PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Conformational and electronic properties of flexible conducting polymer chains

M. Otto and T. A. Vilgis
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Federal Republic of Germany

(Received 29 April 1994)

The conformational and electronic properties of flexible conducting polymer chains are investigated. As a starting point a general Hamiltonian for conjugated flexible chains is presented. The π electrons are described in terms of a Hubbard model confined to the chain modeled by (random) walks. One main result is that electronic degrees greatly affect the conformation which is shown explicitly for a melt of conjugated polymers. The presence of electrons leads to a significant stiffening (rigidification) of the chains, i.e., the effective persistence length is increased. The other important point is the effect of the conformation of the chain on the electron-electron interaction. This leads to a weak disorder-induced localization of the electrons. An effective pair potential is derived using Feynman-graph techniques.

I. INTRODUCTION

The theory of conducting (conjugated) polymers is a generally unsolved problem. For the case of linearly stretched chains the electronic properties are relatively simple, as the classical methods known in solid-state physics can be employed. Such situations are found in crystalline polymers, where the chains are relatively short and the degree of crystallinity is high.[1] More interesting problems are present, when the chains are still significantly flexible and much longer. In such cases the chains have enough entropy to take many different conformations as it is well known in ordinary flexible polymers.[2] Conducting polymers with these properties are solvable in polar solvent and can be found also in the melt state.[1] The well-known methods of quantum mechanics fail in such systems and alternative theories have to be developed. In the present paper this is attempted. A well-defined physical situation is given in experiments with conducting polymer chains in solution that indicate a rod-coil transition at room temperature.[3,4] The conductive properties of conjugated chains have also been shown to depend on conformational properties (see, e.g., Ref. 5). A scaling argument due to Pincus, Rossi, and Cates[6] relates this phenomenon to an interplay between the delocalized π-electron system and conformational entropy. The basic assumption in the approach of these authors is that π electrons are more likely to delocalize along straight monomer sequences than for walk-type chain conformations, such as random walks, walks with finite bending energy, or alternatively, self-avoiding walks (see, e.g., Ref. 2 for a general reference for walk conformations). A simple free-energy ansatz is made using a tight-binding approximation for the one electron band, while supposing a linear dependence on the segment length l for the entropy. An optimum Kuhn segment length, l^*, is thus obtained behaving roughly as $l^*(r) \simeq l_c(r+\frac{1}{2})$; r is the number of electrons on a given segment and $l_c = (2\pi^2 t/3\alpha T)^{1/3}$ where t is the transfer integral, α is a constant of proportionality, and T is the temperature.

Other theoretical work on the conformation of conducting polymer chains concerns the stabilization of rodlike conformations by an interaction between the delocalized electron structure and a polarizable solvent.[7,8]

In this paper we present a detailed model for the interaction between conformational and electronic degrees of freedom based on a Hamiltonian that consists of a purely conformational part and an interaction term that arises due to electrons hopping on the chain. Technically, this interaction is a Hubbard model bound on the chain with arbitrary conformation. In Sec. II we briefly mention the original Hubbard model known in solid-state physics[9,10] to define the notation and review very briefly some of the work presented for conjugated chains in one dimension. The key theory to these issues is the so-called Su-Schrieffer-Heeger (SSH) model.[11,12] In Sec. III we introduce the present model applicable to the case of flexible polymers which carry mobile electrons along the contour, in different representations and generalizations. In Sec. IV consequences of the model presented in Sec. III are derived, mainly in two different directions: (a) the influence of electrons on the conformation of the chain, and (b) the influence of conformation on the interaction between electrons.

II. FROM THE HUBBARD TO THE SSH MODEL

Conjugated carbon-polymer chains are under consideration in the following. A simplified quantum-mechanical model for such macromolecules is the sp^2 hybridization model. The four valence electrons of each C atom are divided into two classes: the three σ electrons that constitute the chain bonds (and the bonds to hydrogen atoms or functional groups) and that are localized on the length scale of these bonds, and one π electron which can delocalize over several bond lengths. Of course, the hybridization picture is not exact; a more realistic model is given by the molecular orbital theory (see, e.g., Ref. 13). On the other hand, one can conceive an even more simplified model for the delocalization of π electrons, i.e., the electrons are imagined to hop between the C atoms

0163-1829/94/50(18)/13228(12)/$06.00

along the chain formed by σ bonds. Additional effects, such as Coulomb correlations between π electrons, have to be taken into account, of course, but complicate the physical picture similar to the case of the classical Hubbard model in solids.

In the discussion that follows, we do not go back to the complete quantum-mechanical description of the conjugated chains because we are interested in the properties on a large length scale (compared to the de Broglie wavelength), i.e., the conformation of these molecules. Large scale properties, and especially the behavior at the critical point (e.g., of the coil-to-rod phase transition), are generally called "universal." Therefore we may use the simplest model neglecting local details, like in the case of the excluded volume problem.

Hopping models for electron delocalization such as those suggested above are very common in solid-state physics. The first one of this kind was proposed by Gutzwiller[9] and Hubbard[10] to describe *d* (and *f*) electrons in transition metals. It is constructed by using Wannier states, which are localized on the atomic scale. In second quantization, creation and annihilation operators $c_\sigma^\dagger(\mathbf{x})$ and $c_\sigma(\mathbf{x})$ for electrons with two spin states, i.e., spin $\sigma=\uparrow,\downarrow$ located at $\mathbf{x}$ are introduced corresponding to the Wannier states. The Hamiltonian for the Hubbard model reads

$$H=\sum_{\mathbf{x},\mathbf{x}'}\sum_{\sigma} t(\mathbf{x},\mathbf{x}')[c_\sigma^\dagger(\mathbf{x})c_\sigma(\mathbf{x}')+\text{H.c.}]$$
$$+U\sum_{\mathbf{x}} n_\uparrow(\mathbf{x})n_\downarrow(\mathbf{x}) \;, \tag{1}$$

in which H.c. means Hermitean conjugate throughout the paper. The first term is purely kinetic describing the motion between atoms at $\mathbf{x}$ and $\mathbf{x}'$, respectively, which are imagined to be points on a lattice. $t(\mathbf{x},\mathbf{x}')$ is the hopping integral between the respective lattice points. In general, the tight-binding approximation is assumed to hold, i.e., the sum in the first term in Eq. (1) is restricted to nearest neighbors. Moreover, translational invariance gives $t(\mathbf{x},\mathbf{x}')=-t$ with $t>0$. The second term is the Coulomb interaction where $U>0$ for electrons. $n_\sigma(\mathbf{x})=c_\sigma^\dagger(\mathbf{x})c_\sigma(\mathbf{x})$ is the particle number operator. The Coulomb interaction is assumed to be screened on the interatomic scales. Therefore we are left with only the onsite term.

The Hubbard model can be also applied to π electrons on conjugate polymer chains. The electrons move in a highly restricted (though not necessarily one-dimensional) geometry, thus validating the assumption of localized states. Similar behavior is found for the restriction of hopping to nearest neighbors. Coulomb correlations are generally neglected for the stretched one-dimensional chain in the SSH model to be discussed shortly. We have included it while discussing an effective pair potential between electrons produced by the conformation. However, for the study of conformational properties local details are not important. Considering Coulomb correlations in the spirit of the original Hubbard model mentioned, they may be neglected as they are screened on interatomic scales.

Su, Schrieffer, and Heeger[11,12] (SSH) applied the Hubbard model to conjugated polymers in order to explain spectra of electronic excitations. Their theoretical ansatz implies the existence of solitons which in the case of conjugate chains appear as moving domain walls separating the two degenerate ground states of the dimerized chain. In contrast to the work presented here, SSH are not interested in the conformation, but rather start out with the linear one-dimensional chain as a fixed configuration. In this particular case the Peierls instability produces dimerization and a doubling of the lattice constant. The σ bonds are modeled by springs with constant K that are fixed between C atoms at the positions u_n and u_{n+1}. The π electrons are treated in the tight-binding approximation via a hopping integral that favors hopping between double bonds as opposed to single bonds:

$$t_{n,n+1}=t_0-\alpha(u_{n+1}-u_n)\;. \tag{2}$$

t_0 is the hopping integral for the undimerized chain and α is the electron-phonon coupling constant. Including the kinetic energy of the C nuclei, one thus obtains the SSH Hamiltonian:

$$H_{\text{SSH}}=-\sum_{n,s} t_{n,n+1}(c_{n+1,s}^\dagger c_{n,s}+c_{n,s}^\dagger c_{n+1,s})$$
$$+\frac{1}{2}\sum_n K(u_{n+1}-u_n)^2+\frac{1}{2}\sum_n M\dot{u}_n^2\;. \tag{3}$$

In analogy to the Hubbard model, $c_{n,s}^\dagger$ and $c_{n,s}$ are creation and annihilation operators for electrons of spin s at the nth C atom.

Coulomb correlations have not been included in the above Hamiltonian, but are assumed to be effectively present in the constants α and t_0. The latter constant will also appear in model discussed below.

