Molecular Dynamics Calculations on Amylose Fragments. I. Glass Transition Temperatures of Maltodecaose at 1, 5, 10, and 15.8% Hydration

Abstract: Molecular dynamics simulations (NPT ensembles, 1 atm) using the all atom force field AMB99C (F. A. Momany and J. L. Willett, Carbohydrate Research, Vol. 326, pp 194–209 and 210–226), are applied to a periodic cell containing ten maltodecaose fragments and TIP3P water molecules. Simulations were carried out at 25 K intervals over a range of temperatures above and below the expected glass transition temperature, \( T_g \), for different water concentrations. The amorphous cell was constructed through successive dynamic equilibration steps at temperatures above \( T_g \) and the temperature lowered until several points of reduced slope (Iff vs volume) were obtained. This procedure was carried out at each hydration level. Each dynamics simulation was continued until the volume remained constant without up or down drift for at least the last 100 ps. For a given temperature, most simulations required 400–600 ps to reach an equilibrium state, but longer times were necessary as the amount of water in the cell was reduced. A total of more than 30 ns of simulations were required for the complete study. The \( T_g \) for each hydrated cell was taken as that point at which a discontinuity in slope of the volume (V), potential energy (PE), or density (p) vs 1/T was observed. The average calculated \( T_g \) values were 311, 337, 386, and 477 K for hydration levels of 15.8, 10, 5, and 1%, respectively, in generally good agreement with experimental values. The \( T_g \) for anhydrous amylose is above the decomposition temperature for carbohydrates and so cannot be easily measured. However, it has also been difficult to obtain a value of \( T_g \) for anhydrous amylose using simulation methods. Other molecular parameters such as end-to-end distances, mean square distributions, and pair distributions are discussed.

Keywords: glass transition temperature; molecular dynamics; AMB99C; maltodecaose

INTRODUCTION

Most carbohydrates form amorphous structures in low-moisture conditions, or when rapidly cooled from the melt, exist as solid “glasses” or liquid-like rubbers. The amorphous state is metastable, and the transition between states is a second-order change in phase that occurs at the glass-transition temperature...
When carbohydrates are heated to temperatures above $T_g$, changes occur in specific heat and viscosity. Vitriﬁcation is described as a discontinuous change in properties such as heat capacity and thermal expansion coefﬁcient. This description suggests that a second-order thermodynamic phase transition underlies the vitriﬁcation process, but $T_g$ is determined by kinetic factors. That is, $T_g$ is accompanied by a change in the rate of molecular translation and rotational diffusion. Anhydrous carbohydrates have $T_g$ values in excess of their decomposition temperatures and so are studied experimentally as mixtures with water, where signiﬁcant decreases in $T_g$ are found for low levels of hydration. For example, adding 10% hydration to maltose reduces the $T_g$ value by 10°C, from 87 to $\sim 18^\circ$C. The glass transition temperature of hydrated starch drops to room temperature upon addition of $\sim 18\%$ water content. 2,3

Computational methods are not limited by complications associated with material decomposition (as are experimental carbohydrate measurements) and for this reason molecular dynamics studies may provide signiﬁcant information on the molecular properties of carbohydrates above and below their $T_g$ values and for very low hydration states. As will be described here, anhydrous amylose $T_g$ values are very difﬁcult to obtain by computational methods as well as by experimental means.

The prediction of the glass transition temperature is not only important for understanding the vitriﬁcation process in carbohydrates, the prediction of PVT/NPT properties of amorphous amylose can also be a strong test of the validity of a particular force ﬁeld. One obtains the glass transition temperature through dynamics simulations (NPT dynamics) by ﬁnding cell volume, potential energy, or density variation with change in the simulation temperature for a given hydration state. Other reported uses of computational methods to study $T_g$ include models of amorphous starch, 2,3 synthetic polymers, 4, 5 and monosaccharides. 6–10 Molecular dynamics NPT methodology was used here to study an ensemble of ten packed maltodecaose fragments at various levels of hydration, and for the subsequent calculation of the ensemble $T_g$ values. End-to-end distances, mean square deviations, and conformational states for the maltodecaose fragments are described. Water molecule diffusion and jump or hopping states are examined in detail elsewhere. 11

