Twin distortions of the Peierls instability

Minghai Li and Xi Lin[*]

Department of Mechanical Engineering and Division of Materials Science and Engineering, Boston University,
Boston, Massachusetts 02215, USA

It is proved analytically that a one-dimensional half-filled polymer chain is subject to two coupled spontaneous conformational relaxations, the well-known Peierls bond length alternation and a uniform bond contraction. These two coupled relaxations work cooperatively against the lattice elastic energy penalty so that all bonds alternate and contract less than the case when these two relaxations are independent. When the fully relaxed neutral chain is taken as reference, creating self-localized charge carriers upon doping results in spontaneous bond contraction within the self-localized domain where the undimerization is enforced. Numeric results based on the Su-Schrieffer-Heeger and extended Peierls-Hubbard models and *ab initio* calculations resolve a long-lasting puzzle observed by x-ray scatterings concerning of the initial zero slope and accompanied sharp knee in the strain response of *trans*-polyacetylene to the Na$^+$ dopant concentration. The demonstrated doping-induced polymer chain length variation mechanism has implications for ultrafast artificial muscle designs.

A one-dimensional (1D) equally spaced metallic polymer chain of one electron per ionic site is unstable with respect to the spontaneous relaxation via optical phonons with the double Fermi wave vector, resulting in a dimerized insulating polymer chain. This is the Peierls instability, originally derived using the free-electron energy dispersion relation.[1] A more rigorous proof was given by Kennedy and Lieb[2] stating that such a dimerization is exact without additional symmetry breakdown, at least for the Su-Schrieffer-Heeger (SSH) type of Hamiltonians[3] in which the nearest-neighbor electron hopping integrals vary linearly with the distance. This work points to the existence of a ubiquitously coupled twin of the Peierls distortion, with validations from previously unresolved puzzling x-ray scattering data on Na$^+$ doped *trans*-polyacetylene.[4–9]

Without loss of generality,[10] we follow Kennedy and Lieb[2] to focus on the SSH Hamiltonian. It is well recognized that the SSH Hamiltonian is subject to a spontaneous contraction. Explicitly, Su proposed a constant tension of $4\alpha/\pi$ to compensate such a undesired global contraction.[11] Later, Stafstrom and Chao[12] suggested a 2% correction to Su's term and attributed such a difference to the discrete energy spectrum of using a finite system. Vos *et al.* expressed the contraction as a function of the electron-phonon coupling coefficient for the perfectly dimerized case and obtained the sound speeds of acoustic and optical modes.[13] Nevertheless, we note that the chain length variation in the above mentioned arguments is independent of the polymer charge state; namely, if the neutral dimerized chain is taken as reference, no further chain length variations would be expected upon charge injections. In addition, Bishop *et al.*[14] observed local contractions at the soliton center via adiabatic exciton dynamics and attributed such local contractions to the coupling between moving solitons and acoustic phonons. In contrast, static contractions via acoustic phonons toward the soliton center were noted by Baeriswyl.[15] Here we present a theory originated from the Peierls distortion to describe how conducting polymers are subject to the chain length variation upon the self-localization of charge carriers without explicit dynamical couplings.

We start from the SSH Hamiltonian for an open polymer chain that contains N carbon-hydrogen (CH) units

$$H_0 = \sum_n \frac{p_n^2}{2M} - \sum_{n,s} [t_0 - \alpha(u_{n+1} - u_n)](c^\dagger_{n+1,s}c_{n,s} + c^\dagger_{n,s}c_{n+1,s})$$
$$+ \sum_n \frac{1}{2}K(u_{n+1} - u_n)^2, \tag{1}$$

where p_n is the nth CHs momentum; M is the mass; u_n is the displacement coordinate of the nth CH with respect to the undimerized chain; and $c^\dagger_{n,s}$ and $c_{n,s}$ are the creation and annihilation operators for π electrons of spin s at site n, respectively. Here t_0=2.5 eV, α=4.1 eV/Å, and K=21 eV/Å^2.[3] A half-filled 1D chain described by Eq. (1) is subject to two spontaneous distortions, the Peierls dimerization and a global chain contraction. The Peierls dimerization has an amplitude of $u_0 = 2t_0\exp[-\pi Kt_0/(4\alpha^2) - 1]/\alpha = 0.0386$ Å if the chain contraction is ignored. The overall chain contraction comes from the shrinkage of every bond by $\delta a = -4\alpha/(\pi K) = -0.2486$ Å when the Peierls dimerization is not considered. Figures 1(b) and 1(c) are denoted for these two distortions, respectively. Here we are going to demonstrate: (1) the two above mentioned distortions are indeed coupled to each other as shown in Fig. 1(d) and (2) charge injections give rise to the dimerization-dependent bond length variation in self-localized domains, shown as Fig. 1(e).