A continuum version of the SSH model has been developed by Takayama, Lin-Liu, and Maki,[14] which is known as the TLM model. More recent work, e.g., by Harigaya, Wada, and Fesser, is concerned with the effect of randomly distributed impurities on electronic properties of conducting polymers within the framework of the SSH or the TLM model[15] and localized electronic states that result form a mutual influence between impurities and nonlinear excitations.[16] Moreover the SSH Hamiltonian has been generalized by Wolf and Fesser to include a disorder term describing hopping between parallel chains via a Gaussian distributed hopping parameter.[17] Most recently, the stability of polarons has been studied depending on chain ends and other effects that break conjugation, by using a generalized SSH model with interchain hopping.[18]

III. A HUBBARD MODEL FOR CHAINS IN ARBITRARY CONFORMATION

A. How to couple electrons to conformation

In order to derive the supposed coupling between conformational and electronic degrees of freedom, the SSH model cannot be used for its starts from a fixed conformation, the stretched out one-dimensional chain. A model that seeks to overcome this deficiency must not exclude a physically reasonable conformation because one of its purposes is exactly to predict how the conformation is altered by the presence of delocalizing electrons. In particular, the dimension of the concerned object is not to be reduced. We remark at this point that the fractal dimension of an ideal flexible chain (random walk) is 2. For a flexible chain with excluded volume (self-avoiding walk) it is approximately $\frac{5}{3}$. In both cases it is not 1. Therefore, when studying a possible stretching of a flexible chain by the presence of delocalizing electrons, it is useless to start from a one-dimensional model.

Accounting adequately for this remark, we start from a self-avoiding walk (SAW) polymer chain on a d-dimensional hypercubic lattice of lattice constant a. To simplify the analysis the electrons are allowed to hop on the lattice under the constraint that they remain within the range a of the chain such that they effectively can jump from the chain to one of the nearest neighbors on the lattice. Below, the continuum limit will be discussed where this effect does not matter, especially for chains with excluded volume. Further simplifying the problem, we consider electrons without spins and neglect the Coulomb interaction as well (it will be included later in the discussion of an effective interelectron potential). As a consequence a modified Hubbard model for the π electrons is obtained:

$$\beta H_{\rm el}=-t\int_0^L ds\sum_{\mathbf{x}}\sum_{\mu=1}^{d}[c^{\dagger}(\mathbf{x})c(\mathbf{x}+a\mathbf{e}_{\mu})+c^{\dagger}(\mathbf{x})c(\mathbf{x}-a\mathbf{e}_{\mu})+\text{H.c.}]\delta_{\mathbf{x},\mathbf{r}(s)}\ . \tag{4}$$

In this equation t is the hopping integral scaled with inverse temperature β, and it has the dimension of inverse length. As above for the Hubbard model, $t>0$. The ladder operators and the δ function are defined on the lattice and are dimensionless. Hence the only reasonable length that exists for our problem is the contour length L. We therefore rescaled

$$t=\frac{\beta t_0}{L}\ . \tag{5}$$

t_0 is the above mentioned hopping parameter in the SSH model. It is found experimentally to be equal to $2.5eV$. Taking for L typical values of 10^4 or 10^5 (times the segment length), we find at room temperatures with $\beta=(\frac{1}{40}eV)^{-1}$ that t is equal to 10^{-2} or 10^{-3}, respectively. Thus an expansion parameter smaller than 1 can be defined; this will become important for later discussions below.

In Eq. (4), 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 corresponding lattice walk. Therefore one might be tempted to introduce an additional δ function for the arguments $\mathbf{x}\pm a\mathbf{e}_{\mu}$. However, this procedure would not give the correct continuum limit. It is the "fuzziness" of the electronic motion which produces the electron-electron interaction that is derived below as well as the stiffening conjectured by Pincus, Rossi, and Cates.[6] In the continuum limit, the apparently superfluous sites fall on the chain [see Eq. (9)]. Constraining the electrons to move *only* along the chain on the lattice, would produce 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. (4).

Before moving to generalizations let us derive the continuum representations of the lattice model, which turn out to be very comfortable in their technical handling.

B. Various continuum models

The continuum limit of lattice theories is very useful if one is interested in the behavior of a system at length scales that are very large compared to the lattice constant. One way to perform this limit is to carry out a Fourier transformation for the ladder operators $c(\mathbf{x})$ and then, an expansion in powers of the wave vector.[19] With $c(\mathbf{x})=\sum_{\mathbf{k}}c_{\mathbf{k}}e^{i\mathbf{k}\mathbf{x}}$ one obtains for the Hamiltonian Eq. (4):

$$\beta H_{\rm el}=-2t\sum_{\mathbf{k}}\sum_{\mathbf{q}}c_{\mathbf{q}}^{\dagger}c_{\mathbf{k}}\sum_{\mu=1}^{d}[\cos(k_{\mu}a)+\cos(q_{\mu}a)]\times\int_0^L ds\, e^{-i(\mathbf{q}-\mathbf{k})\mathbf{r}(s)}\ . \tag{6}$$

As only large scales are of interest, we can expand the cosines to second order in $\mathbf{k}$, which yields

$$\beta H_{\rm el}=-ta^2\sum_{\mathbf{k}}\sum_{\mathbf{q}}c_{\mathbf{q}}^{\dagger}c_{\mathbf{k}}\left[\frac{4d}{a^2}-\mathbf{k}^2-\mathbf{q}^2\right]\times\int_0^L ds\, e^{-i(\mathbf{q}-\mathbf{k})\mathbf{r}(s)}\ . \tag{7}$$

In the parentheses in Eq. (7), the second and third term are obviously of kinetic origin. The first one, which is of order a^{-2}, produces a number operator on the chain, and thus a constant contribution to the energy. In the case of constant electron number it may be dropped. If there are fluctuations in electron number, it has to be renormalized by a chemical potential.

Now we make the coupling between electrons and conformation become apparent. The crucial variable to describe conformation in this specific case is the segment density $\rho(\mathbf{x})=\int_0^L ds\,\delta(\mathbf{x}-\mathbf{r}(s))$. The last factor in Eq. (7) which consists of the integral over the chain contour is in fact the Fourier transform of $\rho(\mathbf{x})$, i.e., $\rho_{\mathbf{q}-\mathbf{k}}$. The coupling term becomes therefore:

$$\beta H_{\rm el}=ta^2\sum_{\mathbf{k}}\sum_{\mathbf{q}}(\mathbf{k}^2+\mathbf{q}^2)c_{\mathbf{q}}^{\dagger}c_{\mathbf{k}}\rho_{\mathbf{q}-\mathbf{k}}\ . \tag{8}$$

The sum in Eq. (8) is usually carried out up to cutoff Λ being of order $1/a$ where a is the lattice constant or fundamental length. In the case of Gaussian chains we set $a=l,l$ being the Kuhn segment. We have thus obtained an interaction term with a second-order dependence on momentum as expected in analogy to the free-electron gas. The kinetic term is, however, directly coupled to the conformation as the electrons are only allowed to move along the chain.

The continuum model can also be derived in position space, when lattice derivatives and lattice Laplacians are used.[20] The interaction term then has the following form:

$$\beta H_{\mathrm{el}} = -ta^2 \int d^d\mathbf{x}[c^\dagger(\mathbf{x})\nabla_{\mathbf{x}}^2 c(\mathbf{x}) + (\nabla_{\mathbf{x}}^2 c^\dagger(\mathbf{x}))c(\mathbf{x})] \times \int_0^L ds\, \delta(\mathbf{x}-\mathbf{r}(s)) \; . \tag{9}$$

Substituting the last factor by the segment density, Eq. (9) yields

$$\beta H_{\mathrm{el}} = -ta^2 \int d^d\mathbf{x}[c^\dagger(\mathbf{x})\nabla_{\mathbf{x}}^2 c(\mathbf{x}) + (\nabla_{\mathbf{x}}^2 c^\dagger(\mathbf{x}))c(\mathbf{x})]\rho(\mathbf{x}) \; . \tag{10}$$

The interaction term due to hopping Eqs. (9) or (10) have to be added to the Hamiltonian for the unperturbed conformation. Assuming this to be the SAW model, one may thus obtain the Hamiltonian for the entire system:

$$\beta H = \frac{d}{2l}\int_0^L ds \left[\frac{\partial \mathbf{r}}{\partial s}\right]^2 + \frac{v}{2}\int_0^L ds \int_0^L dt\, \delta(\mathbf{r}(s)-\mathbf{r}(t)) - tl^2 \int d^d\mathbf{x}(c^\dagger(\mathbf{x})\overleftrightarrow{\nabla}_{\mathbf{x}}^2 c(\mathbf{x}))\int_0^L ds\, \delta(\mathbf{x}-\mathbf{r}(s)) \; . \tag{11}$$

