Spring constant analogy for estimating stiffness of a single polyethylene molecule

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The stiffness of a simple planar polymeric chain is modeled using analogies of mechanical springs arranged in series and in parallel assemblies. The stiffness of chemical bonds is resolved into two perpendicular axes defined by the longitudinal and transverse axes in the molecular plane. Using Hooke's definition of spring stiffness, the molecular stiffness of polyethylene is obtained along the longitudinal and transverse directions. This paper demonstrates the use of physical analogies and mathematical approximations for obtaining an analytical form for the stiffness of a simple single-molecule.

KEY WORDS: analytical approach, bond-bending, bond-stretching, Hooke's Law, mechanical springs, single-molecule

AMS subject classification: 70C20, 74A25, 74B99, 74E40, 74G10

1.   Introduction

Recent advances in optical technology enable the elastic stiffness of single molecules such as DNA [1–4], RNA [5] and extracellular matrix proteins [6,7] to be obtained by optical trapping and stretching. However, the possibility of mounting molecules onto beads for stretching purposes is limited for larger molecules. The objective of this paper is to demonstrate how physical models from elementary cases, such as spring constants, can be applied for estimating physical properties in smaller molecules. Polyethylene (PE), being the simplest of polymeric chains, is selected for illustration. As the name suggests, PE is a polymer of ethylene monomers, as shown in figure 1. To obtain approximate molecular chain stiffness, an analogy is made herein with the mechanical spring whereby the spring constant, or stiffness, is defined according to Hooke's Law as

$$k = \frac{F}{\delta l},\tag{1}$$

where F and δl are the applied force and elongation, respectively. For springs in series, the force across each spring is common while the overall elongation Hooke is the summation of
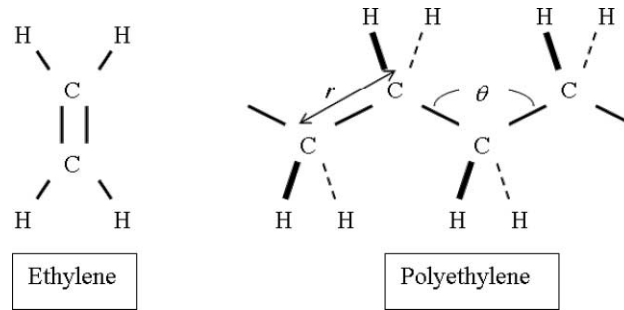
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Figure 1. An ethylene monomer and its polymeric form, polyethylene (PE).

individual spring elongation. Hence

$$\frac{1}{k} = \sum_i \frac{1}{k_i}.$$ (2)

For springs in parallel, the overall load is summed from the force across each individual spring, while the elongation is common for all springs. This leads to

$$k = \sum_i k_i.$$ (3)

Figure 2 shows the two possible combinations of springs. In addition to the spring analogy, one may also apply the electrical circuit and thermal flow analogies shown in table 1.

2.   Analysis

A fully stretched PE chain has its carbon atoms in a zig-zag conformation on a plane. Therefore stretching of the PE chain results in elongation of the C–C bond, r, and widening of the C–C–C angle, θ. For the specific case of a fully stretched PE, no bond twisting occurs on the assumption that this molecule takes the planar zig-zag conformation. As in many other analyses, we begin our analysis by isolating a representative unit. This is shown in figure 3 where two halves of carbon atoms and their corresponding chemical bond are isolated for analysis. The hydrogen atoms are not shown for clarity. Suppose the bond stiffness is k_s and angular stiffness is k_θ, then the effective stiffness will have to be resolved along the direction of interest, as depicted in figure 4, to give the equivalent stiffness constants along the chain longitude (k_R^L, k_θ^L) and along the in-plane transverse (k_R^T, k_θ^T). Since bond stiffness k_s and angular stiffness k_θ has been applied by several groups of researchers [8–11] for computational simulation, these stiffness constants are being employed herein for analytical formulation.