Letting $u_{n+1} - u_n = (-1)^n 2u_0 + \delta a$ or effectively transforming t_0 in Eq. (1) to $t'_0 = t_0 - \alpha\delta a$, one may formally keep the energy dispersion expression,[3]

$$\epsilon(k) = -[(2t'_0 \cos ka)^2 + (4\alpha u_0 \sin ka)^2]^{1/2}. \tag{2}$$

Integrating it up to the Fermi level gives the electronic energy per site $E_e = -4t'_0\mathbf{E}(1-z^2)/\pi$, where $z = 2\alpha u_0/t'_0$ and $\mathbf{E}(1-z^2)$ is the elliptic integral of the second kind. In the small dimerization limit $z \ll 1$, the ground-state energy per site becomes

$$E_0 = -\frac{4t_0'}{\pi}\left[1+\frac{z^2}{2}\left(\ln\frac{4}{z}-\frac{1}{2}\right)\right]+\frac{K}{2}(4u_0^2+\delta a^2)+O(z^4).$$

This energy expression, also presented in Refs. 13 and 16, is now plotted as a function of u_0 and δa in Fig. 1(f). By neglecting $O(z^4)$, one finds the dimerization-dependent δa at equilibrium, defined by $\partial E_0/\partial\delta a=0$, as

$$\delta a = -\frac{4\alpha}{\pi K}\left\{1+\frac{1}{2}\left[\ln\frac{z(u_0,\delta a)}{4}+\frac{3}{2}\right]z(u_0,\delta a)^2\right\}. \quad (3)$$

For given u_0, the optimized δa may be obtained by solving Eq. (3) iteratively. The results are plotted as red crosses in Fig. 1(f), among which the global minimum (red plus) is located at ($u_0'=0.0200$ Å, $\delta a=-0.2478$ Å). It is worthwhile to mention that Yannoni and Clarke have measured the bond lengths of double and single bonds of *trans*-polyacetylene as 1.36 and 1.44 Å, respectively, by the nutation NMR spectroscopy.[17] Their measured bond length difference agrees better with the shrinkage-coupled $4u_0'$ $=0.08$ Å than the shrinkage-decoupled $4u_0=0.15$ Å.[18]

Because z is small, analytic expressions for δa may also be obtained. Explicitly, starting with $z^{(0)}=0$, the first iteration of Eq. (3) gives a constant $\delta a^{(1)}=-4\alpha/(\pi K)$, which is precisely what Su proposed.[11] In turn, one finds $z^{(1)}(u_0)$ $=2\alpha u_0/[t_0(1+2\lambda)]$, where $\lambda\equiv 2\alpha^2/(\pi Kt_0)$. The second iteration of Eq. (3) gives an analytic dimerization-dependent shrinkage

$$\delta a^{(2)}(u_0) = -\frac{4\alpha}{\pi K}\left\{1+\frac{1}{2}\left[\ln\frac{z^{(1)}(u_0)}{4}+\frac{3}{2}\right][z^{(1)}(u_0)]^2\right\}, \quad (4)$$

plotted as the blue line in Fig. 1(f). There is essentially no numeric difference between the analytic blue line and numeric red crosses. Following Stafstrom and Chao[12] by choosing $u_0=0.04$ Å and $\delta a=0$ on the right side of Eq. (3), we obtain a 1.6% correction to Su's term, which suggests that the 2% correction found by Stafstrom and Chao[12] may originate from the dimerization-shrinkage coupling.

In the rest of this work, we will choose the fully relaxed neutral defect-free chain [Fig. 1(d)] as reference to study how dopings would vary the polymer chain length. Due to the strong scattering between 1D Fermi electrons and optical phonons, extra electrons and holes upon dopings will be self-localized to form topological solitons, polarons, and bipolarons.[5] Polarons and bipolarons may be viewed as soliton and antisoliton pairs. The doping-induced self-localized soliton enforces the counter Peierls distortion; namely, u_0 $\rightarrow 0$ at the center of the soliton domain. The exact shrinkage amount ($-\delta a$) depends on the dimerization amplitude u_0, as shown in Fig. 1(f). Because $-\delta a(u_0=0)\geqq-\delta a(u_0)$, bonds in self-localized domains always shrink more than they do in perfectly dimerized domains. Therefore, taking neutral defect-free chains as reference, chains containing *independent* self-localized domains will be shorter, shown as Fig. 1(e). Moreover, shrinkages are expected to saturate at high doping levels when the self-localized domains overlap each other forming the soliton lattice.

