A NEW RISM INTEGRAL EQUATION FOR SOLVATED POLYMERS

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A new RISM integral equation suitable for treating solute–solvent interactions when the solute contains periodicity is presented. The essential feature is the introduction of a new intramolecular correlation function for the solute, which is a sum of the intramolecular correlation functions in the old theory over the periodic cells of the solute. The theory can be used to study polyelectrolyte properties in solution, including solvent effects on biopolymers. As a first application, simple models are considered in which atoms are arranged along a linear chain and on a helix. The results are compared with computer simulations for a linear chain of ions in water.

1. Introduction

Considerable progress has been made in the theory of molecular fluids during the last decade based on the interaction site model (ISM) of liquids in which the interaction energy between a pair of molecules is represented by a sum of pair interaction energies between sites on each molecule [1,2]. The RISM theory, an integral equation method which is particularly suitable for such a molecular liquid model, is characterized by the introduction of an intramolecular correlation coupled with an intermolecular correlation through spatial convolution [3]. The application of the theory to a system in which sites carry partial charges has been made possible by an extended version of the RISM theory which features renormalization of the long-range interaction between charges based on the method which has been developed in ionic solution theory [4]. It has been demonstrated that the theory is able to predict the structure of molecular fluids including hydrogen-bonded liquids in a qualitatively correct manner [5–10].

Although the theory provides a powerful tool for elucidating the structure of liquids in which the component solute and solvent molecules are small, it will find more extensive applications in various fields, if it becomes possible to treat molecules which contain a large number of interaction sites. The extension of

the theory to polymeric systems is in general a formidable task due to the size and complication of the intramolecular correlation matrix which appears in the RISM equation. However, for cases in which one can take advantage of molecular periodicity, the problem may be reduced to a tractable size. Polyelectrolytes in solution constitute one such class of macromolecules. In this article, we present a systematic way of reducing the problem to a size which is comparable to the usual RISM calculations.

2. Theory

We begin with the RISM equation which is generalized to a mixture [3,6]:

$$\rho h \rho = \omega * c * \omega + \omega * c * \rho h \rho , \tag{1}$$

where h is the matrix of site–site intermolecular pair correlation functions, c is the matrix of direct correlation functions, ρ is a diagonal matrix having as elements

$$\rho_{\alpha_M \gamma_{M'}} = \delta_{\alpha_M \gamma_{M'}} \rho_M , \tag{2}$$

where ρ_M is the number density of molecular species M and $\delta_{\alpha_M \gamma_{M'}}$ is a Kronecker delta. The ω is an intramolecular correlation matrix defined as

$$\omega_{\alpha_M\gamma_{M'}} = \rho_M \delta_{MM'}[\delta_{\alpha_M\gamma_M}\delta(r_{\alpha_M}-r_{\gamma_M})$$

$$+ (1-\delta_{\alpha_M\gamma_M})s_{\alpha_M\gamma_M}(r_{\alpha_M}-r_{\gamma_M})] , \qquad (3)$$

where s is the intramolecular distribution function between site α and site γ, which is a delta function for a rigid bond. At infinite dilution (through a limiting process for which the solute density approaches zero), eq. (1) becomes [6]

$$\mathbf{h}^{vv} = \mathbf{w}^v * \mathbf{c}^{vv} * \mathbf{w}^v + \mathbf{w}^v * \mathbf{c}^{vv} * \rho \mathbf{h}^{vv} , \qquad (4)$$

$$\mathbf{h}^{uv} = \mathbf{w}^u * \mathbf{c}^{uv} * \mathbf{w}^v + \mathbf{w}^u * \mathbf{c}^{uv} * \rho \mathbf{h}^{vv} , \qquad (5)$$

where superscripts u,v stand for solute and solvent, respectively, and the matrix $\mathbf{w}$ is defined by $\omega = \rho * \mathbf{w}$. The equations may be solved by an iterative scheme supplemented with a closure relation [6]. The method has been, however, limited to small molecules, due to the large size of the correlation matrices which appear in the equations when one tries to apply them to a large molecule. However, when the solute molecule has spatial periodicity and the number of atoms in the periodic unit is small, the problem may be reduced to a tractable size. We consider a solute molecule which is made up of a periodic array of atoms; for example the sites on a rod-like polyelectrolyte. The group of atoms in the periodic unit is referred to as a cell. In order to perform the reduction, let us rewrite eq. (5) in component form:

$$h_{\alpha_i\beta_M} = \sum_{\delta_{M'}}\sum_j\sum_\gamma w^u_{\alpha_i\gamma_j} * c^{uv}_{\gamma_j\delta_{M'}} * (w^v_{\delta_{M'}\beta_M}+\rho h^{vv}_{\delta_{M'}\beta_M}), \qquad (6)$$