In paving way for resolving forces and displacement, the longitudinal L and transverse T axes are introduced for a PE chain as shown in figure 3, where the L–T plane lies in the zig-zag plane formed by the carbon atoms. The bond axis R lies on the L–T plane,
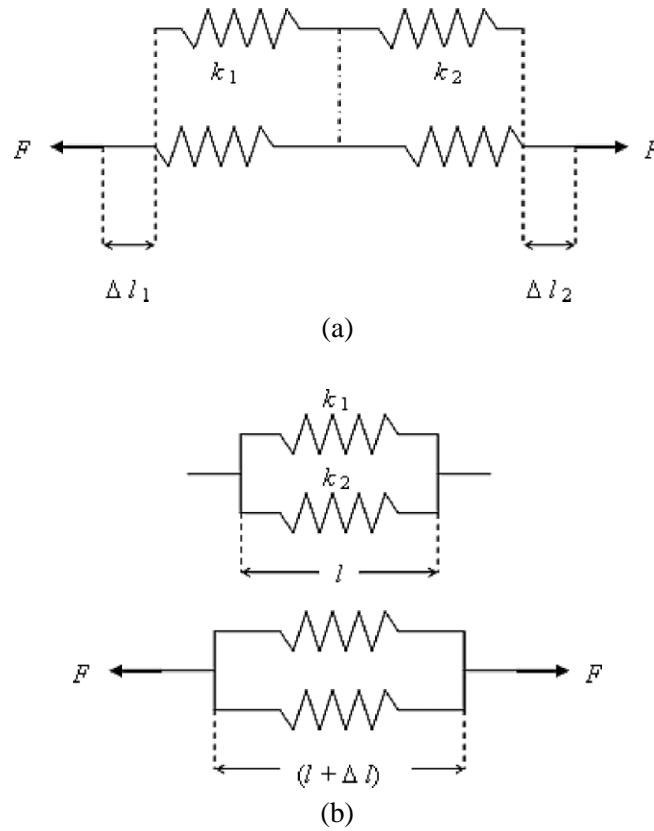
Figure 2. Assembly of two springs in (a) series, and (b) parallel.

Table 1
Analogies for obtaining stiffness of polypropylene chain.

Mechanical spring	Electrical circuit	Thermal flow
Force	Current	Heat flow
Elongation	Potential difference	Temperature difference
Spring constant	Conductance (resistance^{-1})	Thermal conductance[a]

[a] Thermal conductance, $K = kA/L$, where k = thermal conductivity.
 A = cross-sectional area.
 L = thermal transfer distance in each composite slab.

which is subtended by an angle $\theta_0/2$ where θ_0 is the equilibrium bond angle between neighboring carbon atoms. Perpendicular to the R-axis is the θ-axis, which defines the direction of bond bending. In addition, the equilibrium bond length, r_0, is introduced for the distance between two neighboring carbon atoms. For brevity, the changes in bond length $r - r_0$ and bond angle $\theta - \theta_0$ are written as δr and $\delta\theta$, respectively.
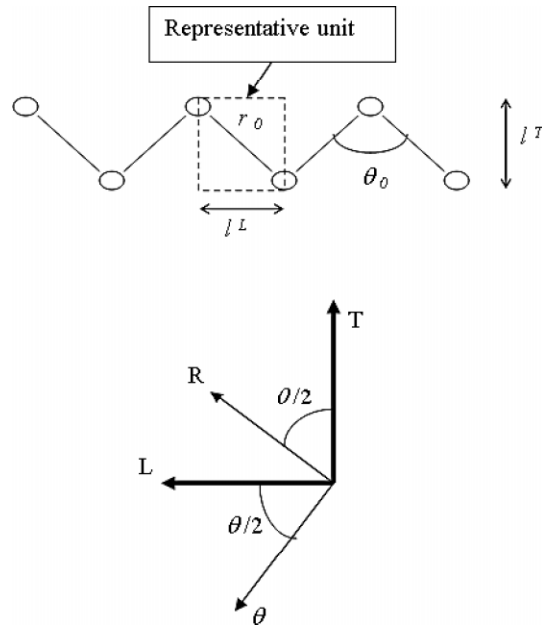
Figure 3. Representative unit for a polyethylene chain.