To demonstrate the total amount of chain length variation upon injecting charges is indeed caused by the presence of
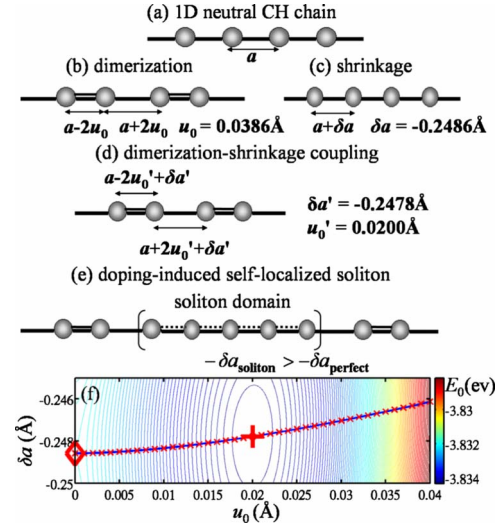

FIG. 1. (Color online) (a) A 1D half-filled neutral CH chain suffers for two types of distortions, (b) the Peierls dimerization via an optical mode, and (c) the bond contraction via an acoustic mode. (d) These two distortions couple to each other. (e) Upon doping, bonds in the self-localized domain contract more than they do in the perfectly dimerized domain. The ground-state energy contour, color coded with the energy scale bar located on the right, is plotted as a function of u_0 and δa in (f). For given u_0, the self-consistent numerical energy minima computed from Eq. (3), red crosses in (f), overlap with the analytic blue line. The global minimum (red plus) and the saddle point (red diamond) correspond to (d) and (c), respectively.

self-localized domains, we introduce the local strain approximation (LSA) for the overall chain length variation ΔL $\equiv u_{N-1}-u_1$ as

$$\Delta L_{LSA} = \int[\delta a(\gamma(r))/a]dr \simeq \sum_{n=1}^{N}\delta a[\gamma(n)]. \quad (5)$$

In Eq. (5) the local shrinkage δa is expressed as a functional of the order parameter $\gamma(n)\equiv(-1)^n(u_{n+1}+u_{n-1}-2u_n)/(4u_0')$ (Ref. 14) which specifies the length difference between neighboring bonds and more importantly has the local shrinkage canceled.[19] As long as the self-localized domains are sufficiently smooth, one can use Eq. (3) derived for homogeneously dimerized chains to define the local shrinkage functional for chains containing self-localized domains. Explicitly, we substitute $u_0'\gamma(n)$ for u_0 in Eq. (3) and solve for δa iteratively. We note that a non-self-consistent solution of the LSA was proposed by Baeriswyl.[15]

Figure 2(a) shows the order parameters $\gamma(n)$ of a neutral (blue) and 1e n-doped (red crosses) CH chain under the free-end boundary condition. Since δa are locally canceled in the definition of $\gamma(n)$,[19] the perfectly dimerized domain is located in the +1 phase and the self-localized polaron domain follows the original continuum expression[5]

$$\frac{\varphi(n)}{u_0'} = 1 - \frac{1}{\sqrt{2}}\tanh\frac{n-n_1}{\sqrt{2}\xi}+\frac{1}{\sqrt{2}}\tanh\frac{n-n_2}{\sqrt{2}\xi}, \quad (6)$$

where $u_0'=0.0200$ Å given in Fig. 1(d); $n_1=115$ and $n_2=142$ are the soliton and antisoliton centers of the polaron,
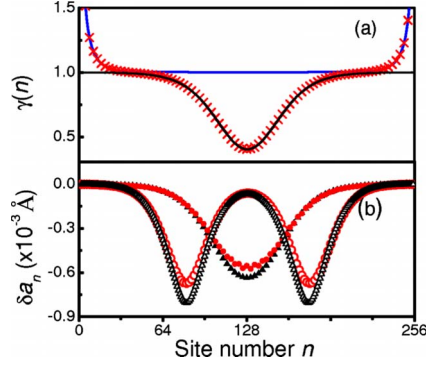
FIG. 2. (Color online) (a) Order parameter $\gamma(n)$ for an open 256-CH chain in its neutral (blue) and $1e$ n-doped (red crosses) states. The fitted polaron order parameter using Eq. (6) is plotted in black. (b) Individual bond length shrinkage δa_n, with respect to the neutral dimerized state, in the $1e$-(filled symbols) and $2e$-(unfilled symbols) n-doped states computed from the direct measurement (red) and the LSA (black).

