The conformation of conducting polymer chains:

Hubbard polymers

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Abstract:

The conformational and electronic properties of conducting flexible random and self-avoiding polymer chains are under investigation. A Hamiltonian for conjugated flexible polymers is introduced and its physical consequences are presented. One important result is that the electronic degrees of freedom greatly affect the conformational statistics of the walks and vice versa. The electronic degrees of freedom extend the size of the chain. The end-to-end distance behaves as $R \propto L^\nu$ with $\nu = (d + 1)/(d + 2)$, where $d$ is the spatial dimension.

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The properties of conducting flexible polymers are widely unknown. On the contrary, quite detailed models exist for linear completely stretched (e.g. crystalline) polymers. In such cases it has been argued that the charge transfer happens only along the chain. Most theoretical investigations on conducting or conjugated (both terms are used interchangeably here) polymers have been devoted to one-dimensional chains studying mainly conductive properties, especially since the SSH model by Su et al. [1] [2]. This Hubbard-type theory predicts the existence of solitons which appear as mobile domain walls between degenerate ground states of the dimerized chain. More recent work focuses on the influence of impurities and non-linear excitations [3] [4], and on the stability of polarons depending on chain ends and other effects that break the conjugation [5]. Experiments with flexible conjugated polymer chains in solution (e.g. polydiacetylenes) indicate a rod-coil transition at room temperatures [6] [7]. Moreover, the structural and conformational dependence of conductivity of these chains has been investigated (see e.g. [8]). These experiments are in particular very interesting, as an important interplay between electronic properties and the conformational properties is demonstrated. Obviously the theories cited above cannot be applied to these cases, as the polymers are flexible, rather than quasi-one-dimensional.

As a first step in this direction a simple scaling argument has been put forward by Pincus et al. [9]. Their idea is to relate this phenomenon to an interplay between the delocalized π-electron system and conformational entropy. A simple free energy Ansatz has been proposed that uses a tight binding approximation for the one electron band together with a simple assumption for the chain entropy, i.e. it depends linearly on the segment length \( l \). By minimization of the free energy an optimum Kuhn segment length, \( l^* \), is found, which behaves roughly as \( l^*(r) \sim l_c \left( r + \frac{1}{2} \right) \). \( r \) is the number of electrons on a given segment and \( l_c = \left( \frac{2\pi^2 t}{3\alpha T} \right)^{\frac{1}{3}} \) where \( t \) is the transfer integral, \( \alpha \) a constant of proportionality and \( T \) temperature.

Other theoretical work on the conformation of conducting polymer chains concerns the stabilization of rod-like conformations by an interaction between the delocalized electron structure and a polarizable solvent [10] [11].

The purpose of this paper is to introduce and show the consequences of a Hamil-
tonian that contains the conformational properties of the polymer chains and the electronic information of the charge carriers. The chains are assumed to be flexible and thus excitations such as phonons play only a minor role, if e.g. a self-avoiding walk is assumed as a model for the bare chain with electrons present. The Hamiltonian presented in the following describes the conformation of conducting polymer chains as a result of chain entropy and the presence of delocalized \( \pi \)-electrons along the chain contour. Our theory elaborates thus on the scaling results by Pincus et al. \cite{9}. It is shown below that the suggested rod-to-coil transition does not take place although the walk stretches significantly. The Hamiltonian put forward here of a flexible chain containing electronic degrees of freedom consists of two parts. The first is the Wiener-Edwards Hamiltonian for a self-avoiding walk, the second is a Hubbard type Hamiltonian that describes the electrons. The electrons are confined to hop along the self-avoiding chain (contour hopping) in the continuum limit. The latter assumption is not necessary, and can be easily relaxed to account for more general situations, where the charge transfer can also take place between excluded volume monomers for a single chain, forming current bridges (bridge hopping), or between different chains (inter chain hopping).