2.1. Longitudinal stiffness

Applying a load F_L along the molecular chain longitude, the force along the R-axis is resolved as

$$F_R = F_L \sin\left(\frac{1}{2}\theta_0\right),$$
(4)

assuming no change in bond angle. By Hooke's Law,

$$F_R = k_s \delta r.$$
(5)

Substituting equation (5) into equation (4), we have

$$F_L = \frac{k_s \delta r}{\sin(\theta_0/2)}.$$
(6)

Corresponding to the change in bond length δr, the change in dimension along the L-axis is

$$\delta l_R^L = \delta r \sin\left(\frac{1}{2}\theta_0\right).$$
(7)

Therefore the longitudinal stiffness according to Hooke's Law, considering bond elongation, is obtained from equations (6) and (7) as

$$k_R^L = \frac{F_L}{\delta l_R^L} = \frac{k_s}{\sin^2(\theta_0/2)}.$$
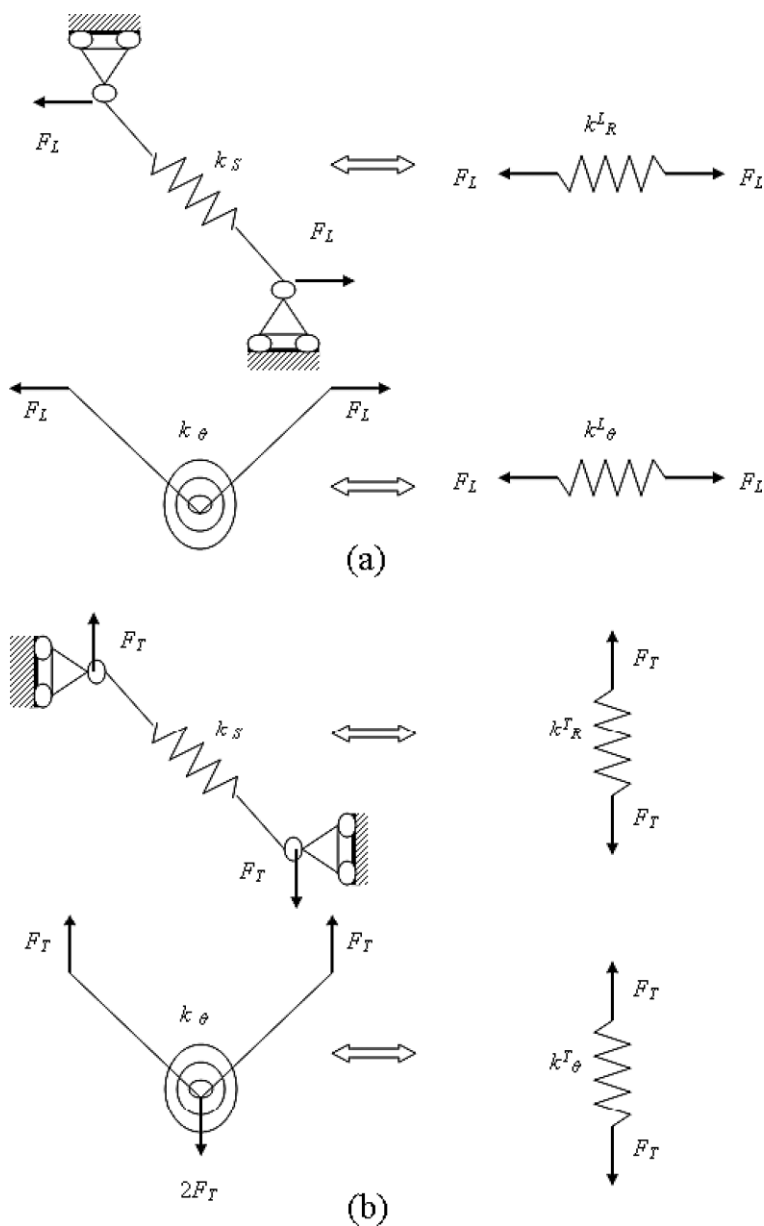(8)

Figure 4. Obtaining individual effective stretching and bending stiffness for (a) longitudinal, and (b) transverse chain directions.