where M,M' specify the solvent molecule, and α,β, etc. specify the atoms or sites as before. The subscript i represents the ith cell of the polymer. So, α_i stands for the αth atom in the ith cell. The i and j may extend over an infinite number of cells. The intramolecular correlation matrix $\mathbf{w}$ is also rewritten in the new notation:

$$w^u_{\alpha_i\gamma_j} = \delta_{\alpha_i\gamma_j}\delta(r_{\alpha_i}-r_{\gamma_j})$$

$$+ (1-\delta_{\alpha_i\gamma_j})s_{\alpha_i\gamma_j}(r_{\alpha_M}-r_{\gamma_M}) . \qquad (7)$$

When the periodic cells extend infinitely or closure is possible, as is the case for models of rodlike and circular polymers, respectively, then $\mathbf{h}^{uv}$ and $\mathbf{c}^{uv}$ are identical for each of the cells.

$$c^{uv}_{\gamma_1\delta_{M'}} = c^{uv}_{\gamma_2\delta_{M'}} = c^{uv}_{\gamma_3\delta_{M'}} = ... = c^{uv}_{\gamma_n\delta_{M'}} = ... = c^{uv}_{\gamma\delta_{M'}} . \qquad (8)$$

Then eq. (6) may be written in compact form:

$$h_{\alpha_i\beta_M} = \sum_{\delta_{M'}}\sum_\gamma W^u_{\alpha_i\gamma} * c^{uv}_{\gamma\delta_{M'}} * (w^v_{\delta_{M'}\beta_M}+\rho h^{vv}_{\delta_{M'}\beta_M}) , \qquad (9)$$

where, a new intramolecular correlation function $W^u_{\alpha_i\gamma}$ is defined by

$$W^u_{\alpha_i\gamma} = \sum_j w^u_{\alpha_i\gamma_j} . \qquad (10)$$

We apparently have an infinite number of equations after the reduction. However, the unique equations are the ones corresponding to the atoms in a cell. The other equations are copies of the unique set. As may be clear from the derivation of eq. (9), the theory may be applied to molecular crystals as well as polymers.

3. Applications

As a first application of the theory explained in section 2, we consider four simple polymeric models, corresponding to linear and helical chains of atoms. For the linear chain model, the new intramolecular correlation matrix (eq. (10)) may be written in Fourier k-space as:

$$W^u(k) = 1 + 2\sum_{n=1}^N \sin(nkl)/nkl , \qquad (11)$$

where l is the separation between adjacent atoms in the molecule. In order for the problem to be strictly reduced by means of eq. (8), N must be infinity; otherwise most atoms in the chain are unique and a very large solvent–solute correlation matrix must be employed. The $k=0$ limit of eq. (11) is required to calculate thermodynamic properties. When N goes to infinity, $W^u(k)$ diverges for $k=0$. This is not a significant problem in practice because the influence of neighbouring cells is limited in spatial extent. That is, the solutions to the RISM equations converges as N increases. Furthermore, the limiting N value provides a measure of the correlation length. Fig. 1 shows the effect of truncation of eq. (11) upon the pair correlation function at several distances between solute and solvent atoms. The figure indicates that for a sufficiently large number N, the effect of truncation upon the correlation function is in fact negligible. For the parameters used in model 2 (see below), $N=10$
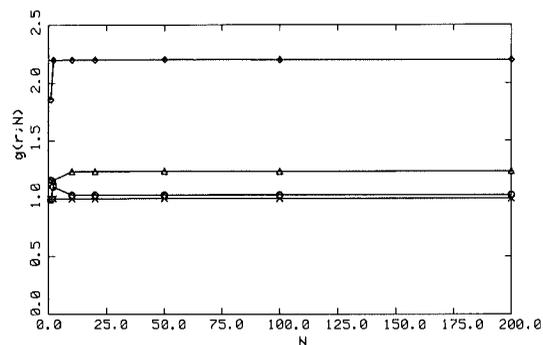
Fig. 1. The effect of truncation of eq. (11) on the correlation function. The result is shown for model 2. The x-axis is the number of terms N in eq. (11), the y-axis is the correlation function at a certain point of the site–site separation r. $\diamond, r=4.0$ Å; $\triangle, r=8.0$ Å; $\bigcirc, r=10.0$ Å; $\times, r=100.0$ Å.

is sufficient.