In this equation we use $a=l$ if no additional bending-energy term is present. Such an assumption can be criticized as unphysical, as realistic polymers are locally stiff. Indeed in intrinsically stiff polymers (e.g., liquid crystalline polymers) a modified persistence length defines the cutoff,[21] which is determined by the bending energy. In most places in this paper we will use the Wiener-type measure for the unperturbed conformation of the polymers to keep the mathematical complications on a minimum. It can be shown, however, that the theory presented in this paper can be generalized to other types of polymers. The formulation of the theory for random and self-avoiding walks is understood to be exemplary to show the possibilities at the simplest level. The general features of the model presented here will not change under the assumptions of local stiffness, more realistic polymer models, etc. As a consequence of this simplification the Kuhn length is the minimum length (lower cutoff) of the system. Equation (11) is very important in order to derive a field theory for conducting polymers.[22]

In density variables βH reads as

$$\beta H = \frac{d}{2l}\int_0^L ds \left[\frac{\partial \mathbf{r}}{\partial s}\right]^2 + \frac{v}{2}\int d^d\mathbf{x}\rho^2(\mathbf{x}) - tl^2 \int d^d\mathbf{x}(c^\dagger(\mathbf{x})\overleftrightarrow{\nabla}_{\mathbf{x}}^2 c(\mathbf{x}))\rho(\mathbf{x}) \; . \tag{12}$$

A further contribution to βH may be the Coulomb interaction between electrons treated like in the Hubbard model Eq. (1). In the continuum representation the respective term is given by

$$\beta H_{\mathrm{Coulomb}} = \frac{U}{V}\int d^d\mathbf{x}\, n(\mathbf{x})n(\mathbf{x}) \; . \tag{13}$$

The operators $n(\mathbf{x}) = c^\dagger(\mathbf{x})c(\mathbf{x})$ are the number operators for the electrons located at $\mathbf{x}$ and U is the on-site term of the transition amplitude and thus the coupling constant of the electron-electron correlation energy.

C. Generalizations: Bridge hopping and interchain hopping

Before we include the unperturbed conformation in the Hamiltonian, we want to discuss some generalizations concerning more complicated hopping processes. So far we considered linear hopping along the chain's contour (hence called "contour hopping"). This is certainly the most important contribution for the case of a single chain in solution. However, even in this case conformations exist where monomers that are very apart along the contour come very close to each other (see Fig. 1). In the purely conformational part in the Hamiltonian, these conformations give rise to excluded volume contributions. As to electron hopping, we may conceive that electrons pass between monomers approaching each other forming bridges (bridge hopping). Moreover we may consider many-chains systems. In this case hopping may occur between different chains touching one another. In the lattice picture we get an impression how these two types of hopping processes look (see Fig. 2). In order to discuss systems of many chains, one has to modify the relevant variables for the conformation. The segment position is now given by $\mathbf{r}_\alpha(s)$ where α is the chain index. For a system of N_p chains, the collective segment density reads

$$\rho(\mathbf{x}) = \sum_{\alpha=1}^{N_p}\int_0^L ds\, \delta(\mathbf{x}-\mathbf{r}_\alpha(s)) \; . \tag{14}$$

The Hamiltonian for the interaction now consists of two terms:

$$\beta H_{\mathrm{el}} = \beta H_0 + \beta H_1 \; . \tag{15}$$

βH_0 is the contribution from contour hopping [see Eq. (4)] of all chains, i.e.,

$$\beta H_0 = -t\sum_\alpha \int_0^L ds \sum_{\mathbf{x}} \sum_{\mu=1}^{d} [c^\dagger(\mathbf{x})c(\mathbf{x}+a\mathbf{e}_\mu) + c^\dagger(\mathbf{x})c(\mathbf{x}-a\mathbf{e}_\mu) + \mathrm{H.c.}]\delta_{\mathbf{x},\mathbf{r}_\alpha(s)} \; . \tag{16}$$

In addition we have to account for the hopping processes in Fig. 2 which are described by βH_1;

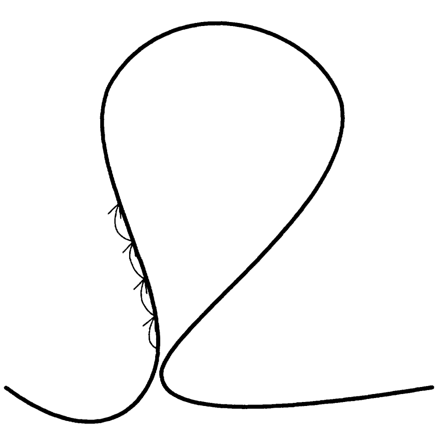

FIG. 1. Excluded volume conformation. The little arrows indicate hopping along the chain.

$$\beta H_1=-t'\sum_{\alpha,\beta}\sum_{\mathbf{x}}\sum_{\mu=1}^{d}\left[c^{\dagger}(\mathbf{x})c(\mathbf{x}+a\mathbf{e}_\mu)\int_0^L dt\,\delta_{\mathbf{r}_\alpha(s),\mathbf{r}_\beta(t)-a\mathbf{e}_\mu}+c^{\dagger}(\mathbf{x})c(\mathbf{x}-a\mathbf{e}_\mu)\int_0^L dt\,\delta_{\mathbf{r}_\alpha(s),\mathbf{r}_\beta(t)+a\mathbf{e}_\mu}+\text{H.c.}\right]\int_0^L ds\,\delta_{\mathbf{x},\mathbf{r}_\alpha(s)}\ . \tag{17}$$

The δ functions within parentheses check whether there are neighboring segments for electrons to hop between. The δ function outside the parentheses ensures that all electrons are constrained to the chains. t' is the respective interchain hopping integral. A dimensional analysis analogous to the one leading to Eq. (5) yields

$$t'=\frac{\beta t_1}{L^2}\ . \tag{18}$$

t_1 is another hopping parameter introduced (in analogy to t_0) for generalized hopping processes. We suppose that $t'<t$ implying that electrons favor linear hopping along the chain.

In the continuum limit of Eq. (17) the δ functions within parentheses become δ functions of the form $\delta(\mathbf{r}_\alpha(s)-\mathbf{r}_\beta(t))$. Similar to Eq. (9), we obtain

$$\begin{aligned}\beta H_1=-t'a^{2+d}\sum_{\alpha,\beta}&\int d^d\mathbf{x}[c^{\dagger}(\mathbf{x})\nabla_{\mathbf{x}}^2c(\mathbf{x})+(\nabla_{\mathbf{x}}^2c^{\dagger}(\mathbf{x}))c(\mathbf{x})]\\&\times\int_0^L ds\,\delta(\mathbf{x}-\mathbf{r}_\alpha(s))\\&\times\int_0^L dt\,\delta(\mathbf{r}_\alpha(s)-\mathbf{r}_\beta(t))\ .\end{aligned} \tag{19}$$

In order to express the generalization hopping term in terms of the segment density, one has to perform a Fourier transformation of Eq. (19) yielding

$$\beta H_1=t'a^2\sum_{\mathbf{k},\mathbf{q},\mathbf{p}}c_{\mathbf{q}}^{\dagger}c_{\mathbf{k}}(\mathbf{k}^2+\mathbf{q}^2)\rho_{\mathbf{q}-\mathbf{k}-\mathbf{p}}\rho_{\mathbf{p}}\ . \tag{20}$$

In contrast to βH_0, the segment density appears in second order. This situation is completely analogous to the density representation of the excluded volume interaction term which is also of second order in ρ. This is not surprising as the conformations contributing to generalized hopping also do so for the excluded volume effect.

From Eqs. (19) or (20), one can also derive a continuum model in position space for many-chains systems in terms of the segment density. Together with the SAW Hamiltonian one obtains for the entire system (neglecting Coulomb correlations due to the reasons discussed above):

$$\begin{aligned}\beta H=&\frac{d}{2l}\sum_\alpha\int_0^L ds\left[\frac{\partial\mathbf{r}_\alpha}{\partial s}\right]^2+\frac{v}{2}\int d^d\mathbf{x}\rho^2(\mathbf{x})\\&-tl^2\int d^d\mathbf{x}(c^{\dagger}(\mathbf{x})\overset{\leftrightarrow}{\nabla}{}_{\mathbf{x}}^2c(\mathbf{x}))\rho(\mathbf{x})\\&-t'l^{2+d}\int d^d\mathbf{x}(c^{\dagger}(\mathbf{x})\overset{\leftrightarrow}{\nabla}{}_{\mathbf{x}}^2c(\mathbf{x}))\rho^2(\mathbf{x})\ .\end{aligned} \tag{21}$$

We have also used $a=l$ for the reason mentioned above [see the discussion following Eq. (11)]. Equation (21) contains two terms quadratic in $\rho(\mathbf{x})$: the excluded volume and the generalized hopping term. The excluded volume interaction is repulsive whereas the generalized hopping term is attractive. The latter one gives an increased delocalization of electrons favoring an effective attraction of segments. This may appear in contradiction to the supposed stretching of the chain which will be derived below. However, one has to keep in mind that the principal mechanism is single-chain hopping leading to a stiffening of the chain. (Only in melts, a correction is expected due to contributions from more general hopping processes which can become important under certain circumstances.)