Some experimental studies of glass transition temperatures for amylose fragments of known size are found in the literature, ranging from dimers to hexamers. 12 In pure maltohexaose for example, 12 the $T_g$ value is estimated to be around 448 K, which is higher than the temperature at which thermal degradation occurs. However, in studies with water content of $\sim 13\%$ this value drops to around 310 K for maltohexaose and rises with fragment size to a range of $\sim 330$ to 370 K for hydrated amylose and amylopectin. 12, 13 The above temperatures are in a reasonable range for molecular simulation studies 14, 15 and from such calculations one may obtain other thermodynamic parameters such as the heat capacity at constant pressure, $C_p$, the change in enthalpy, $\Delta H$, from the change in potential energy calculated at different temperatures, the rms distance traveled, or the end-to-end distances, as well as other parameters associated with the water movement and hydrogen-bonding numbers. Several of the parameters listed above such as the end-to-end distances are reported here and others elsewhere. 16 Further, having an equilibrated box of ten maltodecaose fragments lends itself well to future studies of changes in molecular parameters and thermodynamic values for chemically modiﬁed or cross-linked amylose materials.

**COMPUTATIONAL METHODS**

Molecular mechanics and dynamics simulations were carried out using the software package InsightII/Discover (version 4.0, Molecular Simulations, Inc.). 17 Energy minimization and dynamics were performed using the newly developed all atom force ﬁeld, AMB99C, 14, 15 within the Discover program. A rectangular box with periodic boundaries was constructed such that ten maltodecaose fragments of amylose plus water molecules could be completely enclosed without vacuum holes within a periodic cell. Calculations using the speciﬁc image method 17 (as compared with the simple image method) allowed the application of non-bonded interaction cutoffs of 12 Å with a spline window width of 2 Å at a dielectric constant value of one. There are no charged functional groups in the molecules studied, only alcohols and ethers; thus long-range convergence methods were not required. Atomic charges on the glucose residues may be obtained from Appendix A of Ref. 14. The TIP3P water model 17 was used similarly to the author’s studies on the solution dynamics of maltose and several cyclodextrins. 15 All molecules were deﬁned with all atoms (no group potentials were used) and considered to be fully ﬂexible during energy minimization and molecular dynamics simulations.

The procedure used to construct the amorphous cell included the following steps: A decamer of maltose was constructed from $\alpha$-d-glucose units using the Polymerizer program in InsightII. Atom types and partial atomic charges were assigned to every atom using the atom types and new potentials found from the development of AMB99C (see Appendix A of Ref. 14). The initial single chain backbone dihedral angles for the DP-10 oligomer were those that would create either a double helix conformation, a V-helix, or a more random conformation with backbone dihedral
angles within $10^\circ$ to $15^\circ$ of the normal maltose minimum energy positions.\textsuperscript{1,4,15} Ten chains were generated and each chain was independently allowed to undergo dynamic simulation in vacuo for 100 ps to find an overall conformation in which every set of backbone dihedral angles was in the allowed range as described above. Side-chain hydroxymethyl groups were randomly placed on each chain as either $gg$ or $gt$, and the different side-chain placements allowed different equilibrated conformations to be created as the vacuum dynamics proceeded. Each of the ten maltodecose fragments was then moved to within van der Waals contact distances to each other with random directions of the chains. The cluster was adjusted by moving the chains to create the smallest rectangular structure possible without creating atomic overlaps.

A periodic box was next constructed around the molecular cluster and water molecules added into the void spaces within the box. This box was carried through a series of NVT and NPT dynamics,\textsuperscript{17} each of 200 ps duration to achieve an equilibrated system. The final box dimensions were a result of adding water until the 15.8% hydration level was reached, and that box gave both reasonable density and had no further void space available to add more water molecules. Time steps for integrations were 1 fs, and velocities, volumes, and pressures were collected every 2 ps. Using velocity scaling, the initial temperature was made to be at 300 K although the $T_g$ of this system (15.8% hydration) was predicted from experimental results to be near 300 K. When the box was fully equilibrated it resulted in a density $\sim 1.3$ g/cc with approximately 1.5 water molecules/glucose unit.

