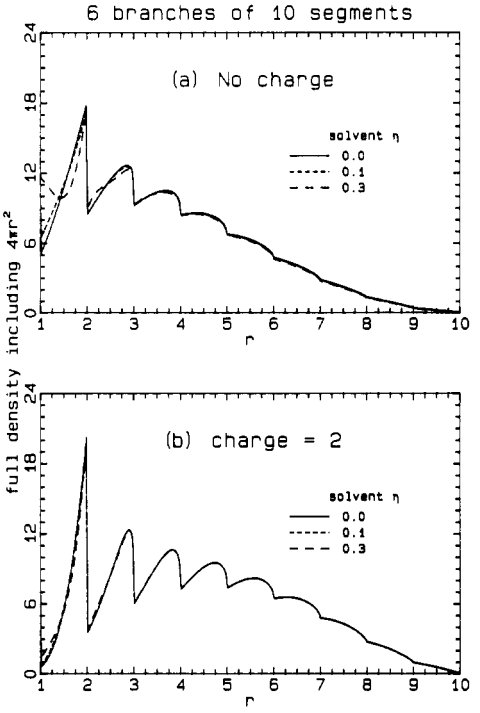

Figure 2. Segment density distribution for hard sphere stars of six branches as a function of solvent density (a) with no charge and (b) with a charge of 2 units per segment.

is of simple reduced Coulombic form

$$\Phi_e(ij) = q_1 q_2 / r_{ij}$$

where we have taken $q_1 = q_2 = 0, 1, 2$ in this study.

Mean-Square Branch Length. In previous publications we have explicitly incorporated the effects of solvent,[2] and although we concede from the outset that our approach, based upon the Percus–Yevick (PY) approximation appropriate to liquids, provides little more than a qualitative indication of the role of a solvent at various packing fractions, the approach nevertheless enables us to incorporate explicitly the effects of a solvent, which does appear to substantially modify the isolated polymer results, particularly in the present case of charged stars. Again, the PY technique in the present context has been extensively described in earlier papers, and to repeat it here would be inappropriate.[2] However, we first determine the radial distribution function $g_{(2)}(r_{ij})$ between two hard sphere segments, which may or may not be charged depending upon the calculation in question. This is done as if the system were a homogeneous liquid of packing fraction η, on the basis of the PY approximation. Having thus determined the radial distribution function $g_{(2)}(r_{ij})$ between two segments, the effective potential of mean force then follows directly as

$$\Psi(r_{ij}) = -\ln g_{(2)}(r_{ij})$$

which we use as the *effective* interaction between the star segments. Such an interaction nevertheless incorporates the packing fraction, electrostatic, and hard sphere features of the system and enables all these features to be simultaneously incorporated into the IC determinations of the star configuration. This technique has been described previously in the literature,[2] although not, of course, for the particular system in question here.

As we might anticipate from the outset, the role of the electrostatic charge is to expand the molecule with respect to its uncharged self-avoiding counterpart, and this is clearly apparent from Figure 1a, in which we show the mean-square length of a flexible hard sphere branch of up to 10 segments for stars of various segment charge for a system of six identical branches. Clearly, the branches are expanded with increasing charge, as would be expected. We note in particular that the mean-square length of a branch develops not only with the magnitude of segment charge but also with the number of segments per branch. This suggests that mean-square length of the branches develops more strongly with increasing branch length in the case of charged systems than with their uncharged counterpart.

In Figure 1b,c we show the effect on the mean-square branch length for a charged star of six branches at a solvent packing fraction of $\eta = (\pi/6)\rho = 0.1, 0.3$, where ρ is the number density of the solvent particles.