The calculation has been carried out for the following models: (1) a linear chain of atoms in liquid argon, (2) a linear chain of ions in an electrolyte solution, (3) a linear chain of ions in water, (4) a helical array of atoms in liquid argon.

The (1-6-12) potential is employed for the interaction between a pair of sites, namely,

$$u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^6\right] + \frac{q_\alpha q_\beta}{r}, \qquad (12)$$

where α and β specify the sites in solute and solvent molecules, r is the separation between the two sites. For each model, eq. (4) for the solvent has been solved first by the standard iterative procedure [6]

to get the pure solvent correlation function $\mathbf{h}^{vv}$. The $\mathbf{h}^{vv}$ has been used to solve eq. (5) for the solute–solvent correlation function by iteration. For the first three models, the HNC closure has been employed, while the PY closure has been used for model 4.

As an initial test of the theory, two sets of molecular dynamics simulations have been carried out with parameters corresponding to model 3. The results of simulations of a single ion in water and an ion chain in water are compared with the polymer RISM results. The simulation of single ion included 215 water molecules (SPC model) [11,12] and one ion at the center of a cubic box with edge length 18.62 Å. The linear chain simulation included nine ions equally spaced ($l=2.07$ Å) along the z-axis. The energy parameters employed are shown in table 1. Ion–water site pair correlation functions are calculated from 10 ps and 5 ps trajectories for the single ion and the chain ion, respectively. Further details of the simulation will be presented elsewhere.

3.1. Model 1

As a first example we consider a linear chain of argon atoms immersed in liquid argon. The parameters employed are shown in table 1. The site–site correlation function between the solute atomic sites on the linear chain and the solvent is shown in fig. 2. The various curves correspond to different spacing of atoms along the solute chain. The curves demonstrate the effect of the spacing, l, of atomic sites along

Table 1
Parameters

		σ (Å)	ϵ (erg/molecule)	q (e)
model 1	solute [a]	3.405	1.6544×10^{-14}	0.0
	Ar	3.405	1.6544×10^{-14}	0.0
model 2 [c]	solute [a]	4.0	1.0×10^{-14}	1.0
	cation	4.0	1.0×10^{-14}	1.0
	anion	4.0	1.0×10^{-14}	-1.0
model 3	solute [a]	1.897	1.116×10^{-13}	1.0
	O	3.166	1.08×10^{-14}	-0.82
	H	1.00 (0.0) [d]	3.790×10^{-15} (0.0) [d]	0.41
model 4	solute [b]	3.405	1.6544×10^{-14}	0.0
		3.405	1.6544×10^{-14}	0.0

[a] An atom in the linear chain molecule.   [b] An atom in the helical chain molecule.
[c] Dielectric constant for model 2 is 78.5.   [d] The values in parentheses were used for the simulations.
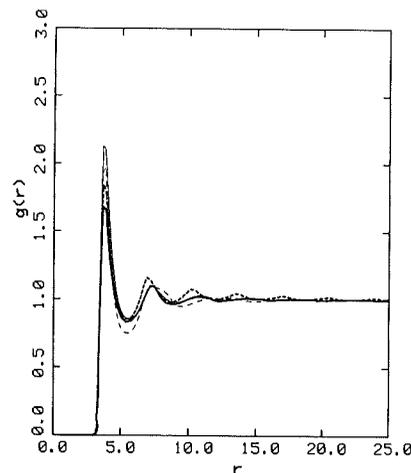
Fig. 2. Solute–solvent correlation function for a linear chain of atoms in liquid argon at density 0.911 g/cm^3 and temperature 153 K. The various curves correspond to the different spacing of atoms in the solute molecule: thin solid line, $l=\infty$; thin dashed line, $l=5.0$ Å; thick solid line, $l=4.0$ Å; thick dashed line, $l=3.405$ Å.

the chain on the solute–solvent correlation functions. For the model linear chain there are two characteristic periodicities which can interfere with each other. One is the periodicity in the pure solvent–solvent correlation function; the other corresponds to the periodicity in the intramolecular correlation between atomic sites on the chain. The curves reflect the interference between the two effects. The correlation function which corresponds to $l=\sigma$ ($=3.405$ Å, σ is the Lennard-Jones diameter of solute and solvent atoms) shows the longest lasting oscillation. This is due to the constructive interference of the two characteristic oscillations. Another interesting trend is the dependence of the height of the first peak on the spacing, where generally, the first peak decreases as the spacing decreases. This reflects the volume exclusion effect of neighboring atomic sites on the correlation function between the central solute atomic site and solvent molecules. The curves corresponding to $l=4.0$ Å and $l=3.405$ Å are reversed; this is due to the dominant effect of the constructive interference of the oscillation for $l=3.405$ Å.

