Monte Carlo simulations to investigate dynamics of concentrated polymer solutions

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Processes on different length scales affect dynamic properties of polymer solutions. The dynamics of chains in concentrated solutions are strongly affected by the local environments of their chain segments. While it is well known that the local density plays an important role (the lower the density of its surroundings, the higher the mobility of a chain segment) it is still difficult to quantify the effect. Furthermore, fluctuations in the local density and concentration lead to a distribution of segmental mobilities whose effect on the overall mobility of the chains is not well understood. In this work, we investigate dynamics of concentrated solutions with Monte Carlo simulations of a generalized bond-fluctuation model. Sites on a simple cubic lattice connected by bonds that can assume three different bond lengths represent the polymer chains. The solvent molecules occupy single sites on the lattice while voids are included to account for the effects of compressibility. The simulations employ local, non bond-crossing moves only and account for attractive interactions between occupied nearest neighbor sites. We present results for static and dynamic properties of concentrated solutions and melts.
Generalized bond-fluctuation model (Shaffer 1994)

- The polymer chain lies on a simple cubic lattice with each polymer segment occupying a single lattice site.

- The model imposes certain constraints on the occupancy of the polymer chain on the lattice:
  - Excluded volume condition (double occupancy of a site forbidden).
  - Bond vectors that are from the 26 (6+12+8) allowed set of values, in other words bond lengths of either 1, \( \sqrt{2} \) or \( \sqrt{3} \).
  - Bond crossings forbidden by not allowing the bond mid-points to overlap.

- The solvent molecule occupies a single lattice site and obeys excluded volume condition.
Simple cubic lattice populated with a polymer chain and solvent molecules according to generalized bond-fluctuation model.
Allowed bond vectors of the generalized bond-fluctuation model

Illegal bond crossing condition

<table>
<thead>
<tr>
<th>bond color</th>
<th>bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>red</td>
<td>1</td>
</tr>
<tr>
<td>blue</td>
<td>$\sqrt{2}$</td>
</tr>
<tr>
<td>magenta</td>
<td>$\sqrt{3}$</td>
</tr>
</tbody>
</table>

- bead
- neighbor sites

- segment of polymer chain A
- segment of polymer chain B
- solvent molecule
- polymer bonds
- bond crossing
Interaction energy

The interaction energies between neighboring elements of the lattice are called by $\epsilon_{pp}$, $\epsilon_{ps}$ and $\epsilon_{ss}$. An example of each of these interactions is illustrated in the figure.

- $\epsilon_{pp}$ represents the interaction energy between non-bonded neighboring polymer segments.
- $\epsilon_{ps}$ represents the interaction energy between polymer segment and solvent molecule.
- $\epsilon_{ss}$ represents the interaction energy between solvent molecules.

The diagram illustrates different elements that interact.
AVS image of the lattice model with size 20 x 20 x 20 (L^3)

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymer chain length (N)</td>
<td>20</td>
</tr>
<tr>
<td>lattice filling fraction ((\phi))</td>
<td>70%</td>
</tr>
<tr>
<td>polymer filling fraction ((\phi_p))</td>
<td>60%</td>
</tr>
<tr>
<td>solvent filling fraction ((\phi_s))</td>
<td>10%</td>
</tr>
<tr>
<td>solvent molecule</td>
<td></td>
</tr>
<tr>
<td>polymer segment</td>
<td></td>
</tr>
</tbody>
</table>
Observed static properties

- Three length scales of polymers that are considered (squared values)
  - end-to-end vector $\mathbf{r}$ is the vector connecting the first and the last bead. end-to-end distance $r^2$ is the squared end-to-end vector.
  - bond length $b_i^2$ is the square of the average bond length (distance between two successive beads) of all the bonds of the chains
  - radius of gyration $R_g^2$ is the sum of the square of the distance between all pairs of atoms. Also defined as the average sum of the distance square of each bead from the center of mass. Center of mass is the average of the position vectors of all beads.