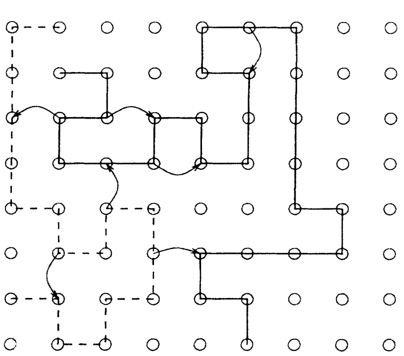

FIG. 2. Inter- and intrachain hopping.

IV. CONSEQUENCES

With this minimal model for conjugate polymers that couples electrons and conformations, different possibilities emerge to discuss consequences. In the complete model for conformation and hopping electrons one may first eliminate the electronic degrees of freedom thus obtaining an effective interaction for the chain conformation (a). Second, one may integrate out the conformational degrees of freedom which gives an effective Hamiltonian for the electrons (b).

This becomes obvious as the partition function for the entire system formally reads as:

$$\begin{aligned}Z=&\int\mathcal{D}\rho(\mathbf{x})\int\mathcal{D}c^{\dagger}(\mathbf{x})\int\mathcal{D}c(\mathbf{x})\\&\times e^{-\beta(H_{\text{conf}}[\{\rho(\mathbf{x})\}]+H_{\text{el}}[\{c^{\dagger}(\mathbf{x})\},\{c(\mathbf{x})\}])}\end{aligned} \tag{22}$$

A. An effective Hamiltonian for the conformation

In order to examine the influence of the electronic degrees of freedom on the conformation, the electron fields are integrated out to yield an effective conformational Hamiltonian:

$$Z=\int\mathcal{D}\rho(\mathbf{x})e^{-\beta H_{\text{conf,eff}}(\rho(\mathbf{x}))}\ . \tag{23}$$

We will elaborate in the discussion that follows on this integration and its consequences. Describing the conformation in terms of the segment density is very efficient for polymer melts. For dilute systems a field theory is more appropriate, and this approach will be presented elsewhere.[22]

For polymer melts the Gaussian approximation is sufficient which neglects terms of order greater than 2 in the density variables.[2] To avoid complications we further restrict the analysis to contour hopping, i.e., the case where $t \gg t'$. The partition function Eq. (23) then reads as

$$Z=\int \mathcal{D}\rho(\mathbf{x}) \int \mathcal{D}c^{\dagger}(\mathbf{x}) \int \mathcal{D}c(\mathbf{x}) \times \exp\left[-\int d^d\mathbf{x} \int d^d\mathbf{y}[\rho(\mathbf{x}) S_0^{-1}(\mathbf{x}-\mathbf{y})\rho(\mathbf{y}) + c^{\dagger}(\mathbf{x}) M(\mathbf{x},\mathbf{y}) c(\mathbf{y})]\right] , \quad (24)$$

where $M(\mathbf{x},\mathbf{y})$ is given by

$$M(\mathbf{x},\mathbf{y})=-ta^2[2\rho(\mathbf{x})\nabla_x^2+2\nabla_x\rho(\mathbf{x})\cdot\nabla_x + (\nabla_x^2\rho(\mathbf{x}))]\delta(\mathbf{x}-\mathbf{y}) . \quad (25)$$

This matrix is obtained by appropriately commuting the ladder operators in Eq. (10) so they appear on the very left and right side of the interaction term.

$S_0(\mathbf{x}-\mathbf{y})=1/V\langle\rho(\mathbf{x})\rho(\mathbf{y})\rangle$ is the structure factor in position space which is assumed to be translationally invariant. The fermion fields can now be integrated out. The arising determinant is then exponentiated again to yield:

$$Z=\int \mathcal{D}\rho(\mathbf{x}) \exp\left[-\sum_{\mathbf{x}}\sum_{\mathbf{y}}[\rho(\mathbf{x}) S_0^{-1}(\mathbf{x}-\mathbf{y})\rho(\mathbf{y})] + \mathrm{Tr}\ln M(\mathbf{x},\mathbf{y})\right] . \quad (26)$$

The negative exponent in this equation is the effective Hamiltonian for the conformation. For the discussion that follows it is more convenient to rewrite the partition function in momentum space. Then it reads

$$Z=N\int \prod_{\mathbf{k}>0} d\rho_{\mathbf{k}} \exp\left[-\frac{1}{V}\sum_{\mathbf{k}} S_0^{-1}(\mathbf{k})\rho_{\mathbf{k}}\rho_{-\mathbf{k}}+\sum_{\mathbf{k}}\ln M(\mathbf{k})\right] . \quad (27)$$

In this representation the effective Hamiltonian is given by

$$\beta H_{\text{conf,eff}}=\beta H_0+\beta H_1=\frac{1}{V}\sum_{\mathbf{k}} S_0^{-1}(\mathbf{k})\rho_{\mathbf{k}}\rho_{-\mathbf{k}}-\mathrm{Tr}\ln M . \quad (28)$$

To treat Tr ln$M$, it turns out to be sufficient to expand the logarithm of M to second order in the density and to determine so corrections to the (inverse) structure factor. First we note that

$$\mathrm{Tr}\ln M=2\,\mathrm{Tr}M-\tfrac{1}{2}\mathrm{Tr}M^2+\text{const terms} . \quad (29)$$

In the present case it is easier to perform the traces in position space whereas the density variables are considered in momentum space. A convenient expression for $M(\mathbf{x},\mathbf{y})$ is obtained from Eq. (8) by transforming the ladder operators back to position space. This yields

$$M(\mathbf{x},\mathbf{y})=ta^2\sum_{\mathbf{k},\mathbf{q}}\rho_{\mathbf{q}-\mathbf{k}}(\mathbf{k}^2+\mathbf{q}^2)e^{-i\mathbf{k}\mathbf{x}+i\mathbf{q}\mathbf{y}} . \quad (30)$$

We now consider βH_1, expanded according to Eq. (29). A straightforward calculation gives

$$\begin{aligned}\beta H_1&=-2\sum_{\mathbf{x}} M(\mathbf{x},\mathbf{x})+\frac{1}{2}\sum_{\mathbf{x}}\sum_{\mathbf{y}} M(\mathbf{x},\mathbf{y})M(\mathbf{y},\mathbf{x})\\&=-4ta^2\rho_0\sum_{\mathbf{k}}\mathbf{k}^2+\frac{t^2a^4}{2}\sum_{\mathbf{k},\mathbf{k}'}\rho_{\mathbf{k}'-\mathbf{k}}\rho_{\mathbf{k}-\mathbf{k}'}(\mathbf{k}^2+\mathbf{k}'^2)^2 .\end{aligned} \quad (31)$$

The first term is constant in $\rho_{\mathbf{k}}$ and can be included in an unimportant overall normalization factor of the partition function Eq. (27). It is neglected in the subsequent discussion. The second term deserves more attention and gives contributions to the structure factor. First, it has to be cast into form comparable to βH_0 so that the product in density reads as $\rho_{\mathbf{k}}\rho_{-\mathbf{k}}$. This is done by transforming the momenta according to $\mathbf{k}\to\mathbf{k}+\mathbf{k}'$. We obtain

$$\beta H_1=\frac{t^2a^4}{2}\sum_{\mathbf{k},\mathbf{k}'}\rho_{-\mathbf{k}}\rho_{\mathbf{k}}[(\mathbf{k}+\mathbf{k}')^2+\mathbf{k}'^2]^2 . \quad (32)$$

Then the square of the expression in parentheses is evaluated. Note that only terms even in $\mathbf{k}$ or $\mathbf{k}'$ contribute to the sums. By introducing a momentum cutoff Λ that is proportional to the inverse of a, the fundamental length, the sum over $\mathbf{k}'$ is performed yielding

$$\beta H_1=\frac{1}{V}\sum_{\mathbf{k}}\rho_{-\mathbf{k}}\rho_{\mathbf{k}}t^2a^4V^2 \times\left[\mathbf{k}^4\frac{\Lambda^d}{2d}A+\mathbf{k}^2\frac{2\Lambda^{d+2}}{d+2}B+\frac{2\Lambda^{d+4}}{d+4}A\right] , \quad (33)$$

where

$$A=\frac{\Omega_d}{(2\pi)^d} \text{ and } B=\frac{1}{(2\pi)^d}\int d\hat{k}(1+\cos^2\theta) . \quad (34)$$

Ω_d is the surface of the d-dimensional unit sphere and $d\hat{k}$ is the corresponding infinitesimal solid-angle element. For $d=3$ we find $A=(2\pi)^{-1}$ and $B=2/3\pi^2$. The result Eq. (33) agrees with intuition because for a chain that is stiffened due to electron hopping, the structure factor is expected to contain a contribution proportional to $\mathbf{k}^4$. Hence the conjecture made in Ref. 6 is justified.