Resolving along the θ-axis, the force responsible for altering the bond angle is

$$F_\theta = F_L \cos\left(\frac{1}{2}\theta_0\right) \tag{9}$$

assuming no change in bond length. Taking Hooke's Law for angular stiffness, we have

$$F_\theta r_0 = k_\theta \left(\frac{1}{2} \delta\theta \right).$$

(10)

Substituting equation (10) into equation (9) gives

$$F_L = \frac{k_\theta (\delta\theta/2)}{r_0 \cos(\theta_0/2)}.$$

(11)

The change in dimension along the *L*-axis, corresponding to the change in bond angle $\delta\theta$, is

$$\delta l_\theta^L = r_0 \left\{ \sin\left(\frac{1}{2}\theta_0 \right) \left[\cos\left(\frac{1}{2}\delta\theta \right) - 1 \right] + \cos\left(\frac{1}{2}\theta_0 \right) \sin\left(\frac{1}{2}\delta\theta \right) \right\}.$$

(12)

For infinitesimal change in bond angle, $\delta\theta \to 0$, the following assumptions are valid: $\sin(\delta\theta/2) = \delta\theta/2$ and $\cos(\delta\theta/2) = 1$. So, equation (12) simplifies to

$$\delta l_\theta^L = r_0 \left[\frac{1}{2} \delta\theta \cos\left(\frac{1}{2}\theta_0 \right) \right].$$

(13)

Therefore the longitudinal stiffness, considering change in bond angle, is obtained from equations (11) and (13) by Hooke's Law:

$$k_\theta^L = \frac{F_L}{\delta l_\theta^L} = \frac{k_\theta}{r_0^2 \cos^2(\theta_0/2)}.$$

(14)

As the bond stiffness and angular stiffness are arranged in series, the effective stiffness *per representative unit* along the longitudinal direction is based on equation (2),

$$\frac{1}{k_{\text{eff}}^L} = \frac{1}{k_R^L} + \frac{1}{k_\theta^L}.$$

(15)

For the entire molecular chain consisting *n* number of carbon atoms, equation (2) applies again with a factor of $n - 1$ and $n - 2$ to the first and second terms on the RHS of equation (15) because there exist $n - 1$ number of C–C bonds and $n - 2$ number of C–C–C angles. Therefore,

$$k_{\text{eff}}^L = \frac{k_s k_\theta}{(n-2)k_s r_0^2 \cos^2(\theta_0/2) + (n-1)k_\theta \sin^2(\theta_0/2)}.$$

(16)

2.2. Transverse stiffness

Where the arrangement of "springs" is not clear as to whether series arrangement or parallel arrangement is to be employed, one considers the independence of the springs in attaining the prescribed deformation. When the prescribed deformation can be attained by any one of the individual spring, then the springs are said to be *in series*. If, on the other hand, deformation of one spring must be accompanied by similar (common) deformation by other springs, they are said to be *in parallel*. For the case of PE chain being
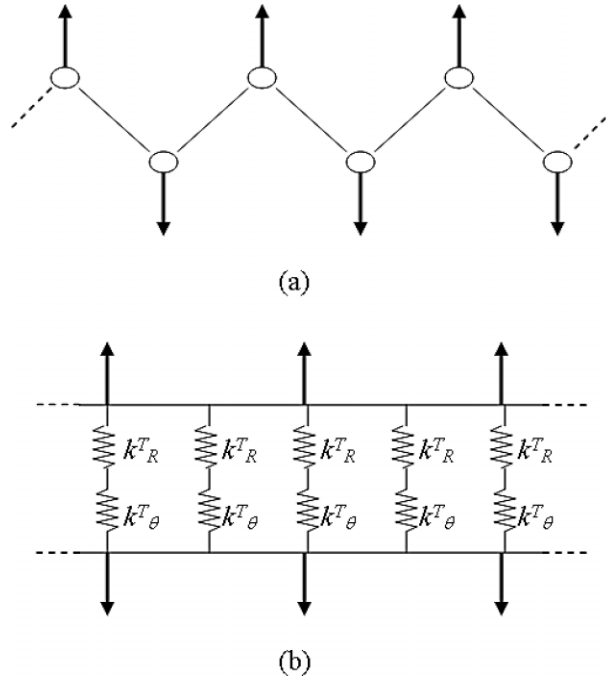
(a)