Preliminary examination of the volume and potential energy plotted as a function of time showed that simulations of the order of 200 ps would be required before both the volume and potential energy would remain constant with time at each temperature. For this reason, more than 1 ns of NVT dynamics simulation was carried out at 300 K prior to reaching a box considered to be near equilibration. After each 200 ps of the 1 ns simulation at 300 K, the complex was energy minimized and an attempt was made to add new water molecules to the box to increase the density. This procedure was carried out five times, and only after no new water molecules could be added for the last two attempts was the NPT simulation started. Initially, slightly less than one atmosphere (0.8 atm) was used for the pressure control during preliminary NPT simulations, moving to 1 atm for the final runs. For each hydration level, runs of 200 ps were carried out at the start of every temperature, starting from different end points of previous runs each time. That is, holding the pressure constant the temperature was increased from 300 to 425 K in 25 K increments (i.e., for 15.8% hydration), and then the direction was reversed and the temperature decreased by the same increments. As the first higher temperature runs were carried out it was observed that at constant pressure, the box volume was not at equilibrium; rather, the volume had a downward drift during the complete 200 ps run. Under these conditions, the simulations were continued, starting from the last dynamics frame of the previous run, until no further change in volume (i.e., drift) was observed for at least the last 100 ps. This criterion for completion was used at each temperature; in particular, the results of two consecutive runs were required to give the same or close average volume without up or down drift in the volume over the time of the run. After reaching equilibrium, the simulation for that temperature was considered complete. Moving down in temperature the volume of the box gets smaller and the final volume measurements for each temperature could be made. For one hydration level, the mass remained constant for every NPT simulation even though the volume changed with temperature. In this way the average density or specific volume was obtained. Simulations were carried out on Silicon Graphics workstations.

**Line Fitting**

Plots\textsuperscript{17} of equilibrated volume ($V$), potential energy ($PE$), or density ($\rho$) vs the reciprocal of the temperature ($1/T$) allows the determination of an inflection point. Using least-squares line fitting, the equation for a straight line passing through the data and the $R$ fitting factor were found. In the cases described here two least-squares fitted lines were obtained, one for data above and one for data below the $T_g$ value. Upon solving the equations, the crossing or inflection point (i.e., $T_g$) is found. All least square fits had $R^2$ fitting factors of $>0.98$. The rather subjective nature of the fitting leads to an error estimate of $\sim \pm 10^\circ$ in $T_g$ value, and an overall error estimate of $\sim \pm 15^\circ$ in $T_g$.

**Torsional Constraints and Hydration Levels**

It was observed that during several simulations, particularly at higher temperatures, the ring conformation of selected residues could flip from the chair (C\textsubscript{4}) into a twisted pseudo boat form. This transition was not predictable and occurred at different positions in the chains and fairly often at the reducing end of one of the maltodecose chains. When these transitions were observed, the run was terminated and a constraining torsional potential applied to the atoms, C5—O5—C1—O1, with a torsional potential constant of 100 kcal/mol-deg. and a dihedral angle of $\sim 65^\circ$—72°. Upon energy minimization and further dynamics the ring returned to its normal chair conformation, and the constraining potential was reduced to a very low value such that the ring freely flexed, but not so far as to flip out of the chair form. At higher temperatures ($>400$ K) and lower hydration levels ($<10\%$), about 10% of the residues could be found to require torsional ring constraints. At 600 K and in the case of the anhydrous cell, volume equilibration could not be reached without constraining all of the glucose residues, and for this reason, extensive dynamics simulations at 0% hydration and high temperatures were not carried out. Further, in the anhydrous cell, it was impossible to obtain a dynamics equilibrated structure in which there were no holes in the cellular matrix. That is, after several dynamics runs of 200 ps on the anhydrous material, it was still possible to add $\sim 1\%$ by weight water to the cell just by filling in available holes.
Table I  Periodic Cell Parameters, Volume, Density, and Potential Energy at Temperatures Between 225 and 600 K for 15.8, 10, 5, and 1% Hydration