We can now assess the influence of hopping electrons on the conformation by looking at the structure factor for the entire system. For a conformation model with excluded volume interaction, it reads

$$
\begin{aligned}
S^{-1}(\mathbf{k}) &= S_0^{-1}(\mathbf{k}) + t^2\tilde{a} + \mathbf{k}^2(t^2\tilde{b}) + \mathbf{k}^4(t^2\tilde{c}) \\
&= S^{-1}_{\text{no interaction}}(\mathbf{k}) + v + t^2\tilde{a} + \mathbf{k}^2(t^2\tilde{b}) + \mathbf{k}^4(t^2\tilde{c})\ .
\end{aligned}
\tag{35}
$$

v is the excluded volume parameter. $S_{\text{no interaction}}(\mathbf{k})$ is the structure factor for the chain conformation without any interaction and has to be calculated for a particular model, e.g., for Gaussian chains where it is equal to the Debye function. The coefficients $\tilde{a}$, $\tilde{b}$, and $\tilde{c}$ are obtained from Eq. (33). They are given by

$$
\begin{aligned}
&\tilde{a} = \frac{2\Lambda^{d+4}}{d+4} A a^4 V^2\ , \quad \tilde{b} = \frac{2\Lambda^{d+2}}{d+2} B a^4 V^2\ , \\
&\tilde{c} = \frac{\Lambda^d}{2d} A a^4 V^2\ .
\end{aligned}
\tag{36}
$$

By considering a concrete model for the conformation without interactions, one can estimate the influence of the electronic parameter t on the conformational parameters of the model used. Taking, e.g., the $\mathbf{k}$ expansion by Shimada, Doi, and Okano[23] for stiff chains in the flexible limit (with no nematic interactions present), one finds

$$
S^{-1}(\mathbf{k}) = \frac{1}{\rho L}\left[1 + \rho L(v + t^2\tilde{a}) + \mathbf{k}^2\left(\tfrac{1}{9} L l_p + t^2\tilde{b}\rho L\right) + \mathbf{k}^4\left[\frac{l l_p}{324} + t^2\tilde{c}\rho L\right] + \cdots\right]\ .
\tag{37}
$$

l_p is the persistence length and is related to the Kuhn length in the flexible limit as $l_p = l/2$. ρ is the mean segment density.

Within a single-chain hopping model, there are contributions to the excluded volume parameter as well as in the second and fourth power of the wave vector $\mathbf{k}$. The two latter contributions imply an effective increase of the persistence length which is proportional to t^2. The next step is to discuss the effect of generalized hopping processes on the conformation. This is a subject of future work.

B. The influence of the conformation on the electrons

We now eliminate the conformational degrees of freedom to discuss their influence in terms of an effective interaction between hopping electrons. We integrate therefore over the density fields $\rho(\mathbf{x})$ which yields the following partition function:

$$
\begin{aligned}
Z = &\int \mathcal{D}c^\dagger(\mathbf{x}) \int \mathcal{D}c(\mathbf{x}) \\
&\times \langle \exp[-\beta H_{\text{el}}(\{c^\dagger(\mathbf{x})\},\{c(\mathbf{x})\})]\rangle_{\text{conf}}\ .
\end{aligned}
\tag{38}
$$

The mean value is with respect to the distribution of conformations and is replaced by a cumulant expansion. This produces an effective Hamiltonian for the electrons:

$$
\begin{aligned}
Z = &\int \mathcal{D}c^\dagger(\mathbf{x}) \int \mathcal{D}c(\mathbf{x}) \\
&\times \exp[-\beta H_{\text{el,eff}}(\{c^\dagger(\mathbf{x})\},\{c(\mathbf{x})\})]\ .
\end{aligned}
\tag{39}
$$

Our next purpose is to calculate the effective Hamilton operator for the electronic degrees of freedom.

We first consider single-chain hopping in the limit $t \gg t'$. The cumulant expansion is only performed for βH_0 up to second order in t, neglecting for the moment βH_1:

$$
\begin{aligned}
\langle e^{-\beta H_0}\rangle &= 1 - \beta\langle H_0\rangle + \frac{\beta^2}{2}\langle H_0^2\rangle + O(t^3) \\
&= e^{-\beta H_{0,\text{eff}}} \\
&= e^{-\beta\langle H_0\rangle + \beta^2/2(\langle H_0^2\rangle - \langle H_0\rangle^2)}\ .
\end{aligned}
\tag{40}
$$

It will be shown below that the expansion in Eq. (40) can be written in terms of graphs that can be constructed from vertices. After identifying the corresponding graphs, one can immediately write down the Fourier transform of the interaction potential. For this purpose we transform βH_0 in Eq. (8) to new momenta $\mathbf{k}$ and $\mathbf{p} = \mathbf{q} - \mathbf{k}$:

$$
\beta H_0 = t a^2 \sum_{\mathbf{k},\mathbf{p}} [\mathbf{p}^2 + 2\mathbf{k}(\mathbf{k}+\mathbf{p})] c^\dagger_{\mathbf{k}+\mathbf{p}} c_{\mathbf{k}} \rho_{\mathbf{p}}\ .
\tag{41}
$$

This expression can be interpretated in terms of a vertex (see Fig. 3). An electron with momentum $\mathbf{k}$ receives the momentum transfer $\mathbf{p}$ from the conformation and leaves with momentum $\mathbf{k}+\mathbf{p}$. The expansion Eq. (40) is now written in terms of graphs that are assembled from the vertices. Finally, when the summation over all conformations is performed, the products of variables $\rho_{\mathbf{p}}$ are replaced by their mean values. We exploit the fact that the system under consideration is translationally invariant which implies that $\langle \rho_{\mathbf{p}}\rangle = \rho_0 = L$ and $\langle \rho_{\mathbf{p}}\rho_{\mathbf{p}'}\rangle = \delta_{\mathbf{p}',-\mathbf{p}}\langle \rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle$. This reduces the number of the momenta to be summed over. Moreover we have to extract the self-energy term in order to isolate the pure pair interaction. This is done by using standard procedures that commute all creation operators to the right and ensure that the same external momenta are written from the inside out in a product of ladder operators.[24] Finally, we obtain for the effective electronic Hamiltonian up to second order in t:

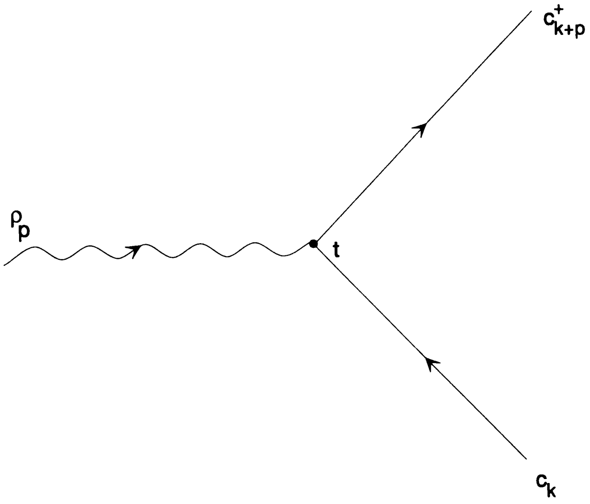

FIG. 3. The vertex for t coupling.

$$\beta H_{0,\mathrm{eff}}=ta^2\sum_{\mathbf{k}}2\mathbf{k}^2c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\rho_0-\frac{t^2a^4}{2}\sum_{\mathbf{k}}\sum_{\mathbf{p}\neq 0}[\mathbf{p}^2+2\mathbf{k}(\mathbf{k}-\mathbf{p})]^2c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\langle\rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle$$
$$-\frac{t^2a^4}{2}\sum_{\mathbf{k},\mathbf{k}'}\sum_{\mathbf{p}\neq 0}[\mathbf{p}^2+2\mathbf{k}(\mathbf{k}+\mathbf{p})][\mathbf{p}^2+2\mathbf{k}'(\mathbf{k}'-\mathbf{p})]c_{\mathbf{k}+\mathbf{p}}^{\dagger}c_{\mathbf{k}'-\mathbf{p}}^{\dagger}c_{\mathbf{k}'}c_{\mathbf{k}}\langle\rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle\ . \tag{42}$$

The three different terms can be identified with different Feynman graphs (see Fig. 4). The first one is related to free electrons. The second type of graph is a second order in t and containing two ladder operators gives the self-energy to the effective electron mass and is to be treated together with the free-electron part. The third graphs represents the effective pair interaction; its analytic counterpart gives the effective pair potential for electrons in presence of conformation in certain approximations to be discussed below. In order to evaluate the graphs, the mean values with respect to certain models for the unperturbed conformation—e.g., random walk or SAW—have to be evaluated.