The mean-square length of the branches, particularly for charged systems, shows the expected electrostatic

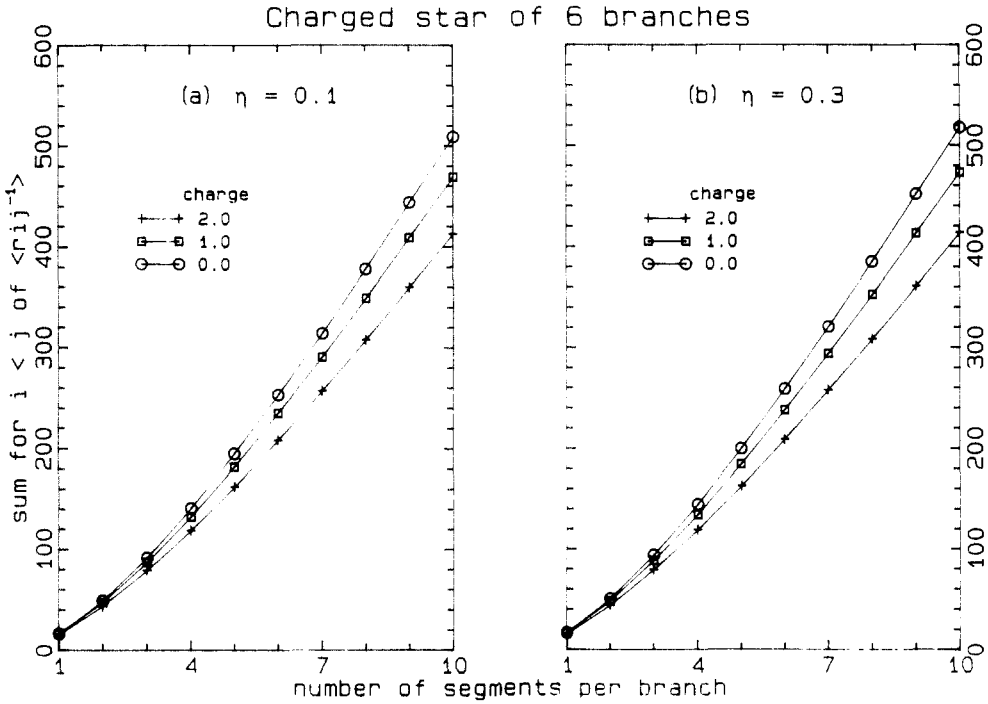

Figure 3. Effects of charge and solvent density on mobility of stars. Parts a and b show that solvent density has minimal effect, while charge, affecting the deployment of the star branches, affects star mobility.

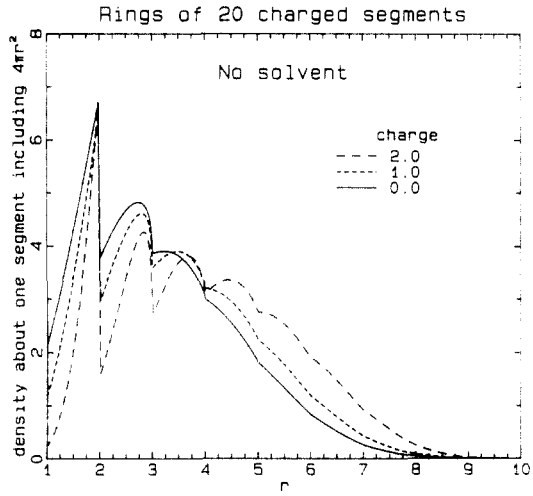

Figure 4. Segment density distribution for charged hard sphere rings of 20 segments as a function of charge, in the absence of solvent. Charge is seen to expand the rings as expected.

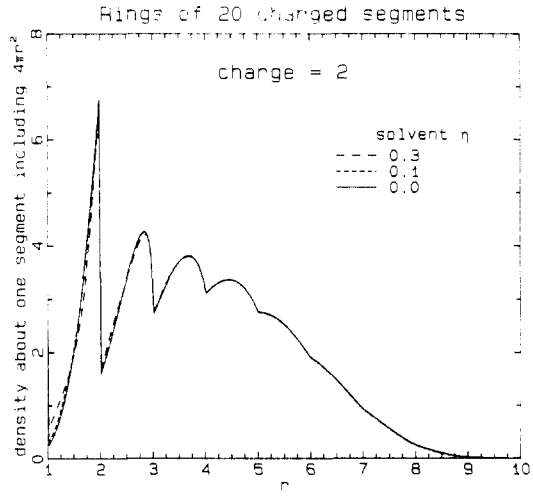

Figure 5. Segment density distribution for charged hard sphere rings of 20 segments. The effect of solvent density is seen to be negligible.

