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Size-dependent elastic properties of crystalline polymers via a molecular mechanics model

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An analytical molecular mechanics model is developed to obtain the size-dependent elastic properties of crystalline polyethylene. An effective “stick-spiral” model is adopted in the polymer chain. Explicit equations are derived from the Lennard-Jones potential function for the van der Waals force between any two polymer chains. By using the derived formulas, the nine size-dependent elastic constants are investigated systematically. The present analytical results are in reasonable agreement with those from present united-atom molecular dynamics simulations. The established analytical model provides an efficient route for mechanical characterization of crystalline polymers and related materials toward nanoelectromechanical applications.

Crystalline polyethylene (PE) is increasingly used in modern industry as structural materials due to its important mechanical and physical properties. Despite its importance and the studies of available molecular dynamics (MD) simulations and constitutive models,1–3 the link between molecular and continuum descriptions of its mechanical properties is still not well established. In order to overcome limitations of atomistic simulations and continuum models, a “stick-spiral” model4 based on interatomic potentials has been calculated7–9 based on the Lennard-Jones (LJ) pair potential function. The size-dependent elastic properties of crystalline PE. In this letter, we use the “stick-spiral” model to simulate united-atom (UA) CH2-CH2 bonds stretching, angle bending potentials along the polymer chain (or z direction), while the vdW force between any two polymer chains can be directly calculated2–9 based on the Lennard-Jones (LJ) pair potential functions.

In the framework of molecular dynamics, the total energy, \( U \), of a crystalline PE at small strains along z direction can be expressed as a sum of energies associated with the variance of bond length, \( U_b \), and bond angle, \( U_\theta \), i.e.,

\[
U = U_b + U_\theta = \frac{1}{2} \sum_i K_{ib}(db_i)^2 + \frac{1}{2} \sum_j K_{ib}(d\theta_j)^2,
\]

where \( db_i \) is the bond elongation of bond \( i \) and \( d\theta_j \) is the variance of bond angle \( j \), and \( K_{ib} \) and \( K_{ib} \) are the related force constant.

To obtain the equilibrium equations of the structure along z direction under tension, we adopt the “stick-spiral” model developed by Chang and Gao.4 As shown in Fig. 2, force equilibrium of bond extension and moment equilibrium lead to

\[
\begin{align*}
\{ f \sin \left( \frac{z}{2} \right) &= K_{ib}db \\
f \cos \left( \frac{z}{2} \right) b &= K_{ib}dz,
\end{align*}
\] (2)

where \( f \) is the external force in z direction on one polymer chain.

We define the z direction strain as

\[
\varepsilon_z = \frac{d(2b \sin \frac{z}{2})}{2b \sin \frac{z}{2}} = \frac{1}{b} \left( \frac{b \cos^2 \frac{z}{2} K_{bb}}{4K_{bb} \sin^2 \frac{z}{2}} \right).
\] (3)

Assuming the structural parameters of every cell remain constant with different-sized structures in Fig. 1, we can obtain the size-dependent elastic properties of crystalline PE. From Eqs. (2) and (3), the elastic property of \( C_{33} \) can be written as

\[
C_{33} = \frac{\sigma_z}{\varepsilon_z} = \frac{m a_0 b_0 \varepsilon_z}{\sum_{m} (1 + \frac{1}{m}) (1 + \frac{1}{n}) 4K_{bb} b \sin^2 \frac{z}{2}} = \frac{a_0 b_0 (4K_{bb} \sin^2 \frac{z}{2} + K_{bb} b^2 \cos^2 \frac{z}{2})}{\sum_{m} (1 + \frac{1}{m}) (1 + \frac{1}{n})},
\] (4)

where \( a_0 \) and \( b_0 \) denote the cell length and \( m \) and \( n \) are the number of cells along the x- and y-direction, respectively.

We find that the result of \( C_{33} \) in one cell wire \( (m = 1, n = 1 \) and periodic boundary in z direction) is about 2.5 times

\[ \text{APPLIED PHYSICS LETTERS 99, 241902 (2011)}\]
higher than that of in bulk PE \((m \to \infty, n \to \infty)\), while \(C_{33}\) is independent of the thickness in \(z\) direction. The constants \(\alpha = 109.5^\circ\), \(K_0 = 700\) Kcal/mol Å\(^2\) and \(K_\beta = 120\) Kcal/mol\(^{11,12}\) are adopted here and in the latter UA MD simulations.

To model vdW interactions between any two chains of crystalline PE, the LJ pair potential \(U_{LJ}\) is adopted as \(^{22}\)
\[U_{LJ} = 4 \epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \]
where \(r\) is the distance between the interacting atoms, \(\epsilon\) is the depth of the potential, and \(\sigma\) a parameter that is determined by the equilibrium distance. Here, we use the available LJ potential’s parameters of \(\sigma = 4.01\) Å and \(\epsilon = 0.112\) Kcal/mol.\(^{11,12}\)

The vdW force \(F_{vdW}\) can be obtained from taking the derivative of the LJ pair potential \(F_{vdW}(r) = -\frac{dU_{LJ}}{dr} = 24 \epsilon \left( \frac{\sigma}{r} \right)^{13} - \left( \frac{\sigma}{r} \right)^7 \). It should be noted that the negative value of the vdW force represents the attractive force of an approaching pair of atoms from a certain distance whereas the positive value represents the repulsive force between a pair of atoms.