3.2. Model 2

The second example is a linear chain of ions

immersed in an electrolyte solution. The electrolyte solution is simply represented by a primitive type model. Here, the short range part of the interionic interaction is replaced by a Lennard-Jones interaction. The parameters are listed in table 1. The results for the site–site correlation function are shown in fig. 3. As is expected, the correlation function displays an oscillatory behavior reflecting the periodic variation of the charge density along the chain. The strongest oscillations occur when the spacing between the ions along the chain is equal to the diameter of
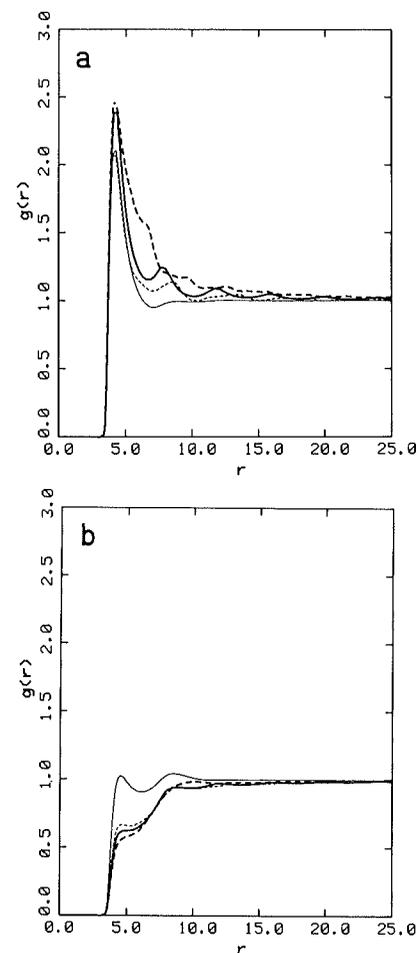

Fig. 3. (a) Solute–solvent correlation function for a linear chain of ions in an electrolyte solution (5 mol/ℓ) at 298 K. Free ions in the electrolyte solution are treated as solvent molecules. Unlike charged pairs. The various curves correspond to the different spacing of ions in the solute molecule: thin solid line, $l=\infty$; thin dashed line, $l=5.0$ Å; thick solid line, $l=4.0$ Å; thick dashed line, $l=3.0$ Å. (b) Same as (a) but for like-charged pairs.

the free ions, as is also observed for the uncharged case (model 1). Another important point concerns the dependence of the correlation function on the charge density along the chain, in which an overall enhancement (unlike charge) or reduction (like charge) of the distribution of solvent ions near the polymers is observed as the charge density increases. The higher charge density, which corresponds to decreased spacing of atomic sites along the chain, results in a stronger attraction of solvent ions and a build up of the solute–solvent ion correlation function close to the chain. This effect dominates the volume exclusion effect observed for model 1.

3.3. Model 3

The next example considered is a linear chain of ions immersed in water. The SPC water model is employed with slight modification [11,12] in order to avoid the numerical catastrophy caused by the possible overlap of hydrogen sites [7,13]. The parameters are shown in table 1. The cation–oxygen correlation functions obtained from the molecular dynamics simulations are compared with the polymer RISM theory in fig. 4. In the results from the simulations two striking features are observed: a significant increase in the height of the first peak of the water distribution around the ion chain as compared with the single ion, and the appearance of a well-defined second peak in the distribution around the ion chain at about 3.73 Å. The new RISM theory reproduces the first peak very well. This increase is not intuitively obvious, because the existence of neighboring chain ions reduces the number of solvent molecules in the first coordination shell due to volume exclusion. The appearance of a second peak corresponds to configurations in which a water molecule is bound by an adjacent ion along the chain. The polymer RISM result also produces a second peak close to the position found in the molecular dynamics simulations, although it is less well developed. A full analysis of the molecular dynamics simulation and comparison with the polymer RISM results will be presented elsewhere.