respectively; and $\xi = 21.08$ is the half width of soliton.[20] Taking the neutral dimerized chain as reference, the LSA approximation of using Eq. (5) gives local bond length variations δa_n that agree well with the directly measured values of $\delta a_n = \frac{1}{4}(u_{n+2} - u_n + u_{n+1} - u_{n-1}) + O(\xi^{-2})$. Integrating the red and black curves in Fig. 2(b) for $1e$ n-doped chain gives the total shrinkage of $\Delta L = -0.0408$ Å and $\Delta L_{LSA} = -0.0439$ Å, respectively.

To test our theory against experiments,[4] we compute the doping-dependent chain length variation using the SSH model. As shown in Fig. 3(a), dilute self-localized domains shorten the polymer chain even though doping weakens π bonds. Competition of these two forces give rise to a flat strain region between 0 and 6% dopings, which explains for the first time the experimentally observed zero initial slope[4] in the Na$^+$-doped $trans$-polyacetylene. Above this threshold, self-localized domains overlap with each other which leaves no space for further undimerization-coupled shrinkages, polymer chain starts to expand. These results are in sharp contrast to the rapid strain variations predicted by conventional delocalized electron theories.[7–9] If a renormalized hopping integral $t_0 + \alpha \delta a$, where δa corresponds to the value obtained by fixing $u_0 = 0.0386$ Å and $\delta a = 0$ on the right side of Eq. (3), is chosen to maintain the original band gap of $2\Delta_g = 8\alpha u_0 = 1.3$ eV, we find stronger shrinkage effects due to the larger dimerization amplitudes, shown as the violet line in Fig. 3(b).

To further explore the electron correlation effects, we perform the Peierls-Hubbard model,[21,22] extended Peierls-Hubbard model,[23,24] and ab $initio$ Hartree-Fock (HF) computations.[22,25,26] Explicitly, we consider the following extended Peierls-Hubbard model Hamiltonian:

$$H = \frac{U}{2}\sum_{n,s}\rho_{n,s}\rho_{n,-s} + \frac{V}{2}\sum_{n,s,s'}\left(\rho_{n,s} - \frac{1}{2}\right)\left(\rho_{n+1,s'} - \frac{1}{2}\right)$$
$$+ \frac{X}{2}\sum_{n,s,s'}(\rho_{n,s} + \rho_{n+1,s})G_{n,s'} + \frac{W}{2}\sum_{n,s}G_{n,s}G_{n,-s} + H_0,$$

where the density operator $\rho_{n,s} = c_{n,s}^\dagger c_{n,s}$ and the bond-charge
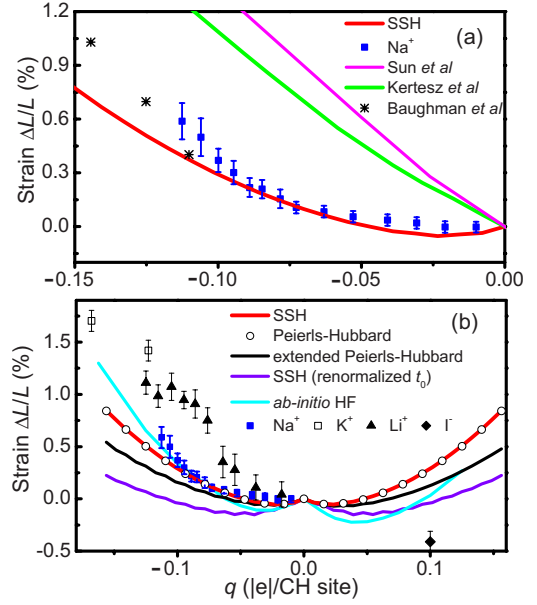