The vdW force exerted on any bead (CH\(_2\)) of a polymer chain can be estimated by summing all forces between the bead and all beads on the other chains. To simplify the calculations, we consider the chain as a straight continuum stick\(^6\) and note that each bead corresponds to the length of \(l/2 = b \sin(a/2) = c_0/2\) (\(c_0\) is the cell length along \(z\)-direction) in Fig. 1(b). Thus, the integration of \(F_{vdW}\) over the entire chain leads to an analytical representation for the initial force contribution \(f_{ij}\) caused by the vdW interaction

\[f_{ij}(Lr_0) = 2Lp_{ij} = \frac{2L}{(c_0/2)^2} \left[ \frac{24 \epsilon}{r_0^6} \arctan(L/r_0) \cos^2 \theta_0 d\theta d\zeta \right] - \frac{24 \epsilon}{r_0^6} \arctan(-L/r_0) \cos^2 \theta d\theta d\zeta \],

where \(\cos \theta = r_0/r, \ z = r \sin \theta, \ L\) is the length along \(z\) direction, \(r_0\) is the initial displacement between two polymer chains, and \(p_{ij}\) is the force per unit length of a chain. Because the distributions of the vdW force \(F_{vdW}\) and its gradient \(dF_{vdW}/dr\) between two polymer beads are both close to zero when \(r_0 > 8.5\) Å, we only consider the vdW interaction with the initial displacement \(r_0 < 8.5\) Å.

In view of the crystalline PE in the PNAM space group, the nine independent elastic constants \(C_{11}, \ C_{12} = C_{21}, \ C_{13} = C_{31}, \ C_{22}, \ C_{23} = C_{32}, \ C_{33}, \ C_{44}, \ C_{55}, \) and \(C_{66}\) should be in the elastic matrix.\(^4\) The four kinds of positions change between two polymer chains are plotted in Fig. 3 under the six direction strains, respectively.

When the strain in the x-direction is \(\epsilon_x\) (see Fig. 3(a)), the \(C_{11}\) and \(C_{12}\) can be expressed as

\[
\begin{align*}
C_{11} &= \frac{\sigma_{xy}}{\epsilon_x} = \frac{4f_{ij}(Lr_0)\cos \theta - f_{ij}(L, r_0)\sin \theta + 2f_{ij}(Lr_0) - f_{ij}(L, r_0)}{2Lr_0} \\
C_{21} &= \frac{\sigma_{yz}}{\epsilon_x} = \frac{4f_{ij}(L, r_0)\sin \theta - f_{ij}(Lr_0)\cos \theta + 2f_{ij}(L, r_0) - f_{ij}(Lr_0)}{2Lr_0} 
\end{align*}
\]

where \(r_0 = \sqrt{b_1^2 + b_2^2}, r_{11} = \sqrt{(1+\epsilon_x)^2b_1^2 + b_2^2}, r_{a0} = a_0, r_{a1} = (1+\epsilon_x)a_0, \cos \theta_1 = \frac{a_0}{\sqrt{a_0^2 + b_0^2}}, \ \cos \theta_0 = \frac{(1+\epsilon_x)a_0}{\sqrt{(1+\epsilon_x)^2a_0^2 + b_0^2}}, \ \theta_1\) is the angle in Fig. 1(a).

When the strain in the y-direction is \(\epsilon_y\) or in the xy-direction is \(\epsilon_{xy}\), the \(C_{22}, \ C_{12}, \) and \(C_{66}\) can be easily obtained in the elastic matrix in view of the similar position change between two chains in Fig. 3(a). The average value of \(C_{21}\) and \(C_{12}\) are shown in Table I (see \(C_{12}\)). For the strain in the \(z\)-direction \(\epsilon_z\) in Fig. 3(b), the \(C_{13} = \sigma_{xy}/\epsilon_z\) and \(C_{23} = \sigma_{yz}/\epsilon_z\) are easily obtained from Eq. (1).

When the strain in the \(zx\)-direction is \(\epsilon_{zx}\) (see Figs. 3(c) and 3(d)), the \(C_{44}\) can be expressed as

FIG. 1. (Color online) Geometry of a single crystalline PE and corresponding coordinates. (a) Each polymer chain’s position view in xoy plane, (b) three-dimensional structure.
TABLE I. Nine elastic constants (GPa) of present analytical model, united-atom molecular dynamics results, and Karasawa et al. all-atom molecular dynamics calculations for bulk PE.

