Solitons in Poly(oxyethylene)

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We introduce a soliton model to describe conformational structure of poly(oxyethylene) in aqueous solution. The model is based on former investigations for twistons in polyethylene, and the soliton solution corresponds to stable excitation that locally transforms the gauche conformation of the O-CH2-CH2-O dihedral angle from the positive (negative) configuration to its negative (positive) partner. The conformational deformation in the polymer main chain is mediated by the unstable cis conformation which changes the physical profile of the chain, contributing to trigger important properties of the polymer. For instance, it may activate the process for the capture of metallic ions in aqueous solution and it may also enlarge solubility of the polymer in water. The soliton solution is used to guide a quantum chemistry investigation that examine, and characterize, a chain containing 40 monomeric units, tracing quantitative correlations with the soliton model.

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Solitons appear under the direct influence of nonlinearity, and may play important role in several branches of nonlinear science. In particular, they may spring as finite energy excitations in nonlinear polymeric chains. A classic example is polyacethylene (PA): in this chain, single and double bonds alternate, generating Peierls instability that gives rise to solitons, as accounted for in the Su-Schrieffer-Heeger model [1]; see Ref. [2] for further details. As one knows, the PA chain admits an interesting field theoretical formulation in terms of bosonic and fermionic fields [3, 4]. Another example of a nonlinear polymeric chain that supports solitonic excitations is polyethylene (PE): in this case the chain only contains single sigma bonds, which activate degrees of freedom of the torsional type, giving rise to twiston excitations in the polymeric chain [5]. The presence of twistons in the PE chain was further explored in Refs. [6, 7], and more recently in Ref. [8] one has shown that these twistons can be seen as topological solitons that appear in a specific model of two real scalar fields.

The work of Ref. [9] follows the investigations on topological solitons initiated in [10], and further explored more recently in [11, 12, 13]. The main idea is that the presence of topological solitons in a polymeric chain may directly contribute to the conformational characteristics of the polymer, a fact important to the understanding of physical, chemical and biological properties of the substance. A singular example is the poly(oxyethylene) (POE), which has long been the subject of great attention due to its various biotechnological and biomedical applications [14]. In this letter we develop the idea that the POE chain is able to support topological solitons, and that these solitons contribute significantly to the understanding of important features of this polymer.

We start with the PE chain, which is a very long chain made of CH2 units. It may be seen as the limit for large n of the chain family [(CH2)n-O-]m. In this family the second member (n = 2) is the POE, which is formed by repetitions of the chain unit CH2-CH2-O-. The POE is a very important polymer in this family, because the peculiar array in the chain provides to this polymer some very impressive features, among them the remarkable ability to entrap metallic ions in aqueous solution and its solubility in water to almost any extent. Besides, one knows that ethylene oxide polymers are amongst the most commonly used substances in pharmaceutical and other industrial formulations [13, 14, 15, 16, 17, 18, 19].