expansion, while the role of solvent, at least for the longer branches, appears to be negligible. This somewhat surprising result suggests that star configuration is primarily determined by electrostatic effects rather than by solvent, a feature which we are able to further investigate by means of a detailed comparison of the radial distribution functions $g_{(2)}(r_{ij})$ determined on the basis of the PY calculations. We see that solvent does have an effect on the interaction between star segments but that for longer branches the role of solvent is minimal since its "penetration" into the star system is small; indeed, all stars, regardless of solvent density, show virtually identical mean-square branch lengths. Accordingly, we conclude that star configuration is primarily determined by geometrical exclusion and electrostatic effects and that solvent packing fraction has a minimal effect on mean-square branch length determined as

$$\int Z(r_{0,10}) r_{0,10}^2 \, d\mathbf{r}$$

where $Z(r_{0,10})$ is the vertex/terminal segment distribution for a branch of 10 segments.

Analogous results for the radius of gyration subject to the effect of electrostatic charge are obtained, and accordingly we do not explicitly present these diagrams. The radius of gyration is dependent upon the *set* of mean-square separations and hence upon the distributions within the central core region of the star where solvent effects are likely to be minimal, with electrostatic expansion dominating the star structure. Again, although in Figure 1a we have presented results for stars of functionality $f = 6$, corresponding results for stars of lower functionality are obtained with results which are qualitatively similar to those presented here.

Star Segment Density Distribution. The effect of solvent packing fraction η upon the radial density distribution for $f = 6$, 10 segment branches is shown in Figure 2a,b for a segment charge 0 or 2, respectively, from which we see that solvent density has a minimal effect, while the effects of electrostatic charge are much greater. It is immediately apparent from these diagrams that solvent effects make a surprisingly small contribution to the detailed form of the density distribution, while electrostatic

effects appear to be much more substantial. This accounts at once for the behavior of the mean-square branch length.

Star Mobility. As we have presented in earlier publications,[3] an estimate of the mobility of the system follows from a knowledge of $\sum_i\sum_j\langle r_{ij}^{-1}\rangle$, which is smaller the more expanded is the star. In the case of uncharged stars for which the geometrical interaction alone determines the clustering of the branch segments, the deployment of the segments is sufficiently compact as to present relatively low viscous impediment to the motion of the star, while for electrostatically expanded systems a substantially greater viscous impediment is presented and the mobility is correspondingly lowered.

The mobility of the stars, based upon the Kirkwood–Riseman approximation[5] according to which mobility is related to $\sum_i\sum_j\langle r_{ij}^{-1}\rangle$, is shown in Figure 3a,b. Again, solvent density appears to have little effect, while electrostatic charge dominates the behavior. As we have discussed on previous occasions, the deployment of the branches for the charged stars presents a greater frictional aspect, and therefore reduced mobility, than does its uncharged, more collapsed counterpart, which presents a smaller frictional aspect.

Rings. Perfectly flexible rings of charged hard spheres exhibit characteristics similar to those of the stars. In particular we see from Figures 4 and 5 that the density distribution function of hard sphere rings depends sensitively upon segment charge. Clearly, the rings expand with charge as would be expected (Figure 4), while the introduction of solvent on a ring of fixed charge is almost negligible. We conclude, as in the case of stars, that the configurational properties of rings depends most sensitively upon charge, while solvent density appears to play a negligible role. Since mean-square diameter (the appropriate parameter in the case of rings) is dependent upon these segment–segment and segment–solvent distributions, they also show similar sensitivity/insensitivity upon the charge/solvent conditions.

References and Notes

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