- Acceptance rates of the moves are calculated for both the polymer segments and solvent molecules.
**Results:** Common parameters $L = 20, \beta = 0.0, N = 20, \phi = 0.7$

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Polymer filling fraction ($\phi_p$)</th>
<th>Solvent filling fraction ($\phi_s$)</th>
<th>MC steps for equilibration</th>
<th>MC steps for production</th>
<th>Polymer acceptance rate</th>
<th>Solvent acceptance rate</th>
<th>(End-to-end distance)$^2$ $R_1^2$</th>
<th>(Radius of gyration)$^2$ $R_g^2$</th>
<th>(Bond length)$^2$ $b_l^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.70</td>
<td>0.00</td>
<td>$1 \times 10^6$</td>
<td>$2 \times 10^5$</td>
<td>11.496</td>
<td>0.000</td>
<td>44.758</td>
<td>0.356</td>
<td>0.0560</td>
</tr>
<tr>
<td>20</td>
<td>0.65</td>
<td>0.05</td>
<td>$1 \times 10^6$</td>
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<td>31.206</td>
<td>44.686</td>
<td>0.4300</td>
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<tr>
<td>20</td>
<td>0.60</td>
<td>0.10</td>
<td>$1 \times 10^6$</td>
<td>$2 \times 10^5$</td>
<td>11.413</td>
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<td>45.196</td>
<td>0.5170</td>
<td>0.0680</td>
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<tr>
<td>20</td>
<td>0.55</td>
<td>0.15</td>
<td>$1 \times 10^6$</td>
<td>$2 \times 10^5$</td>
<td>11.423</td>
<td>30.520</td>
<td>45.643</td>
<td>0.4680</td>
<td>0.0546</td>
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<tr>
<td>20</td>
<td>0.50</td>
<td>0.20</td>
<td>$1 \times 10^6$</td>
<td>$2 \times 10^5$</td>
<td>11.290</td>
<td>31.100</td>
<td>46.194</td>
<td>0.5910</td>
<td>0.072</td>
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</table>
Second set of Results for the same parameters as above to check for sufficient equilibration times – chain dimensions remain same within the error limits

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Polymer filling fraction ($\phi_p$)</th>
<th>Solvent filling fraction ($\phi_s$)</th>
<th>M C steps for equilibration</th>
<th>M C steps for production</th>
<th>Polymer acceptance rate</th>
<th>Solvent acceptance rate</th>
<th>(End-to-end distance)$^2$ $R_1^2$</th>
<th>(Radius of gyration)$^2$ $R_g^2$</th>
<th>(Bond length)$^2$ $bl^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.70</td>
<td>0.00</td>
<td>$1.5 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>11.50</td>
<td>0.000</td>
<td>44.4726 ± 0.3562</td>
<td>7.6659 ± 0.0465</td>
<td>2.0389 ± 0.0005</td>
</tr>
<tr>
<td>20</td>
<td>0.65</td>
<td>0.05</td>
<td>$1.5 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>11.470</td>
<td>30.790</td>
<td>44.9804 ± 0.5176</td>
<td>7.7359 ± 0.0633</td>
<td>2.0425 ± 0.0005</td>
</tr>
<tr>
<td>20</td>
<td>0.60</td>
<td>0.10</td>
<td>$1.5 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>11.43</td>
<td>30.82</td>
<td>45.2432 ± 0.4313</td>
<td>7.7809 ± 0.0543</td>
<td>2.0461 ± 0.0005</td>
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<td>0.55</td>
<td>0.15</td>
<td>$1.5 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>11.39</td>
<td>30.84</td>
<td>45.7083 ± 0.3398</td>
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<td>2.0498 ± 0.0005</td>
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<td>20</td>
<td>0.50</td>
<td>0.20</td>
<td>$1.5 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>11.33</td>
<td>30.85</td>
<td>46.2079 ± 0.4073</td>
<td>7.9203 ± 0.0488</td>
<td>2.0535 ± 0.0006</td>
</tr>
</tbody>
</table>
## Results: Common parameters $L = 20$, $\beta = 0.0$, $N = 20$ $N_{sv} = 0$

