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Are better conductors more rigid?

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Abstract. – The variation of the bending stiffness of various materials is studied from the point of view of the electronic band characteristics. As far as the electronically generated bending stiffness κ_e (which we refer to as electro-stiffness) is concerned, the relevant factors are the orbital overlap t, the gap width u between the valence band and the conduction band, and the electron filling fraction γ. A perturbative calculation leads to the approximate expression $\kappa_e \sim t^2/\sqrt{u^2+t^2}$. This shows that materials with a large overlap and narrow band gap should be stiffer. The electro-stiffness also depends on the electron filling-fraction. We find that $\kappa_e(\gamma) \leq \kappa_e(1/2)$. These kinds of behavior are confirmed by numerical calculations. In addition, we study the variation in the projected length of flexible molecules under a voltage bias. The nonlinear variation of the bending rigidity is shown to give rise to a length contraction or dilation, depending on the voltage bias.

The elastic modulus which characterizes the stiffness of materials shows a broad spectrum ranging from a few k_BT to several eV. The structural stiffness of a material is determined by many factors, such as atomic binding energies, the nature of molecular bonding, inter-polymer adhesion, to mention a few. It seems plausible that inherent electronic properties could be an additional source for mechanical rigidity. If a material is a good conductor, structural deformations which lead to a loss in the electronic orbital overlaps are less favored. Such an effect would be weak for poorly conducting materials. This appears to be true in the case of a polymer like rubber which is a bad conductor and very flexible, while a metal is a good conductor with high rigidity. In fact, there exist materials which are both good conductors and flexible, called conducting polymers. They have π-orbital overlapping along a conjugated backbone and a gap between the highest filled and the lowest unfilled bands, forming a band structure similar to inorganic semiconductors. When an electron is removed or added, the conductivity is greatly enhanced, allowing these semiconductors to be utilized as organic electronic devices. On the other hand, conducting polymers are much more flexible than semiconducting solids. This property has led to many studies for exploring their mechanical deformations, such as bending and expansion/contraction driven by electric triggering.

It seems that the key cause for the mechanical stiffness is material dependent. In the exploration of its possible origins, it is desirable to relate the electronic properties of these materials with their mechanical stiffness. This is essential not only to evaluate the electronic

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contribution to stiffness in relation with the chemistry-based factors, but also to grasp the variation of the mechanical response to an electric signal in various materials. For instance, the extension ratio of Polyalkylthiophene (PAT) is larger than that of Polypyrrole (PPy) [1]. It is interesting to relate this to the difference in their electronic band structures. Although they have comparable orbital overlap, the gap between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels in PAT is about half of that in PPy [2]. This indicates that not only orbital overlap but also band gap comes into play in mechanical stiffness.

The purpose of this work is to give a quantitative estimate of the electronic contribution to the total conformational stiffness. To this aim, we consider a conducting polymer modelled as a one-dimensional chain composed of N-monomers where inter-monomer hopping of electrons is allowed via π-orbital stacking. Assuming that hopping strength to depend on the angular configuration of monomers [3], we focus more specifically on the bending stiffness. Furthermore, to simulate the HOMO-LUMO gap, an alternating on-site potential is included in the Hamiltonian. Following a semi-classical approach, we trace over the electronic degree of freedom and obtain the effective potential for the angle deformations. We find that the bending stiffness associated with electronic properties, which we refer to as electro-stiffness, κ_e, is governed by the molecular orbital, t and gap width between HOMO and LUMO level, u, and scales as $\kappa_e \sim t^2/\sqrt{u^2+t^2}$. Further by analyzing the electron-filling fraction dependence on κ_e, we show that doping would make the molecules more flexible. To evaluate the specific contribution of κ_e to the total bending rigidity, we consider molecules of constant contour length under a voltage bias and examine the variation of the projected length as a function of the bias. It turns out that the applied voltage alters the electro-stiffness, yielding the contraction (dilation) in the projected length of the molecules.

