Journal of Mathematical Chemistry Vol. 34, Nos. 3–4, November 2003 (© 2003)

Elastic properties of a polyethylene single-molecule

Teik-Cheng Lim

Nanoscience and Nanotechnology Initiative, Faculty of Engineering, National University of Singapore, Republic of Singapore

Received 20 June 2003

Analytical closed-form solution of the elastic properties (such as longitudinal stiffness, shear stiffness and Poisson's ratio) of a taut polyethylene single-molecule is developed in this paper in terms of C–C and C–C–C bond parameters. The concepts considered herein include resolution of forces and of displacement, with due application of Hooke's law to determine the longitudinal stiffness and the in-plane Poisson's ratio. Adopting the solid mechanics theory as an analogy, the shear stiffness of a taut polyethylene chain is conveniently obtained. Results reveal unique Poisson's ratio property of a polyethylene single-molecule in comparison to usual bulk materials, thereby suggesting size-dependency of nano-scale materials in terms of the Poisson's ratio. Finally some frequently occurring terms in all three elastic property expressions are grouped to summarize and to reveal some form of uniformity in the analytical solutions.

KEY WORDS: analytical form, bond bending, bond stretching, Hooke's law, Poisson's ratio, polyethylene, single-molecule, solid mechanics, stiffness

AMS subject classification: 70C20, 74A25, 74B99, 92E10

1. Introduction

Miniaturization of objects down to the nano-scale leads to molecular devices, whereby chemical principles are essential for designing these devices. Molecular-scale structures may exist naturally such as bio-molecular motors [1–3] or nano-engineering devices such as molecular machines [4–6] and single-molecule electrical/electronic circuits [7,8]. Where mechanical loading is concerned, an understanding of the molecular stiffness is essential. Previously an analytical approach was adopted in obtaining the longitudinal stiffness – in terms of spring constant – of a polyethylene (PE) molecule [9]. A simpler alternative approach is attempted in this paper which, in addition to longitudinal stiffness, also gives the Poisson's ratio in a convenient manner. Using an analogy from solid mechanics theory, the shear stiffness of a taut PE single-molecule is also obtained.

2. Analysis

Adopting a ball-and-stick model with bond stretching and bond bending stiffness constants as k_s and k_θ, respectively, a stretching force of P acting along the PE chain as

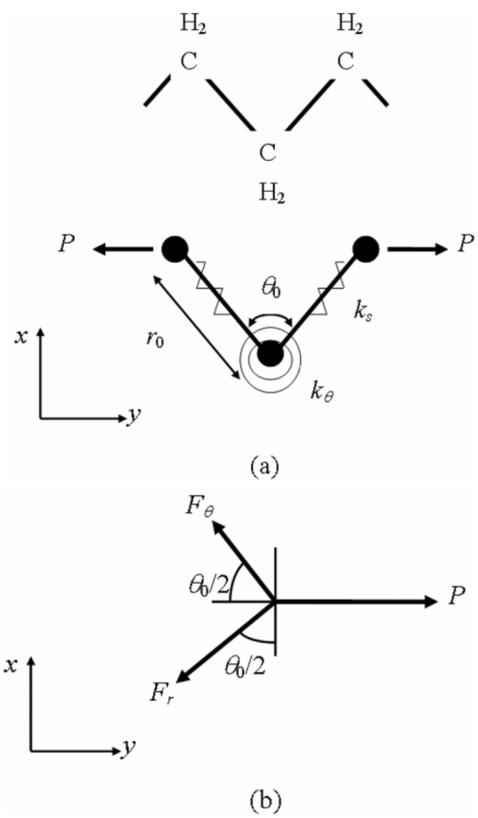

Figure 1. A representative unit of a polyethylene chain consisting three carbon atoms with (a) linear and angular springs for bond-stretching and bond-bending stiffness, respectively, and (b) resolution for forces diagram.

shown in figure 1(a) can be resolved into the stretching force F_r and bending force F_θ, as depicted in figure 1(b). Taking equilibrium about the x- and y-directions, we have

$$F_r \cos\left(\frac{\theta_0}{2}\right) - F_\theta \sin\left(\frac{\theta_0}{2}\right) = 0 \tag{1}$$

and

$$F_r \sin\left(\frac{\theta_0}{2}\right) + F_\theta \cos\left(\frac{\theta_0}{2}\right) = P, \tag{2}$$

respectively. Figure 2 shows the bond elongation by an amount of δr due to F_r and bond bending by an amount of $\delta\theta$ due to F_θ. By Hooke's law,

$$F_r = k_s \delta r \tag{3}$$

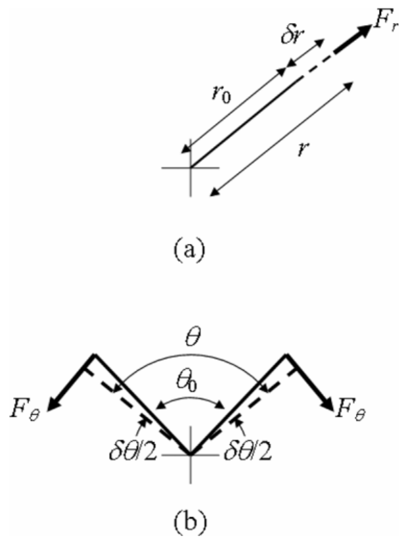

Figure 2. Force-deformation modes via (a) stretching, and (b) bending.