We discuss the third graph in Fig. 4 in order to determine the effective pair potential. It is contained in the coefficient of the operator product in the third term in Eq. (42), i.e., the two factors in parentheses. Assuming that electron momenta are small, multiplication gives only a contribution by the term proportional to $\mathbf{p}^4$. This is, of course, a crude approximation but acceptable for a first assessment of the potential. We thus obtain for the Fourier transform of the pair potential:

$$\beta V(\mathbf{p})=-\frac{t^2a^4}{2}\mathbf{p}^4\langle\rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle=-\frac{t^2a^4}{2}N_pL\mathbf{p}^4g(\mathbf{p})\ . \tag{43}$$

In the last step we replaced the mean value by the single-chain structure $g(\mathbf{p})$ factor times N_pL. We again consider Gaussian chains for simplicity. In this case $g(\mathbf{p})$ is equal to the Debye function[2] and $a=l$. To obtain the pair potential in position space the following integral has to be performed:

$$\beta V(\mathbf{x})=-V\int\frac{d^d\mathbf{p}}{(2\pi)^d}\frac{t^2l^4}{2}N_pL^2\mathbf{p}^4\frac{2}{\mathbf{p}^4(Ll/2d)^2}\left[e^{-\mathbf{p}^2(Ll/2d)}-1+\mathbf{p}^2\frac{Ll}{2d}\right]e^{-i\mathbf{p}\mathbf{x}}$$
$$=-t^2l^4N_pL^2\left[\frac{2d}{Ll}\right]^2V\int\frac{d^d\mathbf{p}}{(2\pi)^d}\left[e^{-\mathbf{p}^2(Ll/2d)}-1+\mathbf{p}^2\frac{Ll}{2d}\right]e^{-i\mathbf{p}\mathbf{x}}\ . \tag{44}$$

The integral cannot be evaluated exactly. Therefore the integrand is expanded as follows:

$$e^{-\mathbf{p}^2(Ll/2d)}-1+\mathbf{p}^2\frac{Ll}{2d}=1-\mathbf{p}^2\frac{Ll}{2d}+\frac{1}{2!}\mathbf{p}^4\left[\frac{Ll}{2d}\right]^2-\frac{1}{3!}\mathbf{p}^6\left[\frac{Ll}{2d}\right]^3+O\left[\mathbf{p}^8\left[\frac{Ll}{2d}\right]^4\right]-1+\mathbf{p}^2\frac{Ll}{2d}$$
$$=\frac{1}{2!}\mathbf{p}^4\left[\frac{Ll}{2d}\right]^2-\frac{1}{3!}\mathbf{p}^6\left[\frac{Ll}{2d}\right]^3+O\left[\mathbf{p}^8\left[\frac{Ll}{2d}\right]^4\right]$$
$$=\frac{1}{2}\mathbf{p}^4\left[\frac{Ll}{2d}\right]^2\left\{1-\frac{1}{3}\mathbf{p}^2\frac{Ll}{2d}+O\left[\mathbf{p}^4\left[\frac{Ll}{2d}\right]^2\right]\right\}\ . \tag{45}$$

The expression in parentheses in the last line can be approximated by an exponential function, yielding the following integral:

$$\beta V(\mathbf{x})=-\frac{t^2l^4}{2}N_pL^2V\int\frac{d^d\mathbf{p}}{(2\pi)^d}\mathbf{p}^4e^{-(1/3)\mathbf{p}^2(Ll/2d)-i\mathbf{p}\mathbf{x}}\ . \tag{46}$$

This is a Gaussian integral which is integrated easily. Substituting for t, Eq. (5), the pair potential in d-space dimensions is given as a function of a scaled distance (without dimensions) $x=r\sqrt{3d/2Ll}$ where $r=|\mathbf{x}|$:

$$\beta V(x)=-\frac{2}{(2\pi)^{d/2}}t_0^2\beta^2\left[\frac{3d}{lL}\right]^{d/2+2}N_pVl^4$$
$$\times\left[\frac{d}{2}\left[\frac{d}{2}+1\right]-(d+2)x^2+x^4\right]e^{-x^2}\ . \tag{47}$$

In $d=3$ we have

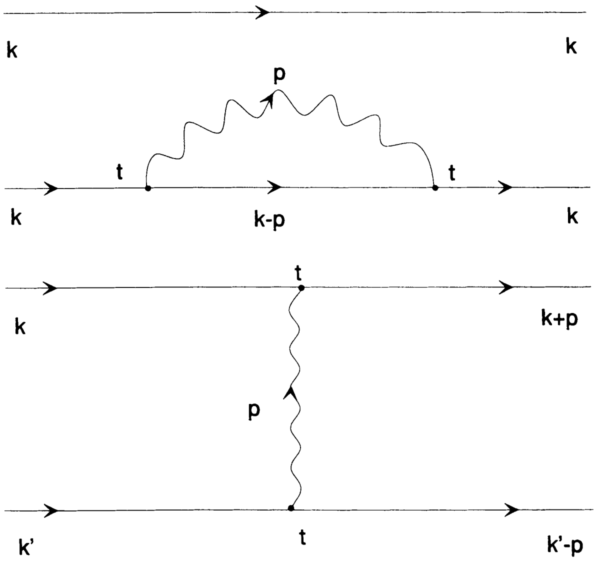

FIG. 4. Feynman graphs in second order of t.

$$\beta V(x) = -\frac{2}{(2\pi)^{3/2}} t_0^2 \beta^2 \left[\frac{9}{L}\right]^{7/2} N_p V l^{1/2} \times \left[\frac{15}{4} - 5x^2 + x^4\right] e^{-x^2} . \tag{48}$$

The corresponding graph in $d=3$ for

$$\beta V(x) = -C\left[\frac{15}{4} - 5x^2 + x^4\right] e^{-x^2} , \tag{49}$$

where the constant C contains all prefactors in Eq. (48), is shown in Fig. 5 for $C=1$. There is obviously an attractive short-range part, a slightly repulsive part on intermediate distances, while for the large distances the potential becomes zero after passing through a weak second minimum that is shown in the inset of Fig. 5.

It is useful to consider the first maximum and the second minimum. A minimization procedure applied to Eq. (49) gives, in $d=3$, $r_{\max}=0.602\sqrt{Ll}$ and $r_{\min}=1.092\sqrt{Ll}$ in dimensions of length. For $l=1$ and $L=10^4$ we find for the extrema in units of the Kuhn length: $r_{\max}=60.2$ and $r_{\max}=109.2$.

To assess the strength of the potential with respect to thermal energy one can make a simple approximation of the prefactors in Eq. (48). One substitutes for the volume V the volume of the chain, where R^3 is the mean end-to-end distance. Using $R=(Ll)^{1/2}$ and estimating the numerical factors by 10^2, one obtains $\beta\Delta V \sim 10^2 t_0^2 \beta^2 L^{-2} l^2$. At room temperature and for $L=10^4$ in units of the Kuhn length, approximately $\beta V \sim 10^{-2}$ is found. Therefore, at room temperature the electrons can easily overcome the attractive range of the potential. On the other hand, βV is of order 1 for temperatures $T \sim 10^1 \cdots 10^2$ (for the same choice of the remaining parameters) where it is useless to discuss the flexibility of polymers as realistic systems are far below the glass transition.[25]

Including the Coulomb interaction term from Eq. (1) in an analysis of the pair potential, a slight modification arises, When spin contributions are neglected, we obtain a contribution proportional to a Dirac delta function: $\beta V_{\text{Coulomb}}(\mathbf{x}) = UV\delta(\mathbf{x})$. Thus, the potential becomes singular at the origin so that the absolute minimum in Fig. 5 is never reached.

We now refine the expansion in terms of graphs by including βH_1 with the hopping parameter t'. Performing the transformation $\mathbf{q}\rightarrow\mathbf{q}+\mathbf{k}$ in Eq. (20) and using $\rho_{-\mathbf{q}} = \rho_{\mathbf{q}}^*$, we obtain the following expression for βH_1:

$$\beta H_1 = t'a^2 \sum_{\mathbf{k},\mathbf{q},\mathbf{p}} c_{\mathbf{k}+\mathbf{q}}^{\dagger} c_{\mathbf{k}} \rho_{\mathbf{p}-\mathbf{q}}^* \rho_{\mathbf{p}} [2\mathbf{k}(\mathbf{k}+\mathbf{q}) + \mathbf{q}^2] , \tag{50}$$

which can be represented by the vertex, Fig. 6. The Fourier transforms $\rho_{\mathbf{p}}$ and $\rho_{\mathbf{p}-\mathbf{q}}^*$ appear as pseudoladder operators, but only to motivate the Feynman graphs. Again, we perform a cumulant expansion up to second order in t and t', now for the entire Hamiltonian $\beta H_0 + \beta H_1$, giving for the effective Hamiltonian

$$\beta(H_{0,\text{eff}} + H'_{\text{eff}}) = +\beta\langle H_0\rangle + \beta\langle H_1\rangle - \frac{\beta^2}{2}[\langle (H_0+H_1)^2\rangle - \langle (H_0+H_1)\rangle^2] . \tag{51}$$