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Polymer filling fraction ($\phi_p$)</th>
<th>Solvent filling fraction ($\phi_s$)</th>
<th>$M$ C steps for equilibration</th>
<th>$M$ C steps for production</th>
<th>Polymer acceptance rate</th>
<th>Solvent acceptance rate</th>
<th>$(\text{End-to-end distance})^2$</th>
<th>$(\text{Radius of gyration})^2$</th>
<th>$(\text{Bond length})^2$</th>
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<tbody>
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<td>20</td>
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<td>$\pm 0.2543$</td>
<td>$\pm 0.0303$</td>
<td>$\pm 0.0003$</td>
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<td>$\pm 0.0023$</td>
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<tr>
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<td>45.9834</td>
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<td></td>
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<td></td>
<td>$\pm 0.1313$</td>
<td>$\pm 0.0255$</td>
<td>$\pm 0.0002$</td>
</tr>
</tbody>
</table>
Radius of Gyration vs Concentration with $\beta = 0.0$ & $N = 20$

**Polymer filling fraction $\phi_p$**

- Without solvent molecules
- With solvent molecules
Bond Length vs Concentration with $\beta = 0.0$ & $N = 20$

- Without solvent molecules
- With solvent molecules
Observed dynamic properties

- $g_1(t)$ represents mean-square displacement of the center monomers of the chains as a function of time.
- $g_3(t)$ represents mean-square displacement of the center of mass of the chains as a function of time.
- $\phi_e(t)$ characterizes the rotational motion of the polymer end-to-end vector as a function of time.
- Self-diffusion coefficient $D_g$, represents diffusion constant of center of mass of the chain. It is a constant at large times for a particular density and temperature.
- $\tau_{ee}$ is the correlation time for the end-to-end vector.
Evaluation

- The microstates recorded during the Monte Carlo simulation are evaluated to determine the dynamic properties.

- $\phi_e(t)$ is the time correlation function of the end-to-end vector:
  \[
  \phi_e(t) = \frac{\langle \mathbf{r}(t) \cdot \mathbf{r}(0) \rangle}{\langle \mathbf{r}(0)^2 \rangle}
  \]

- The end-to-end vector relaxation time is obtained from (Kreer et al., 2001)
  \[
  \phi_e(\tau_{ee}) = 0.29821
  \]

- $g_d(t)$ and $g_{sv}(t)$ are the mean square displacements of the center of mass of the chains and the solvent molecules.
  \[
  g_d(t) = \langle [\mathbf{r}_{CM}(t) - \mathbf{r}_{CM}(0)]^2 \rangle \\
  g_{sv}(t) = \langle [\mathbf{r}_s(t) - \mathbf{r}_s(0)]^2 \rangle
  \]

- The self-diffusion coefficients are determined from
  \[
  D_g = \lim_{t \to \infty} \frac{g_d(t)}{6t} \\
  D_{sv} = \lim_{t \to \infty} \frac{g_{sv}(t)}{6t}
  \]
Simulation results obtained for time correlation and displacement functions.
<table>
<thead>
<tr>
<th>$\phi_s$</th>
<th>$D_g$</th>
<th>$\sigma D_g$ (error)</th>
<th>$D_s$</th>
<th>$\sigma D_s$ (error)</th>
<th>$\tau_{ee}$</th>
<th>$\sigma \tau_{ee}$ (error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>1.792e-04</td>
<td>8.33e-07</td>
<td>No solvents</td>
<td>No solvents</td>
<td>7.364e+03</td>
<td>2.571e+01</td>
</tr>
<tr>
<td>0.65</td>
<td>1.900e-04</td>
<td>1.09e-06</td>
<td>2.704e-02</td>
<td>3.03e-05</td>
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<td>4.950e+01</td>
</tr>
<tr>
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<td>2.329e-04</td>
<td>6.058-07</td>
<td>No solvents</td>
<td>No solvents</td>
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<td>6.667e+01</td>
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<tr>
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<td>2.935e-04</td>
<td>7.298e-07</td>
<td>No solvents</td>
<td>No solvents</td>
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<td>5.634e+01</td>
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<tr>
<td>0.55</td>
<td>2.169e-04</td>
<td>1.21e-06</td>
<td>2.917e-02</td>
<td>1.2e-05</td>
<td>6.332e+03</td>
<td>1.022e+02</td>
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<tr>
<td></td>
<td>3.674e-04</td>
<td>1.189e-06</td>
<td>No solvents</td>
<td>No solvents</td>
<td>3.729e+03</td>
<td>2.712e+01</td>
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<tr>
<td>0.5</td>
<td>2.354e-04</td>
<td>1.38e-06</td>
<td>3.021e-02</td>
<td>1.04e-05</td>
<td>6.100e+03</td>
<td>9.365e+01</td>
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<tr>
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<td>4.521e-04</td>
<td>8.152-07</td>
<td>No solvents</td>
<td>No solvents</td>
<td>3.411e+03</td>
<td>4.328e+01</td>
</tr>
</tbody>
</table>
Self-Diffusion Coefficients of Polymer Chains $\beta = 0.0 \& N = 20$