FIG. 3. (Color online) (a) Doping-induced strain data of $trans$-polyacetylene measured by the x-ray scattering (Ref. 4) and computed by the SSH Hamiltonian of this work, extended Huckel theory by Kertesz et $al.$ (Ref. 7), density-functional theory by Sun et $al.$ (Ref. 8) (jellium $d = 4$ Å), and semiempirical calculations by Baughman et $al.$ (Ref. 9). (b) Doping-dependent strain data computed by the SSH, SSH with renormalized t_0, Peierls-Hubbard, and extended Peierls-Hubbard models as well as ab $initio$ HF calculations in this work with various experimental measurements (Refs. 4 and 6). Doping ratio q is defined as doping charges divided by total CH sites, negative for n-type and positive for p-type dopings. Strain is computed with respect to the corresponding neutral dimerized chain. Chain length variations are computed for a 160-CH chain, with no notable differences seen for shorter or longer chains of $N = 128$ and 256, respectively.

density operator $G_{n,s} = c_{n,s}^\dagger c_{n+1,s} + c_{n+1,s}^\dagger c_{n,s}$. Standard parameters are used, in which $U = 4$ eV (Refs. 21 and 22) and $(V, X, W) = (0, 0, 0)$ for the Peierls-Hubbard model and $(U, V, X, W) = (0.6, 0.3, 0.15, 0.1)t_0$ (Ref. 24) for the extended Peierls-Hubbard model. All these model Hamiltonian calculations are performed on an open 256-CH chain with the self-consistent unrestricted open-shell HF approximation.[21] The Born-Oppenheimer approximation is applied and the systems are fully relaxed to the optimized configurations. Ab $initio$ calculations are performed on a $N = 160$ chain with the 3–21G basis set.[22,25,26] In ab $initio$ calculations, we consider the even doping charge cases, varying from -26 (effectively -16.3% n-doping) to 20 (effectively 12.5% p-doping) and one odd charge case of 3. The restricted HF and restricted open-shell HF approximations are applied for the systems with even and odd charges, respectively. The free-end boundary condition is applied in all calculations, and for ab $initio$ calculations the chain end is terminated with one additional hydrogen atom. The bond length variation results shown in Fig. 3 do not include the counter ion effects. We note that Coulomb interactions among solitons and counter ions do not change the intrinsic electron-phonon nature. Many other intrinsic thermodynamic properties due to self-localizations, such as the negative spin density wave,[21]

soliton-induced bending and twisting,[26] and multiple self-localized states,[22] also show the similar dependence on external defects such as counter ions. Such insensitivity reflects the 1D nature of conducting polymers. External defects are expected to have much stronger influences on kinetic processes, such as the mobility of self-localized domains. Because the on-site U term has little effect on the dimerization for $U < 4t_0 = 10$ eV,[21] the Peierls-Hubbard model (with $U = 4$ eV) preserves the charge conjugation symmetry as the SSH model does. See Fig. 3(b). On the other hand, broken charge conjugation symmetry is observed in both the extended Peierls-Hubbard model and *ab initio* HF calculations, showing stronger shrinkage effects for p doping than n doping. Experimental data of *trans*-polyacetylene with Na^+, Li^+, K^+, and I^- dopants[4,6] are shown in Fig. 3(b) for comparison, among which the Na^+ and Li^+ results have been densely measured and both indeed showed the zero initial slope and the sharp knee. We regard them as the first set of experimental evidences that the well-known Peierls distortion has a coupled twin.

As a summary, we reveal two generic distortions of a 1D polymer chain and prove analytically that these two distortions are indeed coupled. Using the perfectly dimerized neutral chain as reference, we show that the chain length shrinkage within the self-localized domains can be expressed as a functional of the local dimerization amplitude via the LSA specified by perfectly dimerized chains. The long-lasting unresolved initial flat strain response of *trans*-polyacetylene

and the accompanied sharp knee at 6% Na^+ doping are direct experimental evidences of such coupled twin distortions. Furthermore, there are a few implications. First, the coupled twin distortions are independent of detailed boundary conditions. For instance, doping a closed 1D chain would result in shrunk self-localized domains and uniformly expanded perfectly dimerized domains. Such a contrast makes self-localized shrinkages more apparent in rings. Second, because π-π stacks generally have higher α/K ratios along the stacking direction, localized shrinkages are expected to be more pronounced for polarons in DNA.[27] It is important to note that shrinkages are caused by the presence of undimerized polaron cores, independent of the localization origins either intrinsically or extrinsically by the polarizable solvent.[28] Third, many different actuation mechanisms have been proposed to describe fascinating electroactive materials such as conducting polymers and carbon nanotubes.[26,29,30] Since the doping-induced polymer strains revealed in this work are fundamentally associated with the undimerization nature of self-localized charge carriers, propagating such self-localized strain fields at the sound speed may offer a direction for future ultrafast artificial muscle developments.