Molecular dynamics simulations [17, 21, 22] on the conformational structure of the POE and 1,2-dimethoxyethane (DME = CH3-O-CH2-CH2-O-CH3, which is correlated with the POE’s dimer) have shown that the polymeric chain may present a very rich family of conformational possibilities, with preference for tgt conformers in condensed media – we are using standard notation, where ‘t’, ‘c’ and ‘g’ represent trans (t), cis (c) arrangement; in gauche (π/3) arrangements, respectively. The tgt conformer was also observed in POE chains used as hidrophilic moiety of nonionic surfactants, in aqueous solutions, through Raman spectroscopy [23]. The stabilization of the tgt conformer in the liquid or solid state may be understood in terms of polar intermolecular interactions, because this conformer has an appreciable dipole moment while the ttt conformer (all trans conformations) has zero dipole moment [17]. This preference for tgt conformation is also predicted for DME by experimental NMR [24] and infrared [25] spectroscopic studies. The water affinity of POE is directly related to a structural similarity between the POE chain and liquid water, which is not found for other polyethers [24, 27]: when substantially hydrated, the POE chain assumes local conformations mostly with the tgt arrangement; in this case there is almost perfect match between the distance of the oxygen atoms in the structure of liquid water and the distance between the nearest neighbor oxygen...
atoms in the polymer chain. Thus, the POE chain may be easily incorporated into the structure of liquid water, with the ether oxygen atoms replacing some of the water molecules, with the hydrophobic ethylene groups being engaged in voids in between water molecules. There are other conformational possibilities in the POE chain; for instance, the tgg conformer is considered the second most populated in DME, also based on spectroscopic results both for DME and POE, probably because of the presence of an important intramolecular 1,5-CH···O interaction that stabilizes this particular conformation. The nomenclature ttt, tgt, and so forth, that we are using is valid to represent the three most important dihedral angles in the polymer main chain, namely O-CH$_2$-CH$_2$-O, CH$_2$-CH$_2$-O-CH$_2$, and CH$_2$-O-CH$_2$-CH$_2$, as we illustrate in Fig. 1.

![Image of dihedral angles](image1.png)

**FIG. 1:** The three most important dihedral angles in the POE main chain.

We can visualize topological solitons in the POE chain thinking of the tgt conformation, the most stable conformational configuration in the POE chain in liquid water. The symmetry of the chain admits two equivalent possibilities, where the helix can be clockwise, generated by a sequence of tgt$^+$t arrangements, or counterclockwise, generated by a sequence of tgt$^-$t orientations. These two gauche conformations (helixes) are degenerate in energy, and they are typically very populated, according to the previous discussion.[24, 25]. They appear to be the most stable of all the conformational possibilities the POE chain may comprise. Thus, although the POE chain may adopt other distinct conformations, our model considers only the two most important set of degrees of freedom, represented by the O-CH$_2$-CH$_2$-O and CH$_2$-CH$_2$-O-CH$_2$ dihedral angles, and the most stable conformation, the gauche and trans arrangements, respectively. For both angles, the cis conformation is unstable, and is seen as a barrier for gauche and trans orientations to tunnel to its symmetric partner. We illustrate this in Fig. 2 for the gauche conformation of the O-CH$_2$-CH$_2$-O dihedral angle.

![Image of conformations](image2.png)

**FIG. 2:** The cis conformation that intermediates the most stable gauche conformation for the O-CH$_2$-CH$_2$-O dihedral angle. The central circles are drawn to represent the two neighboring carbon atoms between subsequent oxygen atoms.

tg$^+$$t \leftrightarrow$ tgt$^-$ that springs as the topological soliton.

The connection between these detailed information at molecular level with the mathematical representation of the polymer is implemented by the field theoretical model that we now develop. The model is described by two real scalar fields, $\phi$ and $\chi$, which live in the bidimensional space-time $(x, t)$. The Lagrangian density has the form

$$\mathcal{L} = \frac{1}{2} \partial_\alpha \phi \partial^\alpha \phi + \frac{1}{2} \partial_\alpha \chi \partial^\alpha \chi - V(\phi, \chi)$$

(1)

where

$$V(\phi, \chi) = \frac{1}{2} W_\phi^2 - \frac{1}{2} W_\chi^2$$

(2)

Here $\partial_\alpha \phi = \partial \phi / \partial x^\alpha$, $W_\phi = \partial V / \partial \phi$, etc. We are using standard notation, with $x^\alpha = (x^0 = t, x^1 = x)$, and $x_\alpha = (x_0 = t, x_1 = -x)$, and $\hbar = c = 1$. The form of the potential is special, because it allows obtaining static solutions of the equations of motion

$$\frac{d^2 \phi}{dx^2} = W_\phi W_\phi \phi + W_\chi W_\chi \phi$$

(3)

$$\frac{d^2 \chi}{dx^2} = W_\phi W_\phi \chi + W_\chi W_\chi \chi$$

(4)

through the first order differential equations

$$\frac{d \phi}{dx} = W_\phi$$

(5)

$$\frac{d \chi}{dx} = W_\chi$$

(6)

Solutions of the first order equations are stable and are minimum energy solutions – see[11] and references therein for more details.