The starting point is a lattice model for a chain in a \( d \)-dimensional hypercubic lattice of lattice constant \( a \). The electrons hop between lattice points which are nearest neighbors and are constrained to remain within the range \( a \) of the chain. Neglecting electron spin and Coulomb correlations between electrons, the interaction between conformational and electronic degrees of freedom is written as:

\[
\beta H_{el.} = -t \int_0^L ds \sum_x \sum_{\mu=1}^d \left( c^\dagger(x) c(x + a e_\mu) + c^\dagger(x) c(x - a e_\mu) + h.c. \right) \delta_{x,r(s)}. \tag{1}
\]

\( t \) is the transfer integral scaled by inverse temperature, \( \beta \). It has the dimension of inverse length and is supposed to be invariant over the contour; also \( t > 0 \). Therefore we require \( t = \beta t_0 / L \) where \( t_0 \) is the transfer integral of the SSH model in the case of no dimerization (i.e. \( u_n = u_{n+1} \) where \( u_n \) is the position of the \( n \)th C-atom, i.e. the \( n \)th lattice point). This guarantees the righthand side of eq.\((1)\) to be dimensionless as it should.

The assumption that the hopping parameter \( t \) is isotropic and constant is correct in a first approximation. A spatial dependance of \( t \) like in the SSH model cannot be
assumed as phonons are not expected to play a significant role in the case of flexible chains. A dimerized ground state which is vital to the SSH model strictly exists only in one dimension. However, the fractal dimension of flexible chains in solution is 5/3 and not 1 [12]. Nonetheless, the electrons are supposed to move preferably along the chain. This constraint is imposed by the delta function in eq. (1). When "smearing out" this constraint from an interatomic distance \( a \) to the lower cut-off \( l \) of the conformational degrees of freedom, this choice gives the simplest non-trivial coupling between conformation and electronic degrees of freedom in the continuum limit which will be given below.

As indicated above, in eq. (1) the electrons are not strictly confined to hop along the chain. They can also move to and from sites that are next neighbors of the lattice walk. So one might be tempted to introduce an additional delta function for the arguments \( x \pm ae_\mu \). However, this procedure would give a wrong continuum limit. It is exactly the "fuzziness" of the electron hopping which produces the electron-electron interaction that is given below as well as the stiffening conjectured by Pincus et al. [7]. In the continuum limit, the apparently superfluous sites fall on the chain (see eq. (2)). If the electrons were constrained to move only along the chain on the lattice, then there would be no effect on the conformation as the sites passed by the electrons could be numbered systematically. This cannot be done in the case of the interaction given in eq. (1).

The continuum version of the complete Hamiltonian including the term for the unperturbed conformation (SAW) is:

\[
\beta H = \frac{d}{2l} \int_0^L ds \left( \frac{\partial r}{\partial s} \right)^2 + \frac{v}{2} \int_0^L ds \int_0^L dt \delta(r(s) - r(t)) - t l^2 \int d^d x \left( c^\dagger(x) \nabla^2_x c(x) \right) \int_0^L ds \delta(x - r(s)).
\]

In the continuum limit it is natural to set \( a = l; l \) is the Kuhn length that represents the minimum characteristic length scale of the system. The present first model ignores Coulomb interactions between electrons but refinements to account for these can be made some of which are mentioned below in the context of an effective electron-electron interaction (for details see [13]).
In eq. (1) and (2) no preference is given a priori to straighter polymer paths. On the contrary, the aim is first, to choose the SAW for the unperturbed polymer conformation and second, to study (perturbatively) the effect of the interaction term coupling conformation to electronic degrees of freedom. Giving preference to stretched conformations would mean a variational treatment of the problem which is not necessary here.

There are two important aspects to be studied as a consequence of model eq. (2) in finding the interplay of statistical and electronic properties. First, the investigation of the effective conformation after eliminating the electronic degrees of freedom. Second, the derivation of an effective interaction between electrons by summing over all conformations.

For the following it is also useful to rewrite the Hamiltonian in terms of the collective segment density fields of $N_p$ polymers $\rho(\mathbf{x}) = \sum_{\alpha=1}^{N_p} \int_0^L ds \delta(\mathbf{x} - \mathbf{r}_\alpha(s))$, where $\mathbf{r}_\alpha(s)$ is the position of segment $s$ for chain $\alpha$. The partition function to start with is given by:

$$Z = \int \mathcal{D}\rho(\mathbf{x}) \int \mathcal{D}c^\dagger(\mathbf{x}) \int \mathcal{D}c(\mathbf{x}) e^{-\beta(H_{\text{conf}}(\{\rho(\mathbf{x})\}) + H_{\text{el}}(\{c^\dagger(\mathbf{x})\},\{c(\mathbf{x})\})},$$

(3)

where $c^\dagger(\mathbf{x})$ and $c(\mathbf{x})$ are the Grassmann fields for the electrons.