(b)

Figure 5. Transverse stretching of (a) PE molecular chain, and (b) its equivalent system.

longitudinally stretched, such elongation can be attained by bond stretching alone (bond angles being rigid) or by bond bending only (bond lengths fixed), hence the bond length and bond angle stiffness are in series. Similar argument holds for transverse stretching in the molecular plane of PE, as furnished in figure 5(a). Dimensional change of the width, δl^T, can take place due to bond elongation only (bond angle remains unchanged) or due to narrowing of the bond angles alone (constant bond lengths). Hence the pair of bond length "spring" and bond angle "spring" are considered as series spring *within each representative unit*. However, each representative unit is in parallel with other representative units. Hence the arrangement of springs for transverse in-plane stretching is as shown in figure 5(b).

Suppose a transverse load is applied such that the force passing through each representative unit is F_T, then

$$F_R = F_T \cos\left(\frac{1}{2}\theta_0\right) \tag{17}$$

assuming fixed bond angle. Substituting equation (5) into equation (17) gives

$$F_T = \frac{k_s \delta r}{\cos(\theta_0/2)}. \tag{18}$$

For a bond elongation of δr along the R-axis, the corresponding "elongation" along the T-axis is

$$\delta l_R^T = \delta r \cos\left(\frac{1}{2}\theta_0\right). \tag{19}$$

The transverse stiffness, according to Hooke's definition, can be obtained from equations (18) and (19) as

$$k_R^T = \frac{F_T}{\delta l_R^T} = \frac{k_s}{\cos^2(\theta_0/2)}. \tag{20}$$

Resolving along the θ-axis, the force accountable for changing the bond angle is

$$F_\theta = F_T \sin\left(\frac{1}{2}\theta_0\right) \tag{21}$$

assuming no change in bond length. Substituting equation (10) into equation (21) yields

$$F_T = \frac{k_\theta(\delta\theta/2)}{r_0 \sin(\theta_0/2)}. \tag{22}$$

The change in dimension along the T-axis due to a change in bond angle by $\delta\theta$ is

$$\delta l_\theta^T = r_0\left\{\cos\left(\frac{1}{2}\theta_0\right)\left[\cos\left(\frac{1}{2}\delta\theta\right) - 1\right] + \sin\left(\frac{1}{2}\theta_0\right)\sin\left(\frac{1}{2}\delta\theta\right)\right\}. \tag{23}$$

For infinitesimal change in bond angle, equation (23) reduces to

$$\delta l_\theta^T = r_0\left[\frac{1}{2}\delta\theta \sin\left(\frac{1}{2}\theta_0\right)\right]. \tag{24}$$

Therefore the transverse stiffness per representative unit, considering change in bond angle only, can be obtained from equations (22) and (24) by Hooke's definition,

$$k_\theta^T = \frac{F_T}{\delta l_\theta^T} = \frac{k_\theta}{r_0^2 \sin^2(\theta_0/2)}. \tag{25}$$

Since both the bond length "spring" and the bond angle "spring" are in series, equation (2) applies for the transverse stiffness *per representative unit*

$$\frac{1}{k_{\text{eff}}^T} = \frac{1}{k_R^T} + \frac{1}{k_\theta^T}. \tag{26}$$

For the entire molecular chain consisting n number of carbon atoms, equation (3) applies with due consideration to the representative units being in parallel to the transverse stretching.

Therefore,

$$k_{\text{eff}}^T = \frac{(n-1)k_s k_\theta}{k_s r_0^2 \sin^2(\theta_0/2) + k_\theta \cos^2(\theta_0/2)}, \tag{27}$$

where the factor of $n - 1$ refers to the number of representative units for n number of carbon atoms along the molecular chain.