We consider a conducting molecule in the presence of an external electric field. The Hamiltonian for the electrons responsible for the conducting behavior is taken as

$$\mathcal{H}_e = -\sum_n t_{n,n+1}(c_n^\dagger c_{n+1} + \mathrm{H.c.}) + \sum_n [(-1)^n u - \varepsilon x_n] c_n^\dagger c_n. \tag{1}$$

Here the inter-site hopping integral $t_{n,n+1}$ is determined by the degree of π-orbital overlap, and is maximum when the molecule is in a straight form. When the molecule is not in the straight conformation, the overlap is decreased, which tends to suppress electron hopping. We incorporate this fact by introducing an angle dependence in the hopping integral as $t_{n,n+1} = t\cos(\phi_{n+1}-\phi_n) \equiv t\cos\theta_n$. For $\theta_n = 0$, the hopping parameter is spatially uniform and maximized by parallel orbital arrangement. In the second term we introduce an alternating on-site potential, yielding a gap whose width is determined by u. This enables us to investigate semiconducting molecules having a gap between HOMO and LUMO level. Also, the on-site potential is position dependent due to the applied voltage V and $\varepsilon = |e|Va/L$ is the voltage drop across one monomer with electrode spacing L (see fig. 1) with taking the bead spacing as a. Especially, we consider that one end of the polymer is anchored to the grounded electrode, where a nonconductive contact is assumed not to allow current flow between the polymer and the electrodes. The position of monomers (in units of a) coupled to the electric fields, can be written as $x_n = \sum_{i=0}^{n} \cos\phi_i - (1/2)\cos\phi_n$ with the lower index n for the monomer located closer to the grounded electrode. On the other hand, to examine the changes of the projected length in response to the applied fields, the other end is assumed to be detached from the gated electrode.

The Hamiltonian contains several electronic factors that contribute to the structural rigidity: i) the electron hopping favored by a straight configuration; ii) the band gap making the molecules less conducting and tending to diminish the effect of the factor i); iii) the applied

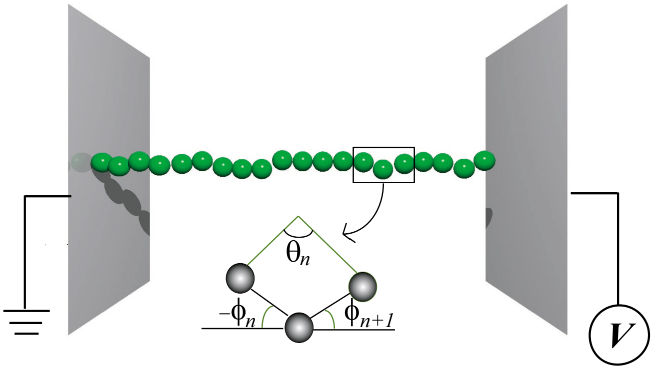

Fig. 1 – Schematic picture of a conducting polymer between two electrodes. The one with the anchored polymer is grounded and the other is fixed at voltage V. The polymer configurations are discretized in a way such that monomers are located at the mean positions of two adjacent beads. Here the local tangent to the polymer at monomer n is defined by the bead-to-bead bond angle $0 \le \phi_n \le \pi/2$.

voltage bias inducing length contraction or extension. In fact, the rigidity also has contributions from molecular bonding and atomic binding potentials, which we denote as κ_m, and the potential governing the structural rigidity is written as

$$\mathcal{H}_m = \sum_n \kappa_n \theta_n^2,$$

where $\kappa_n = \kappa_{e,n} + \kappa_m$ and the rigidity from electronic origin, $\kappa_{e,n}$, can be obtained by

$$\kappa_{e,n} = -\frac{k_B T}{2} \frac{\partial^2}{\partial \theta_n^2} \ln \mathrm{Tr}_{\{c,c^\dagger\}} \exp[-\beta \mathcal{H}_e], \tag{2}$$

which can be site dependent when boundary effects are considered.