For the examination of the effective polymer conformation, an integration over the electron Grassmann fields is performed which yields a determinant $\det M$. The result is an effective Hamiltonian for the conformation including a term $-\text{Tr} \log M$. For a many polymer system (solutions above the overlap concentrations [14] or melts) the unperturbed conformation may be treated in the Gaussian approximation, i.e. only terms up to second order in $\rho(\mathbf{x})$ are considered. This will not represent a limitation for the validity of the results. To handle the determinant the standard procedures of field theory are applied, i.e. the term $-\text{Tr} \log M$ is expanded. To remain consistent with the Gaussian approximation the expansion is carried to second order in the hopping parameter $t$. The term linear in $t$ gives an overall renormalization factor and may be dropped. Finally, the contribution to the effective Hamiltonian due to the hopping electrons is found to be

$$\beta H_1 = \frac{1}{V} \sum_{\mathbf{k}} \rho_{-\mathbf{k}} \rho_{\mathbf{k}} t^2 l^4 V^2 \left( k^4 \Lambda^d \frac{A}{2d} + k^2 \frac{2 \Lambda^{d+2}}{d+2} B + \frac{2 \Lambda^{d+4}}{d+4} A \right),$$

(4)
where \( A = \frac{\Omega}{(2\pi)^d} \) and \( B = \frac{1}{(2\pi)^d} \int d\hat{k} \left( 1 + \cos^2 \theta \right) \). \( \Lambda \) is a cutoff resulting from a \( k \)-space integration and is the inverse of the polymer cut off (Kuhn length) \( \ell \). This results supports the scaling statements of [9] that the chain shows increased stiffness due to electron hopping which yields a non-vanishing contribution in \( k^4 \). The advantage of the present theory is that more results beyond the scaling limit can be predicted.

To be specific let us look at a concrete model for the unperturbed conformation and discuss the influence of the hopping parameter \( t \) on the parameters of the conformational model. This is done by examining the structure factor \( S(k) \). Adopting for a moment the \( k \)-expansion by Shimada et al. [15] which discusses stiff chains in the limit of moderate bending energies, the contribution of the electrons enter the first coefficients as follows:

\[
S^{-1}(k) = \frac{1}{\rho L} \left[ 1 + \rho L(v + t^2\tilde{a}) + k^2 \left( \frac{1}{9} Ll_p + t^2\rho L \right) + k^4 \left( \frac{Ll_p}{324} + t^2\tilde{c}\rho L \right) + \ldots \right].
\]

where \( \tilde{a} = \frac{2\Lambda^{d+4}}{d+4} Aa^4V^2 \), \( \tilde{b} = \frac{2\Lambda^{d+2}}{d+2} Ba^4V^2 \), and \( \tilde{c} = \frac{\Lambda^d}{2d} Aa^4V^2 \). We thus find - for the single chain contour hopping model eq.(1), neglecting other intra and inter chain hopping processes - contributions to the excluded volume effect as well as to terms in second and fourth power of \( k \). Especially the two latter contributions have to be interpreted in terms of an increased persistence length as the hopping parameter is tuned up.

The second aspect of the model, the influence of the conformation on the interaction between the electrons, becomes manifest if the density variables in eq.(3) are integrated out. Then in order to obtain the effective Hamiltonian for the electrons a cumulant expansion may be carried out in momentum space. This expansion can be visualized in terms of Feynman graphs where the structure factor takes the role of a propagator for a "particle exchanged" between electrons. In second order of \( t \) the Fourier transform of the effective inter electron potential is extracted. It is proportional to the conformational structure factor. Different models for the unperturbed conformation can be studied. For simplicity here only Gaussian chains (without excluded volume) are investigated. For such random walk chains the pair
potential in $d$ spatial dimensions as a function of the scaled distance $x = r\sqrt{\frac{3d}{2L}}$ is:

$$\beta V(x) = -\frac{2}{(2\pi)^\frac{d}{2}} t_0^2 \beta^2 (\frac{3d}{LL})^\frac{d}{2+2} N_p Vt^4 \left(\frac{d}{2} (d + 1) - (d + 2)x^2 + x^4\right)e^{-x^2}. \quad (6)$$

Its behavior is shown in fig.1. A magnified view of the non-zero minimum is included. The prefactors in eq.(6) have been set equal to one to give the indicated scale. As fig.(1) demonstrates, the pair potential has an attractive short-range part, a repulsive part for intermediate length scales which gradually decreases to zero for long distances. The attractive short-range part points to a disorder-induced localization of the $\pi$-electrons due to conformational entropy. Coulomb correlations are not included in eq.(6). If they are treated as in the classical Hubbard model, they contribute a positive singularity at the origin (in the form of Dirac’s delta function). At room temperatures $\beta \Delta V \sim 10^{-2}$, so electrons are likely to overcome the attractive part of the potential in this case. The attractive part of the potential becomes important forcing electrons to localize at temperatures where the flexibility of a real polymer is completely lost.

