Interactions in Random Copolymers

Toma Marinov and

Jutta Luettmer-Strathmann

Department of Physics
The University of Akron
Akron, OH 44325-4001

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ABSTRACT

The description of thermodynamic properties of copolymers in terms of simple lattice models requires a value for the effective interaction strength between chain segments, in addition to parameters that can be derived from the properties of the corresponding homopolymers. If the monomers are chemically similar, Berthelot’s geometric-mean combining rule provides a good first approximation for interactions between unlike segments. In earlier work on blends of polyolefins [1], we found that the small-scale architecture of the chains leads to corrections to the geometric-mean approximation that are important for the prediction of phase diagrams. In this work we focus on the additional effect due to sequencing of monomeric units. In order to estimate the effective interaction for random copolymers, the small-scale simulation approach developed in [1] is extended to allow
for random sequencing of the monomeric units. The approach is applied here to random copolymers of ethylene and 1-butene.


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RANDOM COPOLYMERS

Simple cubic lattice

Straight section of the molecule with 3 repeat units (A, B), total of 8 different composites

Unit in the middle (fixed to the origin and aligned to the z-axis) is section of interest, the attached units represent the rest of the molecule

Total number \( n_t \) of nonbonded nearest neighbors of segment of interest

Maximum number \( c_m \) of possible contacts: \( c_m = 4s_f \), where \( s_f \) is the number of lattice sites occupied by the fixed section of interest
COMBINED CONFIGURATIONS

2 molecules: fixed and mobile

Fixed: as described above

Mobile: rotated and translated, so that its section of interest makes contact with the segment of interest of the fixed one

Count:
\( o_k \) – the number of nearest neighbor (nn) sites of the fixed molecule, occupied by the mobile molecule
\( c_k \) – the number of contacts between the two chains

Repeat the procedure until exhausting all possible combined configurations
Repeat the procedure with different combination of composites until exhausting all possible combinations

Result:
For each of the 64 combinations $ij$ of composites statistics about the number of combined configurations for a given pair of $(o_k, c_k)$

The remaining $n_t-o_k$ sites are filled randomly to a density $\xi$, where

$$\xi = \frac{2\phi}{3-\phi}$$

is the contact density for an infinitely long chain with a total filling fraction of $\phi$

The energy $E_k$ for a set of combined configuration $(o_k, c_k)$ is:

$$E_k^{(ij)}(x) = e_{ij}c_k + (\xi_i e_{ii}/(\xi_1 + \xi_2) + \xi_j e_{jj}/(\xi_1 + \xi_2)) \times (n_t^{(i)}\xi - o_k)(c_m^{(i)} - c_k)/(n_t^{(i)} - o_k)$$
The probability $P_k$ of a given energy is:

$$P_k(i,j) = (P_i(x)P_j(x)(m_k/m_{[ii]})\exp(-\beta E_k(x)))/Q,$$

where $Q$ is the total partition function, $x$ is the fraction of $A$ segments in the chain, $m_k$ is frequency of occurrence of $(o_k, c_k)$ and $m_{[ii]}$ is a multiplicity

The average energy $E$ is

$$E = \sum_k \sum_i \sum_j P(k,i,j) E_k(i,j)$$

The interaction energy per contact as a function of concentration is:

$$\varepsilon(x) = E/(\xi c_m)$$
For random copolymers: **ABAABBBBAA**

<table>
<thead>
<tr>
<th>Composite</th>
<th>$P_i(x)$</th>
<th>$m_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAA</td>
<td>$X^3$</td>
<td>1</td>
</tr>
<tr>
<td>AAB</td>
<td>$X^2(1-X)$</td>
<td>4</td>
</tr>
<tr>
<td>BAA</td>
<td>$X^2(1-X)$</td>
<td>4</td>
</tr>
<tr>
<td>ABA</td>
<td>$X^2(1-X)$</td>
<td>4</td>
</tr>
<tr>
<td>BAB</td>
<td>$X(1-X)^2$</td>
<td>16</td>
</tr>
<tr>
<td>ABB</td>
<td>$X(1-X)^2$</td>
<td>16</td>
</tr>
<tr>
<td>BBA</td>
<td>$X(1-X)^2$</td>
<td>16</td>
</tr>
<tr>
<td>BBB</td>
<td>$(1-X)^3$</td>
<td>64</td>
</tr>
</tbody>
</table>

For alternating copolymers

<table>
<thead>
<tr>
<th>Alternating</th>
<th>AAA</th>
<th>AAB</th>
<th>BAA</th>
<th>ABA</th>
<th>BAB</th>
<th>ABB</th>
<th>BBA</th>
<th>BBB</th>
<th>X</th>
</tr>
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<td>ABAB</td>
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<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
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<td>AAABAAAB</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>0</td>
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<td>0.33</td>
<td>0.33</td>
<td>0</td>
<td>0.33</td>
</tr>
<tr>
<td>AABAAB</td>
<td>0</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>AABBAABB</td>
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<td>0.25</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>0.25</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>BABBBBABB</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>
EXAMPLE FOR COMBINING CONFIGURATIONS
Experimental and calculated density for PEB

DENSITY (kg/m³) vs. T(K)

0.1 MPa expt
0.1 MPa calc
10 MPa expt
10 MPa calc
20 MPa expt
20 MPa calc
30 MPa expt
30 MPa calc
Experimental and calculated density for PE
Calculated values of $\varepsilon(X)$ for random copolymers

![Graph showing calculated values and reference values for $\varepsilon(X)$ vs. $X_A$.]
\( \varepsilon \) for alternating copolymers

\[ \begin{align*}
\varepsilon & \approx -1925 \\
\varepsilon & \approx -1945 \\
\varepsilon & \approx -1965 \\
\varepsilon & \approx -1985 \\
\varepsilon & \approx -2005
\end{align*} \]

Concentration \( x \)
Discussion

- Consider random and alternating copolymers of four-carbon segments of PEB (an alternating copolymer of polyethylene and hydrogenated polybutadiene) and polyethylene

- Calculate effective interaction parameters from exact enumerations of all possible combined configurations

- A comparison with reference values based on a random mixing approximation shows that the length of the repeat unit affects the interaction energy.

- A comparison between alternating and random copolymers shows a small effect of sequencing that may, however, be important for blends.