Before proceeding, we first compare how the electronic degrees of freedom are coupled to the lattice motion in our model and in other approaches. For instance, the Su-Schrieffer-Heeger (SSH) model [4] considers π-electron subject to ionic displacement via the tight-binding Hamiltonian given by

$$\mathcal{H}_{SSH} = \sum_n t_{n,n+1}(c_n^\dagger c_{n+1} + \mathrm{H.c.}),$$

where the hopping parameter is taken as $t_{n,n+1} = t - \alpha(\xi_{n+1} - \xi_n)$ with ξ_n being the displacement of the n-th ion from its reference position na. By making an Ansatz as $\xi_n = (-1)^n \xi - (N/2 - n)\delta$ with ξ and δ for the dimerization and bond length variance, the energy for $\mathcal{H}_{SSH}$ together with the lattice Hamiltonian can be calculated and minimized with respect to ξ and δ. In the SSH model there are two competing energetic factors: The electronic energy is lowered and the elastic energy is increased by the dimerization. This kind of Ansatz is appropriate in order to study the appearance of a bond-length alternation in the ground state. In our model however, the bending is neither favored electronically nor mechanically, and hence no competing effect leads to the spontaneous deformation of the lattice. Even if we used the SSH model in our approach, the main concern would still be to figure out an additional potential for the lattice deformation provided by the lattice-electron coupling, rather than the deformation itself.

Let us first consider the small bending of the molecules in the absence of a voltage drop. Expanding the angle to quadratic order, we define

$$\begin{aligned}\mathcal{H}_e^{(0)} &= -t\sum_n (c_n^\dagger c_{n+1} + \text{H.c.}) + u\sum_n (-1)^n c_n^\dagger c_n, \\ \mathcal{H}_e^{(1)} &= \frac{t}{2}\sum_n \theta_n^2 (c_n^\dagger c_{n+1} + \text{H.c.}),\end{aligned} \tag{3}$$

where the position of the n-th monomer for small ϕ's is denoted by x_n. Assuming $\mathcal{H}_e^{(1)}$ to be a small perturbation, we can write $-k_BT\ln\langle e^{-\beta\mathcal{H}_e^{(1)}}\rangle_0 \approx \langle\mathcal{H}_e^{(1)}\rangle_0$, where $\langle X\rangle_0 = \mathcal{Z}_0^{-1}\text{Tr}Xe^{-\beta\mathcal{H}_e^{(0)}}$ with $\mathcal{Z}_0 = \text{Tr}e^{-\beta\mathcal{H}_e^{(0)}}$. It is convenient to work in the Fourier space: $c_n = N^{-1/2}\sum_n e^{ikn}c_k$. The Hamiltonian $\mathcal{H}_e^{(0)}$ can then be straightforwardly diagonalized by the canonical transformation $c_k = \cos\chi_k a_{k,+} + \sin\chi_k a_{k,-}$ and $c_{k+\pi} = -\sin\chi_k a_{k,+} + \cos\chi_k a_{k,-}$ as

$$\mathcal{H}_e^{(0)} = \sum_{k,\alpha=\pm} \lambda(k) a_{k,\alpha}^\dagger a_{k,\alpha},$$

where $\lambda(k,\alpha) = \alpha\sqrt{\epsilon^2(k) + u^2}$ with $\epsilon(k) = -2t\cos k$ and $\tan 2\chi_k = -u/\epsilon(k)$ and $\alpha = \pm 1$. Similarly we can write $\mathcal{H}_e^{(1)}$ in terms of the diagonalizing basis, with off-diagonal components. In evaluating $\langle\mathcal{H}_e^{(1)}\rangle_0$, however, since $\mathcal{H}_{el}^{(0)}$ is quadratic in the c's, the only non-vanishing contributions can be easily traced and we get

$$\kappa_e = \frac{1}{N}\sum_{k,\alpha=\pm 1} \frac{-\epsilon^2(k)}{\alpha\sqrt{u^2 + \epsilon^2(k)}}\langle\mathcal{N}_{k,\alpha}\rangle_0 \tag{4}$$

with the mean number of particles occupying the $\alpha = +1$ and -1 bands being determined by

$$\langle\mathcal{N}_{k,\alpha}\rangle_0 = \langle a_{k,\alpha}^\dagger a_{k,\alpha}\rangle_0 = [e^{\beta(\lambda(k,\alpha)-\mu)} + 1]^{-1}. \tag{5}$$