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>15.8% Hydration</th>
<th>10.0% Hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume (Å³)</td>
<td>Potential Energy (kcal)</td>
</tr>
<tr>
<td>225</td>
<td>23446</td>
<td>-1795</td>
</tr>
<tr>
<td>250</td>
<td>23592</td>
<td>-1662</td>
</tr>
<tr>
<td>275</td>
<td>23666</td>
<td>-1463</td>
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<td>300</td>
<td>23760</td>
<td>-1203</td>
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<td>325</td>
<td>23910</td>
<td>-995</td>
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<tr>
<td>350</td>
<td>24039</td>
<td>-728</td>
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<tr>
<td>375</td>
<td>24318</td>
<td>-449</td>
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<td>400</td>
<td>24711</td>
<td>-168</td>
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<td>425</td>
<td>24832</td>
<td>66</td>
</tr>
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<td>450</td>
<td></td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>5% Hydration</th>
<th>1.0% Hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume (Å³)</td>
<td>Potential Energy (kcal)</td>
</tr>
<tr>
<td>225</td>
<td>21093</td>
<td>-447</td>
</tr>
<tr>
<td>250</td>
<td>21106</td>
<td>-104</td>
</tr>
<tr>
<td>275</td>
<td>21130</td>
<td>265</td>
</tr>
<tr>
<td>300</td>
<td>21188</td>
<td>453</td>
</tr>
<tr>
<td>325</td>
<td>21282</td>
<td>671</td>
</tr>
<tr>
<td>350</td>
<td>21499</td>
<td>867</td>
</tr>
<tr>
<td>375</td>
<td>21729</td>
<td>1071</td>
</tr>
</tbody>
</table>

Different hydration levels were obtained by randomly removing water from the original box with 15.8% by weight hydration. Due to the small number of water molecules per residue of glucose, we consider that all the water molecules are in the "bound" state. That is they are all near one or more sugar residues. The number of water molecules randomly removed was just that necessary to achieve the desired hydration levels of 10, 5, and 1%. As mentioned above, the attempts at 0% hydration were discontinued after significant distortion of the residues took place at the higher temperatures. After removal of the desired number of water molecules, the box was reequilibrated until the density was established and the volume remained constant. This procedure usually required 400 ps or more of dynamics, convergence becoming more difficult to achieve as more water was removed to obtain the 5% and in particular the 1% by weight hydration boxes.

RESULTS AND DISCUSSION

The periodic cell parameters are given in Table I, and the contents of one cell are shown in Figure 1. In such complex systems, it is necessary to look at a variety of parameters in order to judge the quality of the results. In this paper the concentration is on parameters associated with the glass transition temperature, \( T_g \), as well as the distribution of end-to-end distances. Some diffusion and energy parameters are reported here only briefly as they will be included in the discussion of a second computational \( T_g \) study\(^{16} \) in which larger amylose fragments are studied. Further, the individual residue conformations are important to understand the extent of "flipped" (i.e., as determined by values of \( \sim 180^\circ \) or \( 0^\circ \) for \( \phi \) or \( \psi \)) residues because these
abnormal conformations play a role in carbohydrate bends or U-turns. The number and type of "flipped" and "kinked" residues in this paper are noted as well as the backbone conformational properties. Twisted boat conformers were found to be the cause of a type of carbohydrate collapse that manifested itself as a dramatic increase in density and these conformational distortions are eliminated when observed.

In Table I is reported the temperature, volume, potential energy, and density of the final data sets for the different hydration levels. Plots of the reciprocal temperature (1/T) vs V, PE, and p show fairly sharp breaks in the straight line plots, occurring at the glass transition temperatures (see Figure 2). The slopes of the lines at temperatures above and below the glass transition temperature allow determination of parameters such as the thermal expansion coefficient and enthalpy for the transition. In this paper the Ts values are given in Table II. To obtain the Ts values, the plots of V vs 1/T, PE vs 1/T, and p vs 1/T were fitted with two least-squares lines above and below the estimated Ts, each of different levels of hydration were studied in this manner.

**Glass Transition Temperature**

In Figure 2 is shown a plot of V, PE, and p vs 1/T for the data points from equilibrated ensembles obtained from dynamic simulations. The average Ts values for the different hydration levels are given in Table II. To obtain the Ts values, the plots of V vs 1/T, PE vs 1/T, and p vs 1/T were fitted with two least-squares lines above and below the estimated Ts, each of different
15.8% Hydration