On the right-hand side of Eq. (51) there is a number of additional cumulants that have to be determined. The occurring terms are further simplified by exploiting the translational invariance of the conformational degrees of freedom, i.e., the density. In particular one has

$$\langle \rho_{\mathbf{p}_1} \rho_{\mathbf{p}_2} \rangle = \delta_{\mathbf{p}_1, -\mathbf{p}_2} \langle \rho_{\mathbf{p}_1} \rho_{\mathbf{p}_2} \rangle , \tag{52}$$

$$\langle \rho_{\mathbf{p}_1} \rho_{\mathbf{p}_2} \rho_{\mathbf{p}_3} \rangle = \delta_{\mathbf{p}_1, -\mathbf{p}_2 - \mathbf{p}_3} \langle \rho_{\mathbf{p}_1} \rho_{\mathbf{p}_2} \rho_{\mathbf{p}_3} \rangle , \tag{53}$$

and

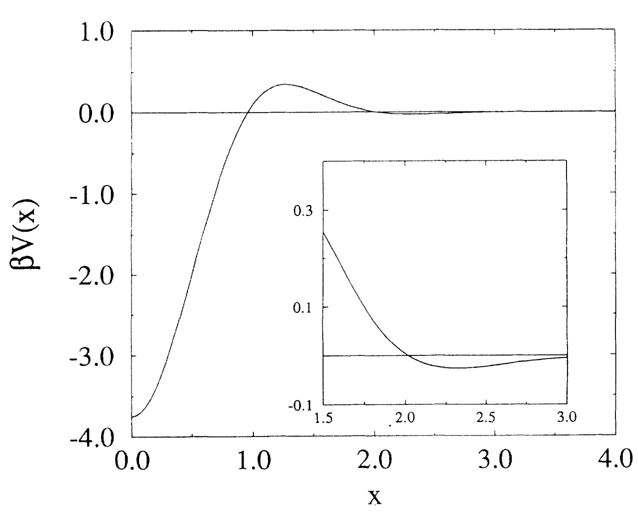

FIG. 5. The pair potential in $d=3$; the inset gives a magnified view of the second minimum.

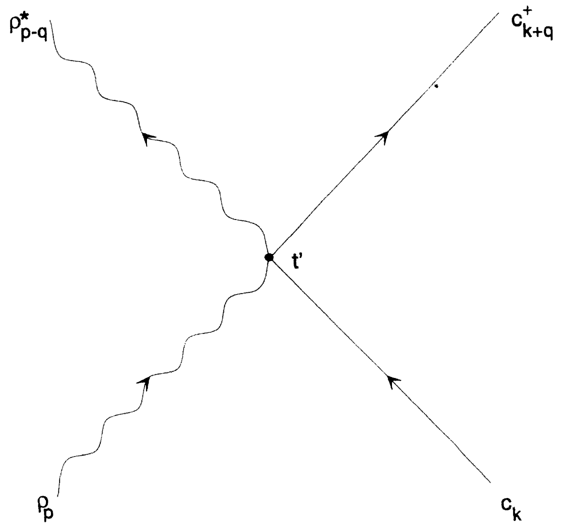

FIG. 6. The vertex for t' coupling.

$$\langle \rho_{\mathbf{p}_1}\rho_{\mathbf{p}_2}\rho_{\mathbf{p}_3}\rho_{\mathbf{p}_4}\rangle = \delta_{\mathbf{p}_1,-\mathbf{p}_2-\mathbf{p}_3-\mathbf{p}_4}\langle \rho_{\mathbf{p}_1}\rho_{\mathbf{p}_2}\rho_{\mathbf{p}_3}\rho_{\mathbf{p}_4}\rangle + \langle \rho_{\mathbf{p}_1}\rho_{\mathbf{p}_2}\rangle\langle \rho_{\mathbf{p}_3}\rho_{\mathbf{p}_4}\rangle + \text{permutations}\ . \tag{54}$$

Apart from the terms arising from contour hopping, we obtain a number of additional terms in the effective Hamiltonian which are denoted by a prime ('). For the electron self-energy we get the following additional contributions:

$$\beta H'_{\text{eff,self}} = 2t'a^2\sum_{\mathbf{k},\mathbf{p}}\mathbf{k}^2 c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\langle \rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle - \frac{t'^2a^4}{2}\sum_{\mathbf{k},\mathbf{p},\mathbf{p}'}\sum_{\mathbf{q}\neq 0}[2\mathbf{k}(\mathbf{k}-\mathbf{q})+\mathbf{q}^2]^2 c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\langle \rho_{\mathbf{q}-\mathbf{p}}\rho_{\mathbf{p}}\rho_{-\mathbf{q}-\mathbf{p}'}\rho_{\mathbf{p}'}\rangle$$
$$-\frac{t'^2a^4}{2}\sum_{\mathbf{k},\mathbf{p},\mathbf{p}'}(2\mathbf{k}^2)^2 c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\langle \rho_{-\mathbf{p}}\rho_{\mathbf{p}}\rangle\langle \rho_{-\mathbf{p}'}\rho_{\mathbf{p}'}\rangle - t'^2a^4\sum_{\mathbf{k},\mathbf{p}}\sum_{\mathbf{q}\neq 0}[2\mathbf{k}(\mathbf{k}-\mathbf{q})+\mathbf{q}^2]^2 c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}\langle \rho_{\mathbf{q}-\mathbf{p}}\rho_{\mathbf{p}-\mathbf{q}}\rangle\langle \rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle\ . \tag{55}$$

These terms correspond to the Feynman graphs in Fig. 7. The term mixing βH_0 and βH_1 which is of order tt' yields an external potential:

$$\beta H'_{\text{eff,ext pot}} = -tt'a^4\sum_{\mathbf{k},\mathbf{q}'}\sum_{\mathbf{p}\neq 0}[2\mathbf{k}(\mathbf{k}+\mathbf{p})+\mathbf{p}^2]^2 c_{\mathbf{k}+\mathbf{p}}^{\dagger}c_{\mathbf{k}}\langle \rho_{\mathbf{p}}\rho_{-\mathbf{p}-\mathbf{p}'}\rho_{\mathbf{p}'}\rangle\ . \tag{56}$$

The corresponding graph is shown in Fig. 8. For Gaussian chains the three-point correlation function in the density variables, like in Eq. (56), vanishes. It is therefore useful to consider a further approximation, by requiring $\mathbf{p}'=-\mathbf{p}$. In solid-state physics, this approximation is known as random-phase approximation (RPA).[26] It yields in our case

$$\beta H'_{\text{eff,ext pot}} = -tt'a^4\sum_{\mathbf{k}}\sum_{p\neq 0}[2\mathbf{k}(\mathbf{k}+\mathbf{p})+\mathbf{p}^2]^2 c_{\mathbf{k}+\mathbf{p}}^{\dagger}c_{\mathbf{k}}\langle \rho_{\mathbf{p}}\rho_{-\mathbf{p}}\rangle\rho_0\ . \tag{57}$$

The contribution to the effective pair potential contains terms of order tt' and $(t')^2$. It reads as:

$$\beta H'_{\text{eff,pair pot}} = -tt'a^4\sum_{\mathbf{k},\mathbf{k}',\mathbf{p}'}\sum_{\mathbf{q}\neq 0}[2k(\mathbf{k}+\mathbf{q})+\mathbf{q}^2][2\mathbf{k}'(\mathbf{k}'-\mathbf{q})+\mathbf{q}^2]c_{\mathbf{k}+\mathbf{q}}^{\dagger}c_{\mathbf{k}'-\mathbf{q}}^{\dagger}c_{\mathbf{k}'}c_{\mathbf{k}}\langle \rho_{\mathbf{q}}\rho_{-\mathbf{q}-\mathbf{p}'}\rho_{\mathbf{p}'}\rangle$$
$$+\frac{t'^2a^4}{2}\sum_{\mathbf{k},\mathbf{p},\mathbf{k}',\mathbf{p}'}\sum_{\mathbf{q}\neq 0}[2\mathbf{k}(\mathbf{k}+\mathbf{q})+\mathbf{q}^2][2\mathbf{k}'(\mathbf{k}'-\mathbf{q})+\mathbf{q}^2]c_{\mathbf{k}+\mathbf{q}}^{\dagger}c_{\mathbf{k}'-\mathbf{q}}^{\dagger}c_{\mathbf{k}'}c_{\mathbf{k}}\langle \rho_{\mathbf{q}-\mathbf{p}}\rho_{\mathbf{p}}\rho_{-\mathbf{q}-\mathbf{p}'}\rho_{\mathbf{p}'}\rangle\ . \tag{58}$$

The arising terms may also be identified with graphs (Fig. 9). For the first term we may perform a RPA as in Eq. (56). Considering all additional terms arising in the effective Hamiltonian [Eqs. (55), (57), (58)] the term βH_1, Eq. (50), leads to a dependence on three-point and four-point correlation functions in the cumulant expansion. In terms of the conformational degrees of freedom, this amounts to including the second and third virial coefficient.