Let us first consider when the system is half-filled so that $\langle\mathcal{N}_{k,+}\rangle = 0$. From eq. (4), it is clear that as far as the electronic contribution to the bending stiffness is concerned, the hopping integral plays a dominant role: while the denominator in eq. (4) characterizes the band width, the numerator is proportional to t^2. On the other hand, for molecules having comparable hopping strengths, those with large band gap would be more flexible. The numerical evaluation of eq. (2) has been performed and the resulting stiffness is presented in fig. 2. It is in good agreement with the perturbative result, eq. (4). While the analytic expression for the stiffness can be easily obtained for an infinitely long polymer, a finite-sized polymer has boundary effects that are characterized by a site-dependent stiffness. As shown in fig. 2, the stiffness is weaker in the polymer bulk than in the ends, indicating that when a force is applied, the bending of the polymer would be more localized in the bulk rather than being uniform all over.

Even more interesting is the filling factor dependence of κ_e. When hole/particles are introduced in the system by doping, the electrostiffness becomes weaker than that for a half-filled system, as displayed in fig. 3. We evaluated the stiffness difference $\Delta\kappa_e \equiv \kappa_e(\gamma) - \kappa_e(1/2)$, where γ denotes the filling fraction as $\gamma = N_e/N$. When the system is half-filled, $\alpha = (+1)$ band would be empty so that in eq. (4), the contribution to the stiffness is solely due to the $\alpha = (-1)$ band. On the other hand, when holes are doped, the $\alpha = (-1)$ band becomes partially filled, and the corresponding reduction in $\langle\mathcal{N}_{k,-}\rangle$ results in a decrease of κ_e. Here we have assumed that doping makes no changes in the orbital overlap. Since the doping effect is to enhance the electric conductivity, it can be assumed that a doped system has a larger

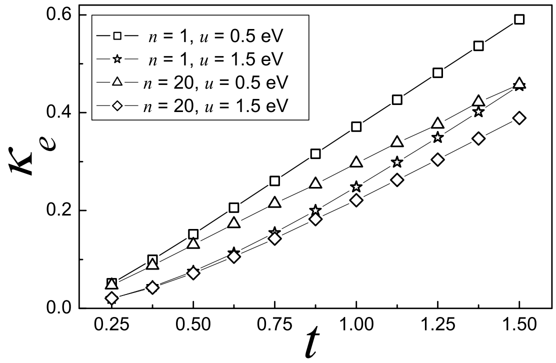

Fig. 2 – The electro-stiffness κ_e *vs.* the hopping integral for $N = 40$ in the absence of a voltage bias. The values of κ_e depend on the monomer position, those near the boundaries, *e.g.* $n = 1$ being smaller than those at $n = 20$. For a given n, κ_e is estimated for $u = 20$ and $u = 60$ to show that an increase in the gap width suppresses the stiffness. The energy parameters are in units of eV throughout this paper.

orbital overlap than a non-doped one. In that case, doping leads to two competing effects: increasing κ_e by enhancing t and decreasing κ_e by reducing γ. In order to discriminate which of the two is the dominant factor, some experimental measurements on bending as a function of doping should be performed, and our results could be used as a benchmark.