![Graph showing self-diffusion coefficients for polymer chains with and without solvent molecules.](image-url)
End-to-End Vector Relaxation Times with $\beta = 0.0$ & $N = 20$

Without solvent molecules

With solvent molecules
Self-Diffusion Coefficients of Solvent Particles $\beta = 0.0 & N = 20$

![Graph showing the relationship between polymer filling fraction $\phi_p$ and self-diffusion coefficient $D_s$]
Reduced self-diffusion coefficient with $\beta = 0.0$ & $N = 20$

- **Without solvent molecules**
- **With solvent molecules**
Effect of Polymer and Solvent Concentrations

- Chain dimensions - radius of gyration and bond length decrease with increasing polymer concentration.
- The self-diffusion coefficient of both the polymer chains and solvent molecules (in the case of solutions) decreases with increasing polymer concentration.
- The relaxation time increases with increasing polymer concentration.
- The chain dimensions depend on the polymer concentration only, they are unaffected by the presence of explicit solvent molecules.
- The segmental mobility of the polymers, measured by the acceptance rate for polymer moves, is almost independent of polymer concentration for fixed total filling fraction.
- The self-diffusion coefficients of the polymer chains at a given polymer concentration are greatly reduced when explicit solvent molecules are present.
- Results of diffusion coefficients divided by polymer acceptance rates show that the difference in the dynamics between systems with explicit and implicit solvents is mostly due to the difference in segmental mobility.
### Results: Common Parameters $L = 20, N_{sv} = 0$