<table>
<thead>
<tr>
<th>Elastc constants</th>
<th>C11</th>
<th>C12</th>
<th>C22</th>
<th>C33</th>
<th>C32</th>
<th>C23</th>
<th>C13</th>
<th>C44</th>
<th>C55</th>
<th>C66</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anal. pure LJ</td>
<td>14.52</td>
<td>6.89</td>
<td>2.92</td>
<td>/</td>
<td>0.72</td>
<td>1.28</td>
<td>0.02</td>
<td>0.03</td>
<td>7.53</td>
<td></td>
</tr>
<tr>
<td>Anal. All potential</td>
<td>14.50</td>
<td>6.97</td>
<td>2.83</td>
<td>195.08</td>
<td>0.70</td>
<td>1.27</td>
<td>0.03</td>
<td>0.04</td>
<td>7.57</td>
<td></td>
</tr>
<tr>
<td>MD pure LJ</td>
<td>15.3 ± 0.3</td>
<td>7.1 ± 0.4</td>
<td>4.9 ± 1.4</td>
<td>0.9 ± 0.4</td>
<td>0.3 ± 0.2</td>
<td>0.5 ± 0.3</td>
<td>0.6 ± 0.2</td>
<td>1.1 ± 0.2</td>
<td>6.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>MD all potential</td>
<td>15.6 ± 0.5</td>
<td>7.0 ± 0.4</td>
<td>5.1 ± 1.2</td>
<td>200 ± 0.6</td>
<td>1.61 ± 1.0</td>
<td>3.03 ± 2.0</td>
<td>5.58 ± 0.3</td>
<td>5.97 ± 0.3</td>
<td>6.48 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>Karasawa MC (Ref. 1)</td>
<td>13.9</td>
<td>7.9</td>
<td>13.5</td>
<td>237.9</td>
<td>4.8</td>
<td>2.3</td>
<td>5.4</td>
<td>3.0</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

where $l = c_0$, $l' = l\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}$, $r_{e} = \frac{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}}{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}}r_e$, $r_{a} = \frac{1}{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}}r_a$, $\cos(\Delta \theta) = \frac{1}{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}}F_{\text{stick}}$, and $\eta = \frac{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}} \cos \theta_1 - \frac{\sin^2 \theta_1}{4l^2} \sin \theta_1}{\sqrt{1 + \frac{\sin^2 \theta_1}{4l^2}}}$.

We find that the most elastic constants using the present UA MD simulations of all potentials (include all bond, angle, and LJ potentials) are very different with those of Karasawa et al. all-atom MD calculations (Ref. 1) in Table I. The possible reason is that the present analytical model is based on the UA potentials, in which the torsion potential, out-of-plane bending potentials, and coulomb interactions are neglected. Therefore, we should compare present analytical model with UA MD simulations. Compared with the two

![Figure 3](https://example.com/figure3.png)

FIG. 3. (Color online) Schematic illustration of the position change between two “sticks” in one PE cell after deformation. (a) Under x or y tension or xz shear, (b) under z tension, (c) any two corner sticks under xz or zy shear, (d) between corner and center sticks under xz or yz shear.
UA MD results using all potentials and the pure LJ potential in Table I, we find that the difference of the values of $C_{23}$, $C_{33}$, $C_{13}$, $C_{44}$, and $C_{55}$ are large. It indicates that the bond and angle potentials have a large effect on these elastic constants. The present analytical result $C_{33} = 195$ GPa is in excellent agreement with the value of $C_{33} = 200 \pm 0.6$ GPa using all potentials’ UA MD simulations. The analytical values of $C_{11}$, $C_{12}$, $C_{23}$, $C_{13}$, and $C_{66}$ are also in good agreement with those of this UA MD method, while the difference of $C_{44}$ and $C_{55}$ are very large. It indicates that the present analytical model is effective to predict the most elastic constants, while it has some limitations to predict $C_{44}$ and $C_{55}$. One possible reason is that the shear and torsion properties of the “stick” in the present analytical model are neglected; another reason is that the present simplified straight stick has a little effect on the predictions of the elastic constants.

To understand the size-dependent elastic properties of PE, the effect of the polymer thickness along the $z$-direction on the elastic constants is further studied in Fig. 4, in which the periodic boundary is only adopted along the $x$- and $y$-directions. The elastic constants of $C_{11}$, $C_{12}$, $C_{22}$, and $C_{66}$ increase with decreasing thickness, while $C_{13}$ and $C_{23}$ decrease with decreasing it. The values of $C_{44}$ and $C_{55}$ are both independent of it. The results mean that the change tendency of the size-dependent elastic constants is not in accordance with one another, which strongly depends on the lattice direction. When $L/c_0 > 10$, all of the elastic constants are close to the corresponding constants in Fig. 4, respectively.

In summary, on the basis of the molecular mechanics approach, we present an analytical model to obtain the size-dependent elastic properties of crystalline PE. We obtain a set of closed-form expressions for nine size-dependent elastic constants of crystalline PE. Compared with the present united-atom molecular dynamics calculations, we find that the present analytical model can be used to effectively simulate the van der Waals interactions between any two polymer chains. This work is a new effort to establish analytical models of molecular mechanics for crystalline polymers, and is helpful for further analytical studies of elastic properties of other crystalline polymers.

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\[C_{33} = 195 \text{ GPa}\]

Reference:

FIG. 4. (Color online) Eight size-dependent elastic constants with different thickness along $z$ direction using the present analytical model.