V. DISCUSSION

This paper discusses the statistical behavior of conducting random and self-avoiding walks. It has been shown that the presence of mobile and delocalizable electrons as present in conjugated polymers have considerable consequences on the conformation. Vice versa a similar statement holds, i.e., the conformation of the polymers deeply influences the electronic behavior. The model introduced in this paper combines the classical Edwards-Wiener theory of self-avoiding walks with the Hubbard model for electron hopping. Unlike in quasi-one-dimensional electron systems the usual quantum-mechanical formalisms cannot be used and wave functions cannot be calculated by the Schrödinger theory. The combination of the standard polymer theory and the Hubbard model for electron hopping leads to several new consequences for the theory of conducting and conjugat-

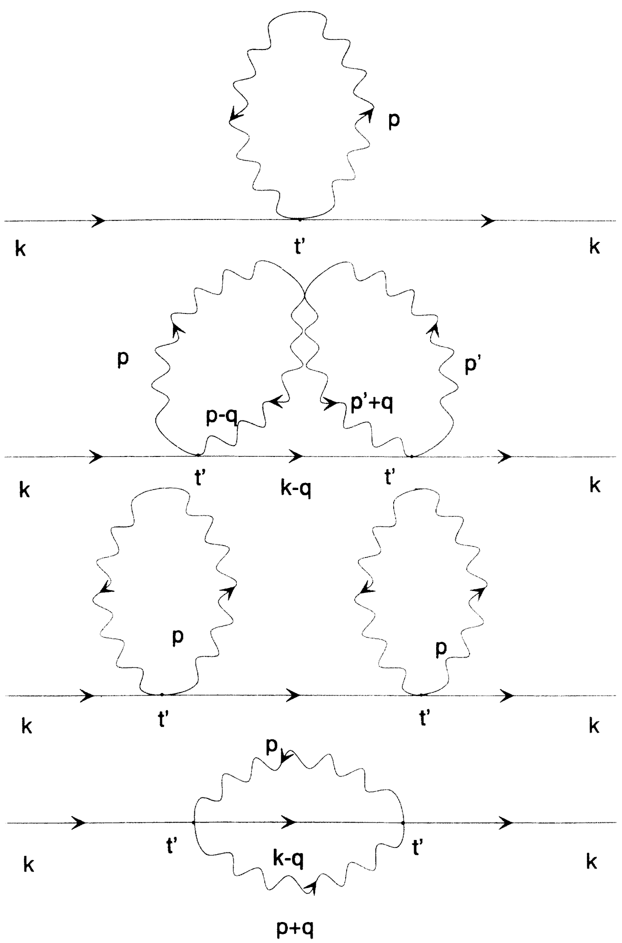

FIG. 7. Self-energy graphs due to t' coupling.

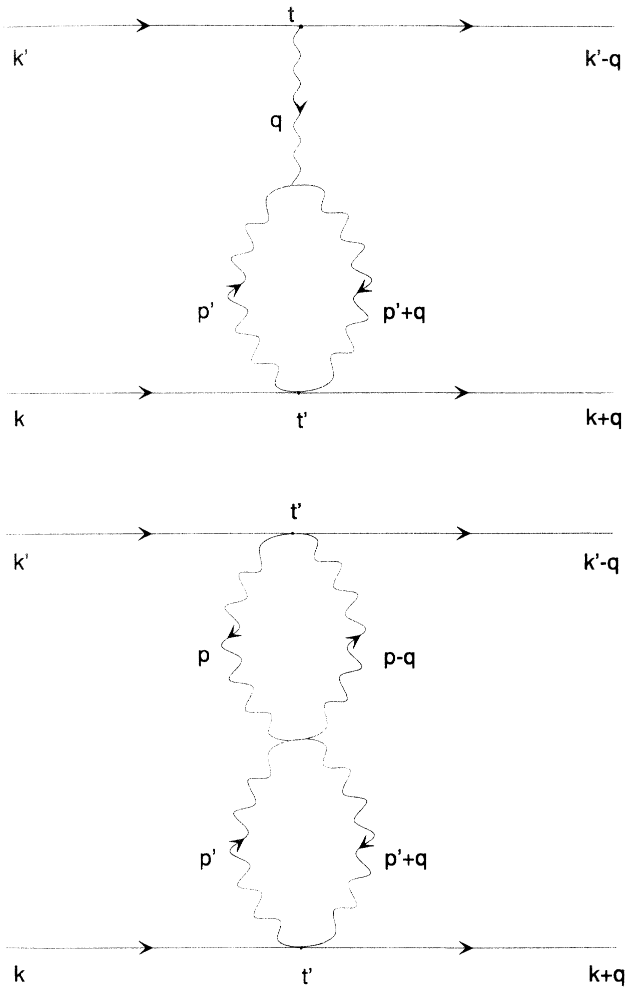

FIG. 9. Contributions to the effective pair potential.

ed polymers.

The first result confirms the scaling conjecture of Pincus, Rossi, and Cates[6] that the delocalization of charge carriers stiffens effectively the polymers. The physical reason is that the hop along the chain becomes more probable than if the chain is locally very flexible. This is in accordance with the quantum-mechanical picture that the transition element of an electron to hop to the next segment is larger if the chain is locally one dimensional. The conclusion whether a complete rod-to-coil transition is theoretically possible in conjugated systems requires more detailed single-chain field-theoretic studies, that use an $O(n)$-symmetric field theory. Corresponding results will be presented elsewhere.[22] The advantage of the path-integral formulation presented in this paper is that several consequences can be discussed. The effective pair potential between electrons shows anomalies, in particular the (weak) disorder-induced localization of π electrons, which is clearly the effect of the conformation. Moreover the theory itself is not limited to intrachain hopping (contour and bridge hopping) but interchain hopping in strong solutions or melts of flexible conjugated polymers can be treated within the same framework as we have demonstrated.

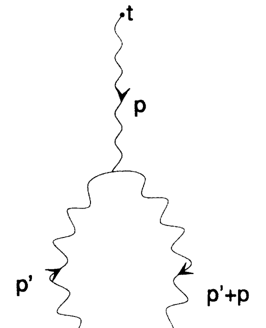

FIG. 8. The external potential.

In most equations we have used flexible "Wiener polymers" for reasons of simplicity and clarity in this paper. Indeed the choice of the simplest polymer model allowed several cross checks as their conformational behavior is well known. The formalism presented here is not bound to the use of Wiener-type conformations and can be generalized indeed to more realistic polymers which include a local stiffness and a local bending energy at the segmental level. This generalization has been used in the section where a melt of conjugated polymers has been treated, where implicitly the stiff chain Hamiltonian by Saito, Takahashi, and Yunoki[27] has been employed.[23] The general conclusions derived in this paper do, however, not significantly depend on the polymer model under consideration.

---

[1] S. Schmidt, Ph.D. thesis, University of Mainz, 1994.

[2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[3] L. A. Harrah and J. M. Ziegler, J. Polym. Sci. Polym. Lett. **23**, 209 (1985).

[4] K. C. Lim, A. Kapitulnik, R. Zacher, and A. J. Heeger, J. Chem. Phys. **84**, 1058 (1986).

[5] G. Wegner and J. Rühe, Faraday Discuss. Chem. Soc. **88**, 333–349 (1989).

[6] P. A. Pincus, G. Rossi, and M. E. Cates, Europhys. Lett. **4**, 41 (1987).

[7] K. S. Schweizer, Chem. Phys. Lett. **125**, 118 (1986).

[8] K. S. Schweizer, J. Chem. Phys. **85**, 1156 (1986).

[9] M. C. Gutzwiller, Phys. Rev. Lett. **10**, 159 (1963).

[10] J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).

[11] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

[12] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[13] H. Kaufmann, *Grundlagen der Organischen Chemie* (UTB Birkhäuser, Basel, 1981).

[14] H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).

[15] K. Harigaya, Y. Wada, and K. Fesser, Phys. Rev. B **42**, 11 303 (1990).

[16] K. Fesser, J. Phys. Condens. Matter **4**, 9347 (1992).

[17] M. Wolf and K. Fesser, J. Phys. Condens. Matter **3**, 5489 (1991).

[18] H. A. Mizes and E. M. Conwell, Phys. Rev. Lett. **70**, 1505 (1993).

[19] C. Itzykson and J. M. Drouffe, *Statistical Field Theory* (Cambridge University Press, Cambridge, 1989).

[20] H. J. Rothe, *Path Integral Method, Lattice Gauge Theory and Critical Phenomena*, edited by A. Shaukat (World Scientific, Singapore, 1989).

[21] M. Otto, J. Eckert, and T. A. Vilgis, Macromol. Th. Simul. **3**, 543 (1994).

[22] M. Otto and T. A. Vilgis (unpublished).

[23] T. Shimada, M. Doi, and K. Okano, J. Chem. Phys. **8**, 2815 (1988).

[24] R. P. Feynman, Statistical Mechanics (Addison-Wesley, Reading, MA, 1972).

[25] S. Matsuoka, *Relaxation Phenomena in Polymers* (Hanser, Munich, 1992).

[26] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[27] N. Saito, K. Takahashi, and Y. Yunoki, J. Phys. Soc. Jpn. **22**, 219 (1967).