3.4. Model 4

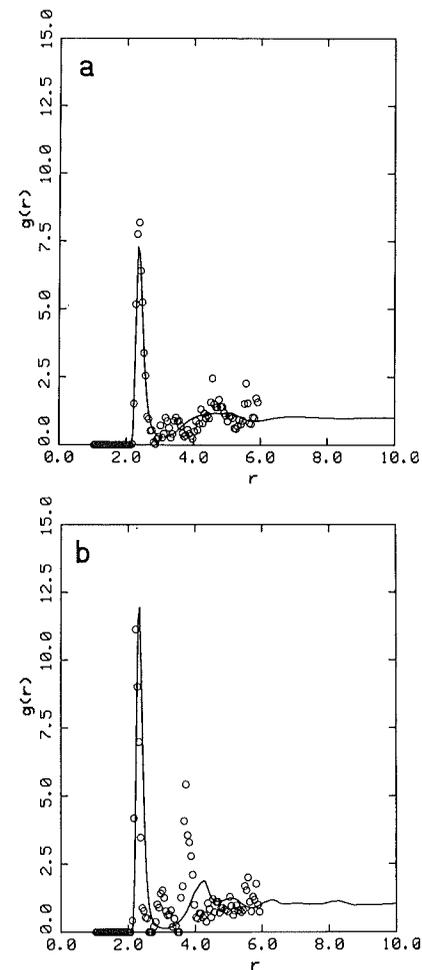As a final example, we consider a solute composed

Fig. 4. The solute–oxygen distribution function for a linear chain of cations in water (1 g/cm^3) at 298 K, (a) single ion ($l=\infty$); (b) ion chain ($l=2.07$ Å). Circles: simulation, solid lines: RISM.

of atoms arranged along a helix interacting with solvent. The same Lennard-Jones parameters are used for the atomic sites on the helix and the solvent. The distance between atomic sites on the helix has been calculated using cylindrical coordinates:

$$x = R \cos(n\Delta\phi), \quad y = R \sin(n\Delta\phi), \quad z = n\Delta z ,$$

where R is the helix radius, $\Delta\phi$ and Δz specify the rotational and translational coordinates of the atomic sites on the helix. The helix site–solvent correlation function is shown in fig. 5 for helix parameters $R = 3.0$ Å, $\Delta\phi = 30°$ and several values of Δz. As may be seen in fig. 5, the main feature of the correlation function
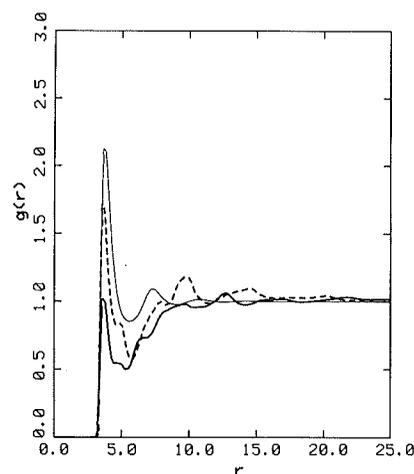
Fig. 5. The solute–solvent correlation functions for a helix chain of atoms in liquid argon at density 0.911 g/cm^3 and temperature 153 K. The various curves correspond to different spacing in the axis direction, Δz: thin solid line, $\Delta z = \infty$; dashed line, $\Delta z = 0.5$ Å; thick solid line, $\Delta z = 0.4$ Å.

is the drastic decrease in the first peak which becomes more and more significant as Δz becomes smaller. The behavior is a consequence of the volume exclusion effect, similar to the first model. The more the helix is packed, the more solvent molecules are excluded from the neighborhood of the central atom in the solute molecule.

4. Concluding remarks

We have introduced a new RISM equation which can be used to treat the interactions of a polymeric solute molecule with solvent. The essential feature of the theory is the introduction of a new intramolecular correlation function for the solute, which is a sum of the intramolecular correlation functions in the old theory over the periodic cells of the polymeric molecule. By means of the new function, a large number of equations, each of which corresponds to correlations between an atomic site on the polymer with solvent, is reduced to a small number of equations for the atoms in a periodic unit of the polymer. It has been demonstrated by several simple examples that the theory can treat the correlations between polymeric structure and solvent structure for a variety of polymer geometries and choices of solvent. Compar-

isons of the predictions of the theory with the results of molecular dynamics simulations are encouraging. Most standard treatments of polyelectrolyte solutions employ a rod-like model with a continuum charge density [14–17]. The rod-axis–ion-center correlation function is expressed in terms of cylindrical coordinates, which is different from our atom–atom radial correlation function written in the spherical coordinate system. A significant advantage of the method proposed here is the flexibility permitted in choosing a model for the polyelectrolyte. For example, polyelectrolytes can be modeled using ions arranged along a helix. Both uniform and alternating charge models can be solved. Correspondence between standard polyelectrolyte treatments which employ continuum charge distributions and the theoretical formalism proposed here may be established in two ways: (1) translating the correlation function from one system to the other through some averaging process; (2) calculating thermodynamic quantities. Both of these approaches are being pursued. Applications of the theory to several interesting problems, particularly solvent effects on the B to Z DNA transition [18] will be the subject of future communications.

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