The model we consider is defined by the superpotential $W = W(\phi, \chi)$, which has the specific form

$$W = \lambda a^2 \phi + \nu a^2 \chi - \frac{1}{3} \lambda \phi^3 - \mu \phi \chi^2$$

(7)
We consider $\lambda, \mu, \nu$ real, and $a$ real and positive. This model is new, and reproduces the model first considered in Ref. [6] in the limit $\nu \to 0$. We calculate $W_{\phi\phi}$ and $W_{\chi\chi}$ to see that

$$W_{\phi\phi} = -2\lambda \phi, \quad W_{\chi\chi} = -2\mu \phi$$

(8)

We notice that the superpotential is harmonic for $\mu + \lambda = 0$, thus the equations of motion can be reduced to a family of first order equations for $\lambda + \mu = 0$ [28].

The potential presents absolute minima at the points $(\phi_i, \chi_i)$, where $\chi_i/a = \nu a/2\mu \phi_i$ are given in terms of $\phi_i$, which represent the real solutions of

$$\left(\frac{\phi}{a}\right)^2 = \frac{1}{2} \pm \frac{1}{2} \sqrt{1 - \frac{\nu^2}{\mu \lambda}}$$

(9)

There are two solutions for $\nu^2/\mu \lambda < 0$, four solutions for $0 < \nu^2/\mu \lambda < 1$, two solutions for $\nu^2/\mu \lambda = 1$, and no solution for $\nu^2/\mu \lambda > 1$. We consider the case $0 < \nu^2/\mu \lambda < 1$. We write $\mu = \lambda r$, and $\nu = \lambda s$, to get to $0 < s^2/r < 1$. This implies that $r > 0$, and we take $-\sqrt{s} < s < \sqrt{s}$.

The equations of motion for static fields are solved by solutions to the first order differential equations, after changing $\phi \to a \phi$, $\chi \to a \chi$, and $x \to \lambda ax$

$$\frac{d\phi}{dx} = 1 - \phi^2 - r \chi^2$$

(10)

$$\frac{d\chi}{dx} = s - 2r \phi \chi$$

(11)

We notice that this system does not allow one-field solutions for $s \neq 0$. This peculiar behavior of the model is important, and is in good agreement with the quantum chemistry investigation that we have implemented, as we comment on below. We can find true two-field solutions to the above first order equations. They are described by the field configurations

$$\phi_s(x) = a \sqrt{\frac{1}{2r} \tanh(\lambda a \sqrt{2r} x)}$$

(12)

$$\chi_s(x) = \pm a \sqrt{\frac{1}{r} - \frac{1}{2r^2} \tanh(\lambda a \sqrt{2r} x)}$$

(13)

which are valid for $s = \pm \sqrt{2 - 1/r}$, with $r > 1/2$. We notice that the limit $r \to 1/2$ transforms the above solution back to the one-field solution of the simpler model, where $s = 0$. We see that the amplitude of $\phi$ is $A_\phi = a/\sqrt{2r}$, and that of $\chi$ reads $A_\chi = |s| A_\phi$. Thus, for $1/2 < r < 1$, we get $0 < s^2 < 1$, and the amplitude of $\chi$ is always smaller then that of $\phi$. For $r > 1$ we get $s^2 > 1$, and in this case the amplitude of $\chi$ is greater then that of $\phi$. A complete investigation of the two-field model will be published elsewhere.