10.0% Hydration

5% Hydration

1% Hydration

```
Vol
2.18e+04
0.0024 1/T 0.0044

PE
-3.07e+03
0.0024 1/T 0.0044

Density
1.29
0.0024 1/T 0.0044

Vol
2.30e+04
0.0022 1/T 0.0044

PE
-2.28e+03
0.0022 1/T 0.0044

Density
1.31
0.0022 1/T 0.0044

Vol
1.04e+04
0.0020 1/T 0.0040

PE
-1.65e+03
0.0020 1/T 0.0040

Density
1.30
0.0020 1/T 0.0040

Vol
2.11e+04
0.0017 1/T 0.0024

PE
2.560
0.0017 1/T 0.0024

Density
1.372
0.0017 1/T 0.0024
```
Table II  Calculated and Experimental Values of the Glass Transition Temperatures, \( T_g \) (K), for Different Hydration Levels

<table>
<thead>
<tr>
<th>Hydration Level</th>
<th>15.8%</th>
<th>10.0%</th>
<th>5.0%</th>
<th>1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g ) from volume</td>
<td>315</td>
<td>337</td>
<td>394</td>
<td>490</td>
</tr>
<tr>
<td>( T_g ) from potential energy</td>
<td>318</td>
<td>333</td>
<td>373</td>
<td>453</td>
</tr>
<tr>
<td>( T_g ) from density</td>
<td>300</td>
<td>342</td>
<td>390</td>
<td>488</td>
</tr>
<tr>
<td>Average ( T_g )</td>
<td>311</td>
<td>337</td>
<td>386</td>
<td>477</td>
</tr>
<tr>
<td>Experimental ( T_g )</td>
<td>310(^b), 295(^b)</td>
<td>325(^b)</td>
<td>355(^b)</td>
<td>440(^c), 500(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Thirteen percent hydration for maltohexaose.\(^{12}\)
\(^b\) Estimated from Figure 2 of Ref. 12 for maltohexaose.
\(^c\) Anhydrous maltohexaose and dry amylose respectively.\(^{12}\)
\(^d\) Estimated from Figure 3 of Ref. 12 for DP-10 degree of polymerization and 13% hydration.
\(^e\) Estimated for starch from Figure 4 of Ref. 13 and private communication.

The average \( T_g \) values show an increment between hydration levels that increases as you go down in hydration levels. Between 15.8 and 10.0% \( \Delta T_g \) is 26 K, whereas between 10 and 5% hydration the change is 49 K. The jump from 5 to 1%, is even larger being 71 K. At the 5% hydration level the \( T_g \) value is approaching the decomposition temperature, \( \sim 450 \) K, and at 1% hydration the \( T_g \) exceeds the experimental decomposition temperature. A calculation of the rate of change in \( T_g \) as a function of change in hydration level as water content approaches zero gives a value of 1775 for the maltodecaose cell as compared to an experimental value of 1950 for maltohexaose.\(^{12}\) Our calculated value is in quite good agreement with the experimental value when compared to a classical thermodynamic theory (1250) for maltohexaose.\(^{12}\)

Conformations of “Normal,” “Kinked,” and “Flipped” Residues

A snapshot of the different conformations (10% hydration, 300 K) of one set of DP-10 maltodecaose chains is shown in Figure 3. To simplify viewing, the chains were removed from the cell. They are ordered in Figure 3 depending upon the degree of bend, from most twisted (shortest end-to-end distance) to least twisted (longest end-to-end distance). Residues in which the \( \alpha(1 \rightharpoonup 4) \)-linked dihedral angles are in the “flipped” conformation are denoted by arrows and can be found by looking for those residues in which the hydroxymethyl group is located \( \sim 180° \) relative to that observed in the previous residue. Location of residues that are in a “kinked” conformation are somewhat more difficult to observe since the dihedral angles are not greatly different from “normal” values. The average \( \langle \phi, \psi \rangle \) values defined as \( \phi(1--4) \)-linked \( \psi \) values were corrected by eliminating the “flipped” residues \( \phi, \psi = 77 \text{ to } 103, -7 \text{ to } -146 \) and “kinked” residues \( \phi, \psi = 31 \text{ to } 91, 33 \text{ to } 86 \). The dihedral angle values observed above compare favorably with the best experimentally defined structures of the large cyclodextrins,\(^{18,19}\) in particular, the CA10 and CA14 cyclodextrins. In these structures the normal \( \phi, \psi \) values are in the range 94°-102° for \( \phi \), 96°–122° for \( \psi \) in CA10, 97°–110° for \( \phi \), and 104°–
FIGURE 3 Individual maltodecaose chains taken from a 10% hydration, 300 K simulation. The end-to-end distances, and “flipped” (arrow), and “kinked” (circle) residues, are shown.