The electrostiffness depends also on the applied electric field which contributes to the energy of the system via a coupling to the charges of the electrons: when $\varepsilon \ll t$ and u, we may approximate the energy due to the field as $E_f = -\varepsilon \sum_n x_n \langle c_n^\dagger c_n \rangle$. When a positive voltage bias is applied, the molecule increases its length, and hence the effective stiffness increases. For a negative voltage bias, the molecule tends to contract, resulting in the reduction of its stiffness. Investigating the length deformation as a function of the electric field is thus very useful to evaluate the contribution of κ_e to the total rigidity κ. As we mentioned earlier,

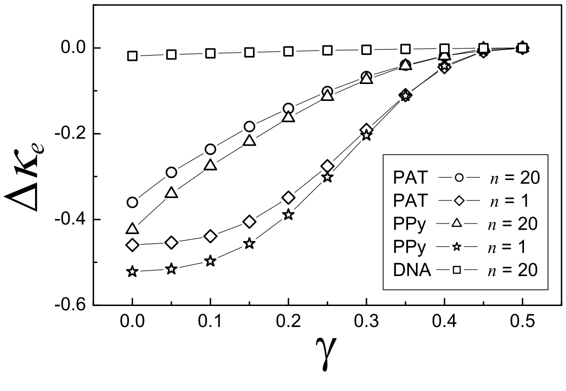

Fig. 3 – The stiffness difference $\Delta\kappa_e$ *vs.* the electron filling fraction γ for $N = 40$ in the absence of a voltage bias: for a given n, κ_e is estimated for $t = 60$, $u = 40$ (PPy) and $t = 48$, $u = 20$ (PAT) to show that the increase of the gap width suppresses the stiffness. For a DNA molecule, the parameters $t = 8$ and $u = 40$ are used to show that κ_e barely changes with the filling fraction.

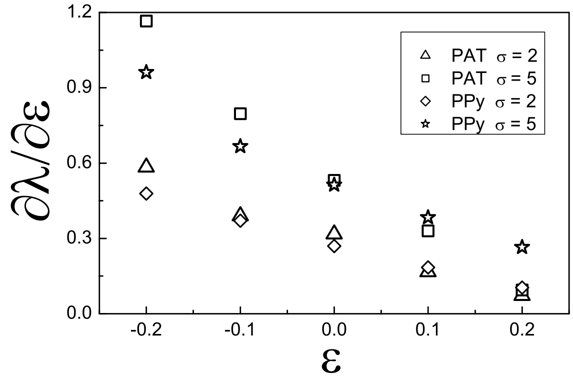

Fig. 4 – The derivative of the length contraction ratio λ *vs.* the voltage drop ε for various parameter sets. Here, the parameters for PPy and PAT are the same as the ones used in fig. 3, and σ represents the ratio $\sigma = \kappa_m/\kappa_e$.

the structural rigidity comes not only from those electronic degrees of freedom but also from the molecular binding potentials. Since for the latter, the deformation is presumably rather insensitive to the applied electric potential, the length deformation caused by the electric field would directly relate the contribution of κ_e to the total rigidity. To see this more clearly, let us define the length contraction (extension) ratio λ as

$$\frac{1}{\lambda} \equiv 1 - \frac{L_p}{L_c} \approx \frac{1}{2}\langle\phi^2\rangle \tag{6}$$