---

*linx@bu.edu

[1] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

[2] T. Kennedy and E. H. Lieb, Phys. Rev. Lett. **59**, 1309 (1987).

[3] W. P. Su *et al.*, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).

[4] M. J. Winokur *et al.*, Solid State Commun. **68**, 1055 (1988).

[5] A. J. Heeger *et al.*, Rev. Mod. Phys. **60**, 781 (1988).

[6] N. S. Murthy *et al.*, J. Chem. Phys. **87**, 2346 (1987).

[7] M. Kertesz *et al.*, Chem. Phys. Lett. **90**, 430 (1982).

[8] G. Sun *et al.*, J. Chem. Phys. **117**, 7691 (2002).

[9] R. H. Baughman *et al.*, Phys. Rev. B **46**, 10515 (1992).

[10] It can be proved that the coupled twin distortions exist for the free-electron case. Details will be provided separately.

[11] W. P. Su, Solid State Commun. **35**, 899 (1980).

[12] S. Stafstrom and K. A. Chao, Phys. Rev. B **30**, 2098 (1984).

[13] F. L. J. Vos *et al.*, Phys. Rev. B **53**, 14922 (1996); **53**, R5986 (1996).

[14] A. R. Bishop *et al.*, Phys. Rev. Lett. **52**, 671 (1984).

[15] D. Baeriswyl, in *Theoretical Aspects of Band Structures and Electronic Properties of Pseudo-One-Dimensional Solids*, edited by H. Kamimura (Reidel, Dordrecht, 1985), pp. 1–44.

[16] Mikrajuddin *et al.*, Phys. Rev. B **61**, 8224 (2000).

[17] C. S. Yannoni and T. C. Clarke, Phys. Rev. Lett. **51**, 1191 (1983).

[18] Note that the single- and double-bond length difference is $4u_0$ not $2u_0$. If bond angles of $120°$ are considered, this difference becomes $4u_0/\cos 30° = 0.08$ Å, which gives $u_0 = 0.017$ Å. Using $2u_0/\cos 30° = 0.08$ Å so that $u_0 = 0.035$ Å, p. 797 in Ref. 5, seems to be a typo.

[19] For a soliton with the bond-length order parameter that follows $\phi_{n+1/2} = \tanh[(n+1/2-n_0)/\xi]$, one finds $\gamma(n) = \tanh[(n-n_0)/\xi] + O(\delta a_n - \delta a_{n-1})/u_0$.

[20] Due to the shrinkage effect, there is a factor of $e = 2.718$ difference in the soliton half width between a free-end chain and a chain with the linear shrinkage term compensated. Detailed proof will be provided separately.

[21] K. R. Subbaswamy and M. Grabowski, Phys. Rev. B **24**, 2168 (1981).

[22] X. Lin *et al.*, Proc. Natl. Acad. Sci. U.S.A. **103**, 8943 (2006).

[23] S. Kivelson *et al.*, Phys. Rev. Lett. **58**, 1899 (1987).

[24] S. J. Xie *et al.*, Phys. Rev. B **46**, 6169 (1992); A. Painelli and A. Girlando, *ibid.* **39**, 2830 (1989).

[25] M. J. Frisch *et al.*, (2003) *Gaussian 03*, Pittsburgh.

[26] X. Lin *et al.*, Phys. Rev. Lett. **95**, 198303 (2005); Int. J. Quantum Chem. **102**, 980 (2005).

[27] S. V. Rakhmanova and E. M. Conwell, J. Phys. Chem. B **105**, 2056 (2001); E. M. Conwell and S. V. Rakhmanova, Proc. Natl. Acad. Sci. U.S.A. **97**, 4556 (2000).

[28] D. M. Basko and E. M. Conwell, Phys. Rev. Lett. **88**, 098102 (2002).

[29] J. D. W. Madden *et al.*, IEEE J. Ocean. Eng. **29**, 706 (2004); E. Smela, Adv. Mater. **15**, 481 (2003).

[30] R. H. Baughman *et al.*, Science **284**, 1340 (1999).