135° for ψ in CA14. The experimental18,19 “flipped” (ϕ, ψ) values for CA10 and CA14 are (84°, -65°) and (82°, -69°) respectively, while the “kinked” values are (76°, 84°) and (93°, 92°) respectively. These experimental18,19 dihedral angle values are limited to very few cases; thus one must be wary of setting them as limiting values. The range of deviations from the dynamics calculations are considerably larger for these distorted conformations, but the “normal” values are very close to the average “normal” values found experimentally in the large cyclic systems.

In this particular simulation cell, there were six “flipped” residues and seven “kinked” residues, leaving eighty seven conformationally “normal” residues. It is interesting to note that there are “flipped” residues in both the most bent and the most extended conformers. A pronounced feature to be pointed out is the persistence of a partial 6-residue helical turn, similar to that found structurally in single chain V₅-amylose, usually with ligands located in the core of the helix. In the studies described here only water and other amylose chains are available for stabilizing the V₅-helical turn and thus only short segments of this turn are found.

The endocyclic torsional angle of interest is defined by the atoms O5—C5—C6—O6, and is found here only in the gauche (+ or gt) and (− or gg) conformation, where the gt and gg designations are from consideration of the O5—C5—C6—O6 and C4—C5—C6—O6 dihedral angles respectively. These two gauche conformers are not equally common, with the gt conformer of average dihedral angle χ = +53° being twice as populated as the gg conformer with the average value of χ = −52°. The (+) gauche dihedral places the O6—H6 atoms pointing away from the glucose ring while the (−) places the O6—H6 over the glucose ring. The experimental conformational preferences of χ taken from cyclodextrins in their crystal environments shows some preference for the gauche(−) form.18,19

Characteristic Ratio

The conformational energy surfaces of the DP-10 polymers considered here have been used to calculate the mean square end-to-end distance, ⟨r²⟩, and the characteristic ration, CN, where CN is defined as,

\[ C_N = \langle r^2 \rangle / N \bar{l}^2 \]  

N is the number of sugar residues in the chain, and \( \bar{l}^2 \) is the mean-square length of the conventional glyco-
FIGURE 4  End-to-end distances plotted as a function of temperature for each of the ten maltodecaose chains.
Table III  The Average End-to-End Distance, \( R_{ij} \), and Characteristic Ratio, \( C_N \), at Each Temperature for All the DP-10 Chains at 15.8% Hydration

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>225</th>
<th>250</th>
<th>275</th>
<th>300</th>
<th>325</th>
<th>350</th>
<th>375</th>
<th>400</th>
<th>425</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{ij} )</td>
<td>22.4</td>
<td>22.4</td>
<td>22.4</td>
<td>22.3</td>
<td>23.1</td>
<td>22.9</td>
<td>23.6</td>
<td>23.4</td>
<td>23.7</td>
</tr>
<tr>
<td>( C_N )</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.6</td>
<td>2.5</td>
<td>2.7</td>
<td>2.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The characteristic ratios of Table III appear to be in the correct range for this size amylose chain, comparing favorably to the amylose values obtained by Perico et al.,\(^{20}\) where a Rouse–Zimm local dynamics (ORZLD) theoretical method was utilized. The \( C_N \) value for an amylose fragment of ten glucose residues (taken from Figure 5 of Ref. 20) is \( \sim 2 \). Considering the differences in methods, the agreement is quite satisfactory.

Mean Square Displacement and Self Diffusion Coefficient

The calculation of the mean square displacement (MSD) is of interest as it leads to the determination of the self-diffusion coefficient of an atom or molecule. That is, as a dynamics simulation proceeds over time, the position of an atom or molecule in the periodic system changes relative to its three dimensional coordinates at the start of the simulation. Thus, knowing the position vector of the atom and averaging over all choices of time origin within a dynamics trajectory, one can obtain the MSD. The self diffusion coefficient \( \langle D_o \rangle \) is defined for the number \( \langle N_o \rangle \) of bodies as

\[
D_o = \left[ \frac{1}{6N_o} \right] \lim(t \to \infty) \langle [\text{MSD}] / dt \rangle
\]  

\( D_o \) is evaluated from the limiting slope of the MSD from a plot of MSD vs. time for the particular group (i.e., solvent) and dynamics simulation. These partic-