3. Results

As an illustration to the longitudinal stiffness and transverse stiffness described by equations (16) and (27), respectively, we employ the physical data from [12] as listed in table 2. Since the Morse potential for bond stretching

$$U_M = D\{1 - \exp[-a(r - r_0)]\}^2 \tag{28}$$

is known to be more realistic than the harmonic potential

$$U_H = \frac{1}{2}k_s(r - r_0)^2, \tag{29}$$

the stretching stiffness k_s coefficient is obtained from the Morse parameters (D, a) as [13,14]

$$k_s = 2Da^2. \tag{30}$$

Result of the longitudinal and transverse stiffness as a function of molecular chain length, in terms of the number of carbon atoms n, is shown in figure 6. As expected, results reveal that transverse chain stiffness is higher than the longitudinal chain stiffness, and the gap widens for longer molecular chains.

Though the non-bonded potential should be included for more accurate description of the intramolecular interaction, it is negligible in comparison to the covalent bond stiffness. Another type of stiffness not included here is the twisting of bonds. This is because no torsion of chemical bond occurs for stretching a planar molecule as in the case of PE [15]. Twisting of bonds is expected, however, either in prescribed twisting of a planar molecule [16] or in stretching of a helical polymeric chain such as isotactic polypropylene.

Table 2
Physical data for illustration.

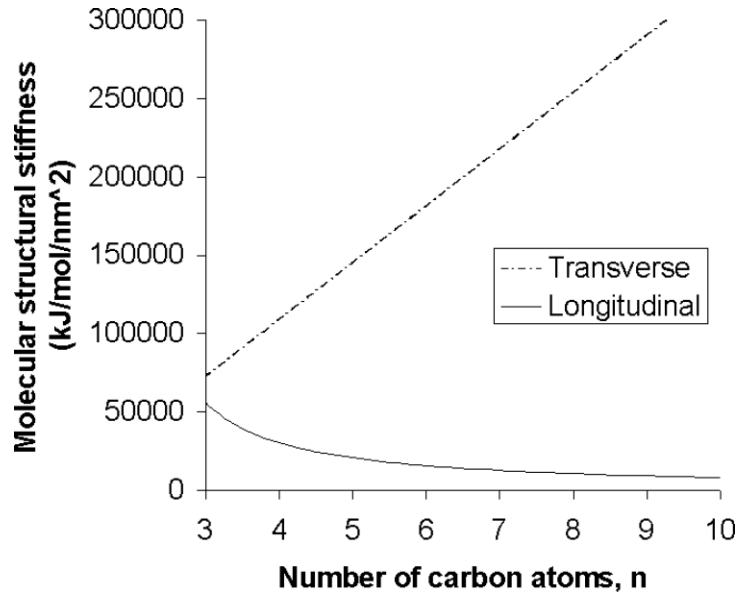|	Data from [12]	Equivalent SI units applied herein
D	80.0 kcal mol^{-1}	334.72 kJ mol^{-1}
a	1.94 Å^{-1}	19.4 nm^{-1}
k_s	Nil	251950 kJ mol^{-1} nm^{-2}
k_θ	144.6 kcal rad^{-2} mol^{-1}	605.0 kJ rad^{-2} mol^{-1}
r_0	1.53 Å	0.153 nm
θ_0	111.0 deg	1.9373 rad

Figure 6. Stiffness of in-plane PE molecule for *n* number of carbon atoms in longitudinal direction (continuous curve) and transverse direction (dashed line).

4. Conclusions

An analytical approach in formulating the stiffness of a planar molecular chain has been demonstrated by means of the mechanical springs assembly. Major criteria adopted in this paper include:

(a) Resolution of forces and of displacements;

(b) Quantitative description for stiffness of springs arrangement in series and parallel; and

(c) Assumption of $\sin(\delta\theta) \approx \delta\theta$ and $\cos(\delta\theta) \approx 1$ for simplicity in infinitesimal deformation.

Results reveal that with increasing length of PE molecule, the structural longitudinal stiffness decreases while the structural transverse stiffness increases.

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