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Polymer filling fraction ($\phi_p$)</th>
<th>Beta ($\beta$)</th>
<th>MC steps for equilibration</th>
<th>MC steps for production</th>
<th>Polymer acceptance rate</th>
<th>Relaxation time ($\tau_{ee}$)</th>
<th>Self-diffusion coefficient ($D_g$)</th>
<th>(Radius of gyration)$^2$ $R_g^2$</th>
<th>(Bond length)$^2$ $b^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.70</td>
<td>0.1</td>
<td>$5 \times 10^6$</td>
<td>$3 \times 10^6$</td>
<td>10.40</td>
<td>8.7e+03 $\pm$ 3.0e+02</td>
<td>1.54e-4 $\pm$ 3.42-7</td>
<td>7.7253 $\pm$ 0.039</td>
<td>2.0593 $\pm$ 0.0003</td>
</tr>
<tr>
<td>20</td>
<td>0.70</td>
<td>0.2</td>
<td>$5 \times 10^6$</td>
<td>$3 \times 10^6$</td>
<td>9.33</td>
<td>1.0e+04 $\pm$ 3.0e+02</td>
<td>1.32e-4 $\pm$ 4.87e-7</td>
<td>7.768 $\pm$ 0.0395</td>
<td>2.0787 $\pm$ 0.0003</td>
</tr>
<tr>
<td>20</td>
<td>0.70</td>
<td>0.3</td>
<td>$4 \times 10^6$</td>
<td>$5 \times 10^6$</td>
<td>8.29</td>
<td>1.3e+04 $\pm$ 5.0e+02</td>
<td>1.11e-4 $\pm$ 3.2e-7</td>
<td>7.8071 $\pm$ 0.0441</td>
<td>2.0973 $\pm$ 0.0004</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td>0.1</td>
<td>$2 \times 10^6$</td>
<td>$5 \times 10^6$</td>
<td>16.87</td>
<td>4.5e+03 $\pm$ 5.0e+02</td>
<td>3.99e-4 $\pm$ 5.09e-7</td>
<td>7.8839 $\pm$ 0.0244</td>
<td>2.0687 $\pm$ 0.0002</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td>0.2</td>
<td>$2 \times 10^6$</td>
<td>$5 \times 10^6$</td>
<td>14.88</td>
<td>5.0e+03 $\pm$ 5.0e+02</td>
<td>3.41e-4 $\pm$ 5.09e-7</td>
<td>7.8556 $\pm$ 0.0245</td>
<td>2.0834 $\pm$ 0.0002</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td>0.3</td>
<td>$4 \times 10^6$</td>
<td>$2 \times 10^6$</td>
<td>12.84</td>
<td>5.2e+03 $\pm$ 2.0e+02</td>
<td>2.79e-4 $\pm$ 2.0e+2</td>
<td>7.8071 $\pm$ 0.051</td>
<td>2.0975 $\pm$ 0.0003</td>
</tr>
</tbody>
</table>
Self-Diffusion Coefficient vs $\beta$ for $N = 20$ & $Nsv = 0$

- For $\phi = 0.5$:
  - Red diamond line

- For $\phi = 0.7$:
  - Green square line

Y-axis: $D_g (a^2 / MCS)$
X-axis: Reduced inverse temperature $\beta$
Relaxation Times vs $\beta$ for $N = 20$ & $N sv = 0$

- Reduced inverse temperature $\beta$
- Reduced time $\tau_{ee}$ (MCS)

Datasets:
- $\phi = 0.5$
- $\phi = 0.7$
Radius of Gyration vs $\beta$ for $N = 20$ & $N_{sv} = 0$

$R_{g}^2 (a^2)$ vs Reduced inverse temperature $\beta$

- $\phi = 0.5$
- $\phi = 0.7$
Bond Length vs $\beta$ for $N = 20$ & $Nsv = 0$

Reduced inverse temperature $\beta$

$B_i^2 \left( a^2 \right)$

Reduced inverse temperature $\beta$

- $\phi = 0.5$
- $\phi = 0.7$
Polymer Melts - Relative Values of $\tau_{ee}$ and $D_g$

![Graph showing the relative values of $\tau_{ee}$ and $D_g$ as a function of reduced inverse temperature $\beta$. The graph includes lines for different volume fractions $\phi = 0.5$ and $\phi = 0.7$. The x-axis represents reduced inverse temperature $\beta$, and the y-axis represents the relative values of $\tau_{ee}$ and $D_g$.](image-url)
Effect of Temperature for Systems Without Explicit Solvents

- The bond length increases with increase in $\beta$ or decreasing temperature.
- For $\phi = 0.5$ the chain dimensions decrease with decreasing temperature. This is typical for (concentrated) solutions.
- For $\phi = 0.7$ the chain dimensions increase with decreasing temperature. This behavior has been observed for melts such as poly(ethylene) (Han et al., 1997) and poly(oxy-ethylene) (Smith et al., 1996).
- The self-diffusion coefficient decreases with decreasing temperature.
- The relaxation time increases with decreasing temperature.
- The system with the higher filling fraction has
  - Smaller chain dimensions
  - Smaller self-diffusion coefficients
  - Larger relaxation times
Outlook

• Compare local chain environments in the presence and absence of explicit solvent molecules.
• Extend explicit solvent calculations to finite temperatures and longer chains
• Employ parallel tempering methods (Hansmann et al., 1997) with parallel implementation to increase efficiency.
• Use Message Passing Interface (MPI) to implement the parallel tempering algorithm.

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References