with L_c and L_p being the contour length and the projected length of the polymer, respectively, and $\langle\phi^2\rangle$ being the average angle fluctuation per monomer, given by $\langle\phi^2\rangle = \mathrm{Tr}_{\{\phi\}} e^{-\beta\mathcal{H}_m} \sum_i \phi_i^2 / \mathrm{Tr}_{\{\phi\}} e^{-\beta\mathcal{H}_m}$. Here, let us disregard the site dependence in $\kappa_{e,n}$ (which as we saw is uniform, except for a few boundary sites), and write $\mathcal{H}_m = \sum_{\langle i,j\rangle} \kappa(\phi_i - \phi_j)^2$, where $\kappa = \kappa_m + \kappa_e$ and κ_m is the bending rigidity due to molecular bonding. It is clear that $\langle\phi^2\rangle \propto 1/\kappa$ and hence, $\partial\lambda/\partial\varepsilon$, which is measurable in experiments, would be simply related to the electric-field dependence of κ_e. Evaluating λ as a function of the voltage bias for molecules having different κ_m, *e.g.*, $\sigma \equiv \kappa_m/\kappa_e (\sigma = 2, 5)$, we confirm in fig. 4 that $\partial\lambda/\partial\varepsilon$ is indeed not very sensitive to κ_m. It is also shown that the length contraction ratio increases nonlinearly with ε and its derivative with respect to ε is positive. This clearly demonstrates the expected feature that the molecules adjust their length to the voltage, allowing for their use as electro-mechanical switches. For experimental investigation on the length variation, to suspend a single molecule would be a highly demanding task. Yet, experiments would be possible with a layer of polymer chains. It is known that due to the excluded-volume effect polymer chains grafted onto solid substrate form a brush-like layer, the so-called polymer brush [5]. Our results on a single molecule might not be directly comparable to the case of polymer brush. Nonetheless, when the grafting density is low, it is expected that a single-particle feature would be dominant over the collective properties arising from the steric interaction between polymers, for which our theory can provide a lucid explanation.

In summary, the electronic origin of bending stiffness was investigated. It was shown that the electro-stiffness, κ_e, is governed by the molecular orbital overlap and the gap width between HOMO and LUMO levels: molecules with wider band width are more flexible. The electro-stiffness can be controlled by molecular doping or by applying a voltage bias. Analyzing the electron filling-fraction dependence on κ_e, we showed that doping makes molecules more flexible. In addition, we considered molecules under a voltage bias to extract the κ_e contribution to the total stiffness. In response to the applied voltage, the molecules are contracted or dilated with a very nonlinear increase of κ_e with the applied bias.

To conclude this study, we mention the value of κ_e for a few molecules. For example, DNA has an extremely narrow band width ($\approx 0.01 \sim 0.04\,\mathrm{eV}$) [6] and its electrostiffness is estimated here to be roughly just a few k_BT. It is well known that the persistence length of ssDNA is about $\ell_p \sim 5\,\mathrm{nm}$ [7], which is related to the bending energy by $\kappa = (\ell_p/a)k_BT$. Taking the inter-base distance $a = 3.4\,\text{Å}$, $\kappa \approx 14k_BT$, showing that the contribution of κ_e to the stiffness is significant. For a dsDNA $\ell_p \approx 50\,\mathrm{nm}$ and hence κ is ten times bigger than that for ssDNA [7], while the doubling of κ_e cannot account for the difference. This suggests that among the energetic factors which govern dsDNA bending, the electronic motions via orbital overlap is not as crucial as the electrostatic repulsion between phosphate groups and the helical structured base staking [8]. On the other hand, the persistence length of carbon nanotubes (CNT) lies in the macroscopic range $\ell_p = 0.1$–$1\,\mu\mathrm{m}$ [9], which shows that the bending rigidity of CNT is hundreds times larger than that of dsDNA. Noting that the orbital overlap is $t \sim 2.5\,\mathrm{eV}$, and the band gap is small, $u = 0 \sim 0.5\,\mathrm{eV}$ [10], we find $\kappa_e \approx 10^2k_BT$, which shows the important contribution of electro-stiffness to the total stiffness of CNT. In addition, the HOMO and LUMO level of PPy and PAT can be simulated by taking $u = 1\,\mathrm{eV}$ and $t = 1.5\,\mathrm{eV}$, and $u = 0.5\,\mathrm{eV}$ and $t = 1.2\,\mathrm{eV}$, respectively [2]. This leads to $\kappa_e \approx 34k_BT$ for PPy, and $\kappa_e \approx 28k_BT$ for PAT. Although no direct measurement of the bending rigidity of these materials has been made, this goes in the direction of showing that the latter is more responsive than the former [1].

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