and

$$F_\theta r_0 = k_\theta \frac{\delta\theta}{2}. \tag{4}$$

Solving equations (1) and (2) simultaneously gives

$$\begin{Bmatrix} F_r/P \\ F_\theta/P \end{Bmatrix} = \begin{Bmatrix} \sin(\theta_0/2) \\ \cos(\theta_0/2) \end{Bmatrix} \tag{5}$$

which, upon substitution into equations (3) and (4), leads to

$$\begin{Bmatrix} \delta r \\ \delta\theta \end{Bmatrix} = P \begin{Bmatrix} (1/k_s)\sin(\theta_0/2) \\ (2r_0/k_\theta)\cos(\theta_0/2) \end{Bmatrix}. \tag{6}$$

The combined elongation along the PE chain is thus

$$\delta l_L = \delta r \sin\left(\frac{\theta_0}{2}\right) + \delta s \cos\left(\frac{\theta_0}{2}\right), \tag{7}$$

where

$$\delta s = r_0 \left(\frac{\delta\theta}{2}\right) \tag{8}$$

as shown in figure 3. Substituting equations (6) and (8) into equation (7), we have

$$\delta l_L = P\left[\frac{1}{k_s}\sin^2\left(\frac{\theta_0}{2}\right) + \frac{r_0^2}{k_\theta}\cos^2\left(\frac{\theta_0}{2}\right)\right]. \tag{9}$$

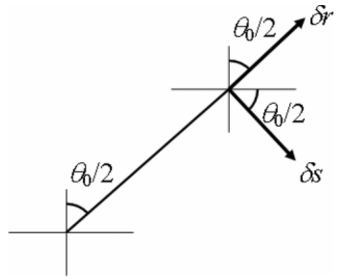

Figure 3. Diagram for the resolution of displacement.

Hence the effective longitudinal stiffness of a PE chain is

$$k_{\text{eff}}^{L} = \frac{P}{\delta l_L} = \frac{2k_s k_\theta}{(k_s r_0^2 + k_\theta) + (k_s r_0^2 - k_\theta)\cos\theta_0}. \tag{10}$$

To obtain the Poisson's ratio, we first obtain the overall widening of the PE molecule as

$$\delta l_T = \delta r \cos\left(\frac{\theta_0}{2}\right) - \delta s \sin\left(\frac{\theta_0}{2}\right). \tag{11}$$

Substituting equations (6) and (8) into equation (11) leads to

$$\delta l_T = \frac{P}{2}\sin\theta_0\left[\frac{1}{k_s} - \frac{r_0^2}{k_\theta}\right]. \tag{12}$$

Therefore, the in-plane Poisson's ratio for a taut PE molecule is simplified as

$$\nu \approx -\frac{\delta l_T}{\delta l_L} = \frac{(k_s r_0^2 - k_\theta)\sin\theta_0}{(k_s r_0^2 + k_\theta) + (k_s r_0^2 - k_\theta)\cos\theta_0}. \tag{13}$$

In solid mechanics, the inter-relationship between the Young's modulus E, the shear modulus G, and the Poisson's ratio ν is

$$G = \frac{E}{2(1+\nu)}. \tag{14}$$

Using the solid mechanics principle as an analogy, we have the shear stiffness of a taut PE molecule in terms of the longitudinal stiffness and Poisson's ratio

$$k_{\text{shear}} = \frac{k_{\text{eff}}^{L}}{2(1+\nu)} \approx \frac{k_s k_\theta}{(k_s r_0^2 + k_\theta) + (k_s r_0^2 - k_\theta)(\sin\theta_0 + \cos\theta_0)}. \tag{15}$$

3. Results and discussion

Based on some bond parameters shown in table 1 [9], the elastic properties of a taut PE chain are calculated using equations (10), (13) and (15). Results are shown in table 2. Theory predicts that the Poisson's ratio of a PE molecule is slightly above unity, thereby

Table 1
C–C and C–C–C bond parameters [9].

k_s (kJ · nm^{-2} · mol^{-1})	k_θ (kJ · rad^{-2} · mol^{-1})	r_0 (nm)	θ_0 (rad)
251950	605.0	0.153	1.9373

Table 2
Elastic properties prediction of PE single-molecule.

k_{eff}^L (kJ · mol^{-1})	k_{shear} (kJ · mol^{-1})	ν
66185	15965	1.0728

implying a unique property at molecular-level as compared to bulk materials whereby the Poisson's ratio of a bulk isotropic material has been shown to be between -1 and $1/2$ [10], although Poisson's ratio is usually between $1/4$ and $1/3$ for most materials [11]. The present result is, nonetheless, not surprising as it has been recently shown that certain bulk cellular polymers can have Poisson's ratio exceeding unity [12–14].

4. Conclusions and summary

The elastic properties of a taut PE single-molecule has been modeled in terms of bond parameters such as the equilibrium bond length, equilibrium bond angle, bond stretching stiffness and bond bending stiffness. Using the analogy from solid mechanics, the shear stiffness of the taut PE chain is conveniently obtained from the longitudinal stiffness and the Poisson's ratio. Theoretical result for the Poisson's ratio reveals unique properties at the nano-scale level. In view of some frequently occurring terms, the elastic stiffness of a PE single-molecule can be summarized, for convenience, as

$$k_{\text{eff}}^L = \frac{2K_A}{K_B + K_C \cos\theta_0}, \tag{16}$$

$$k_{\text{shear}} \approx \frac{K_A}{K_B + K_C(\sin\theta_0 + \cos\theta_0)}, \tag{17}$$

$$\nu \approx \frac{K_C \sin\theta_0}{K_B + K_C \cos\theta_0}, \tag{18}$$

where

$$\begin{Bmatrix} K_A \\ K_B \\ K_C \end{Bmatrix} = k_s \begin{Bmatrix} k_\theta \\ r_0^2 \\ r_0^2 \end{Bmatrix} + \begin{Bmatrix} 0 \\ k_\theta \\ -k_\theta \end{Bmatrix}. \tag{19}$$

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