In the POE polymer, the topological soliton represents a conformational distortion in the tgt chain: it describes the change from the $tg^+t$ conformation to the $tg^-t$ conformation. This modification is done with the chain passing through the unstable cis conformations, in a way such that the topological distortions locally increase the dipole moment in the chain, which are evenly distributed along the entire chain in both the $tg^+t$ and $tg^-t$ conformations. The presence of a topological soliton breaks the dipole moment uniformity in the chain, increasing the polar nature of the chain in the soliton core, and this is the mechanism that triggers the process for capturing metallic ions in aqueous solution, or that favors the presence of hydrogen bonds in water solutions.

To make our investigations more quantitative we now examine the connections between the detailed information obtained in the model described by two real scalar fields and the POE chain at molecular level. This can be obtained through quantum chemistry calculations, with the mathematical representation of the polymer as given by the model theoretical model. We investigate the chain $H(-\text{CH}_2-\text{CH}_2-O-)...\text{H}$, a POE chain with 40 monomeric units. We suppose that the topological soliton represents the transition state between the positive and negative helix conformations for the polymer main chain. The transition state between the two most stable conformations of the POE is represented by a polymer that mixes the gauche and the energetically unfavorable cis conformations at the same molecule, in a way such that it makes possible the application of quantum chemistry machinery to do the investigation, since the soliton excitation is a continuum phenomenon that needs an extended molecular representation. In Fig. 3 one depicts the polymer molecules considered as reagent, named positive helix (lower figure), and as transition state, named soliton (upper figure). We established that the dihedral angle C-O-C-C was maintained at configuration trans $(\pi)$ throughout the entire polymer molecule, and that the other two dihedral angles in the main chain – namely O-CH$_2$-CH$_2$-O and CH$_2$-CH$_2$-O-CH$_2$ – are chosen according to the field theoretical model, in which we are identifying the $\phi$ and $\chi$ fields with the two dihedral angles CH$_2$-CH$_2$-O-CH$_2$ and O-CH$_2$-CH$_2$-O, respectively. [In fact, we have done several other investigations: for instance, if the CH$_2$-CH$_2$-O-CH$_2$ angle is also frozen, the results are very unusual, showing that the polymer main chain visit very energetic configurations, returning along the same chain axis, but reversing its direction; also, if all the three dihedral angles are free, the polymer main chain bends considerably, breaking the unidirectional character of the polymer].

We use results of the two field model to see that the modification of the two dihedral angles that are correlated with important degrees of freedom of the main chain follow the hyperbolic tangent behavior. We identify the two dihedral configurations O-CH$_2$-CH$_2$-O and CH$_2$-CH$_2$-O-CH$_2$ with the $\chi$ and $\phi$ fields, respectively, and so we use the quantitative pattern of the soliton solution...
The results reveal that the soliton is 98.09 kJ more energetic than the normal gauche conformation, in agreement with the fact that the soliton induces a localized transition between positive and negative helicities of the gauche conformation. This energy difference is explained by the instability of the cis or near-cis conformations in both O-CH₂-CH₂-O and CH₂-CH₂-O-CH₂ dihedral angles, found in the soliton core. We believe that it can be minimized in condensed media, particularly in polar solvents like water, for example, because of the greater polarity of the soliton molecule ($\mu = 11.53$ D) in comparison to the positive or negative helicity ($\mu = 1.42$ D).

The soliton model that we have used seems to be limited, since it does not account for intermolecular interactions between neighbour POE chains. However, this is a good approximation in aqueous solutions, even at high concentrations, since interactions between POE chains via hydrogen bonds are scarce \cite{2}. In fact, there are more interactions between oxyethylene units in the same chain \cite{2}, mediated by hydrogen bonds via neighbour water molecules, but this we have empirically taken into account by considering the positive and negative helix conformations for the POE main chain as the most populated conformations in aqueous solutions.

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\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Heat of Fomation (kJ) & $\mu$ (Debye) \\
\hline
-7621.47 & 11.53 \\
-7719.56 & 1.42 \\
\hline
\end{tabular}
\end{table}

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