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Table IV  Individual End-to-End Distances at Each Temperature for Each of the DP-10 Chains at 15.8% Hydration

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<td>225</td>
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<td>29.6</td>
<td>26.8</td>
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<td>20.3</td>
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<td>19.7</td>
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<td>250</td>
<td>18.7</td>
<td>30.6</td>
<td>26.1</td>
<td>20.8</td>
<td>21.2</td>
<td>21.3</td>
<td>10.2</td>
<td>19.8</td>
<td>32.5</td>
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ular plots must be carefully analyzed as the initial dynamics time periods are affected by previous energy minimization, and so one must use only the longer time periods. The end of the run also has termination effects which may cause some distortion in the curve. The middle time regions, although somewhat short (~ 150 ps), can lead to a reasonable slope. These slopes can be used to get values of the diffusion coefficient of water or the maltodecamers. The slope units obtained here are in A^2 ps^{-1} and are converted to m^2 s^{-1} for comparison with experimental values. Equation (3) allows the calculation of the activation energy ($\Delta E$) for the diffusion of water,

$$D_T = D_0 e^{-\Delta E/RT}$$

where $R$ is the gas constant. Plotting the natural log form of Equation (3) for the final simulations at the 10% hydration level gave a value of $\Delta E/R = -1333$ or an activation energy of $\Delta E \sim 2.6$ kcal/mole. This value can be compared to the excess enthalpy of 2.79 kcal/mol for the concentration range of 1.9–9.1% and 1.24 kcal/mol for the range 9.1–16% of water in native starch\(^3,13\) and compares favorably with the energy of evaporation value of 3.4 kcal/mol for 8–14% water from Trommsdorff and Tomka's\(^5\) calculations on starch models. The self diffusion coefficient of water at this hydration level and at a temperature above the $T_g$ value was evaluated to be $D_0 \sim 3 \times 10^{-9}$ m^2 s^{-1} which is in reasonable agreement with the experimentally measured diffusion coefficient of water $(2.3 \times 10^{-9}$ m^2 s^{-1})\(^{21,22}\). Water "hopping" or jumping observations and the calculated diffusion coefficients for low hydration amylose systems are described elsewhere\(^6\) for the maltodecaose and a recent $T_g$ study on 30-mer amylose fragments.

**Conclusions**

Calculated and experimental values for $T_g$ are given in Table II. The experimental data is available for several small fragments of amylose, the closest to this study being the maltohexaoose. It is observed that the fragments longer than the maltohexaoose will have higher $T_g$ values at different hydration levels. Clearly, this trend is shown in Table II where the maltodecaose $T_g$ values are consistently higher than the maltohexaoose experimental values at the same hydration level. In fact, the experimental data for a 10-mer at 13% hydration is approximately\(^12\) halfway between the calculated 10 and 15.8% calculated values. The agreement with experimental results is very good, and both the volume measures and energy measures give very similar $T_g$ values for all the different hydration levels. This would appear to be a very favorable test of the force field, AMB99C.\(^14,15\) Other properties obtained from the maltodecaose containing cells, such as the mean square deviation, characteristic ration, enthalpy, density, etc., also compare very well with equivalent experimental studies. In particular, density values for the DP-10 oligomers in Table I and Figure 2 are in the range of 1.3–1.4 g/cc and the equivalent experimental values are ~ 1.3–1.6 g/cc for starch,\(^23\) with the lower values being lower molecular weight fragments. Amorphous amylose and air-dried potato starch containing 10–16% water have densities of ~ 1.45 g/cc,\(^25\) close to that found here even though the more densely packed amyllopectin molecules are not included in the calculations reported here.

The attempts to study the anhydrous cell were not successful since after exhaustive dynamics (with constraints throughout to hold the residue rings correctly) it was always possible to add further water (~ 1%) back into the cell. It appears that the structural constraints of the linked cyclic rings of amylose fragments do not allow sufficient flexibility to fill all space and leave holes or voids between chains where water can be added. This would suggest that anhydrous amylose material may need to deform to distorted or ring puckered configurations in order to fill the void spaces, and because of the strain energy in the puckered ring it is more easily degraded in this state.

**REFERENCES**

17. Molecular Simulations, Inc., 9685 Scranton Road, San Diego, CA 92121-3752.