The analysis of effective electron-electron interactions may be carried further by including more complicated hopping processes. They lead to seagull-type and other Feynman graphs which will be discussed elsewhere [13]. These depend on higher (3-point and 4-point) correlation function of the density variables. In terms of conformational interactions these correspond to the inclusion of the second and third virial coefficient. Thus the series remains finite if these coefficients vanish which they actually do in the case of Gaussian chains. A proper $O(n)$-field theory (in the limit $n \to 0$) for such conducting chains can be easily constructed, if a SAW [16] is used for the underlying conformation of the non-conducting chain. The $n$ component vector fields $\phi$ are coupled to fermion fields for the hopping electrons [17]. An effective field theory for the conformation can be obtained by integrating over the electron fields. This gives rise, among other effects, to a renormalized excluded volume parameter:

$$v_1 = v + const \frac{1}{d + 4} \frac{\beta^2 t_0^2}{L^2} V^2 l^{-d}. \quad (7)$$

$v$ is the excluded volume parameter of the non-conducting SAW. One also obtains higher gradient terms in the conformation fields that can be eliminated by counter
terms. A supersymmetric field theory following [18] may also be conceived. Indeed such a theory confirms the results found in the bosonic version together with the limit $n \to 0$.

How does $v_1$ affect the conformation? A simple estimate is given by a Flory-type argument that starts from a crude approximation to the free energy for the modified SAW:

$$\beta F = \frac{dR^2}{2L} + \frac{v_1 L^2}{2 R^d}. \quad (8)$$

Now $v_1$ has to be implemented according to eq.(7). The volume $V$ is given by the mean volume of the chain, $R^d$. If $R$ is expressed in terms of the contour length $L$, one finds in the case of Gaussian chains $V \sim L^{\frac{d}{2}}$. The excluded volume parameter $v_1$ is therefore given by $v_1 = v_0 + C\beta^2 t_0^2 L^{d-2}$. Substituting this expression for $v_1$ in eq.(8) and minimizing with respect to $R$ yields the mean end-to-end vector. For $\beta^2 t_0^2 L^{d-2} \gg v_0$ we find $R \propto L^\nu$ with a new Flory exponent:

$$\nu_{Flory,Hopping} = \frac{d + 1}{d + 2}. \quad (9)$$

In $d = 3$ it is 0.8 whereas the common exponent for SAW reads roughly as 0.6. This implies a strong swelling and stretching of the chain. Although the term induced by the hopping of the electrons dominates over the excluded volume we do not find a completely stretched chain, i.e. we cannot find a rod-to-coil transition. It has to be pointed out also that this term yields no finite upper critical dimension. The hopping term is important in all space dimensions, which is in accord with the physical intuition. The hopping of the electron is purely local from segment to segment and is not sensitive to the space dimension, whereas the usual excluded volume interaction becomes irrelevant in $d > 4$.

We have presented a field theory for conducting, flexible self-avoiding walks. Starting from the path integral formulation of the chain Hamiltonian and a Hubbard model where the electron hopping is bound to take place on the chain, several results could be found. First the hypothesis of Pincus et al. could be confirmed that stiff or rod-like conformations are favored due to a strong interplay of entropic conformation of the polymers and the electronic energy. Moreover a new exponent for the size of a conducting SAW could be derived. The chains are significantly stretched. However,
even in the Flory approximation no rods are formed. This is in contrast to Pincus et al. as far as the explicit assumption of extended rod-like segments made in [9] is concerned. The result found above agrees with the physical picture that the $\pi$-electrons are likely to delocalize more easily when the chains are stretched. Therefore they are able to contribute to the electronic properties. One advantage of the field theoretic formulation is that the influence of the conformation on the effective pair potential between the electrons can be calculated. It shows a repulsive and an attractive part, which produces a second minimum. Several extensions and modifications of this theory are possible and will be reported separately.

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Figure 1: The pair potential in $d = 3$; the inset gives a magnified view of the second minimum.
