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Molecular Dynamic Simulations of Water Contaminated Biodiesel

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Abstract

The hydrophilic nature of biodiesel, as compared to conventional petroleum based fuel, results in the absorption of water from the environment and is one of the main critical issues hampering its widespread use as a petroleum alternative. Fatty acid methyl esters (FAMES) are a major component of biodiesel, and have been found to possess ordering in the liquid phase that is driven by head group interactions. Presented here are two representative biodiesel mixtures, rapeseed and soy, in the presence of 1% (kg/kg) of water. It is found that the water favorably interacts with the carbonyl oxygen of the ester head group in FAMES.

Motivation

- FAMES are a potentially environment-friendly source of transportation fuel
 - Reduced CO₂ for full carbon cycle
 - Currently implemented as petroleum diesel blends (e.g. B5, B10, and B20)
- Projected future increase in biodiesel usage
 - United States Navy initiative indicating new fuels possess 20% biodiesel fuel

Issues

- Hygroscopic molecules result in relatively hydrophilic fuel²
 - Biodiesel absorbency rates of 3016 mg/kg at 300K (B100)¹
- Water in system adversely impacts calorific value, oxidative & biological stability, fuel injection systems *etc.*²
- Water adversely impacts cold flow properties, cloud point, *etc.*

Methods & Parameterization

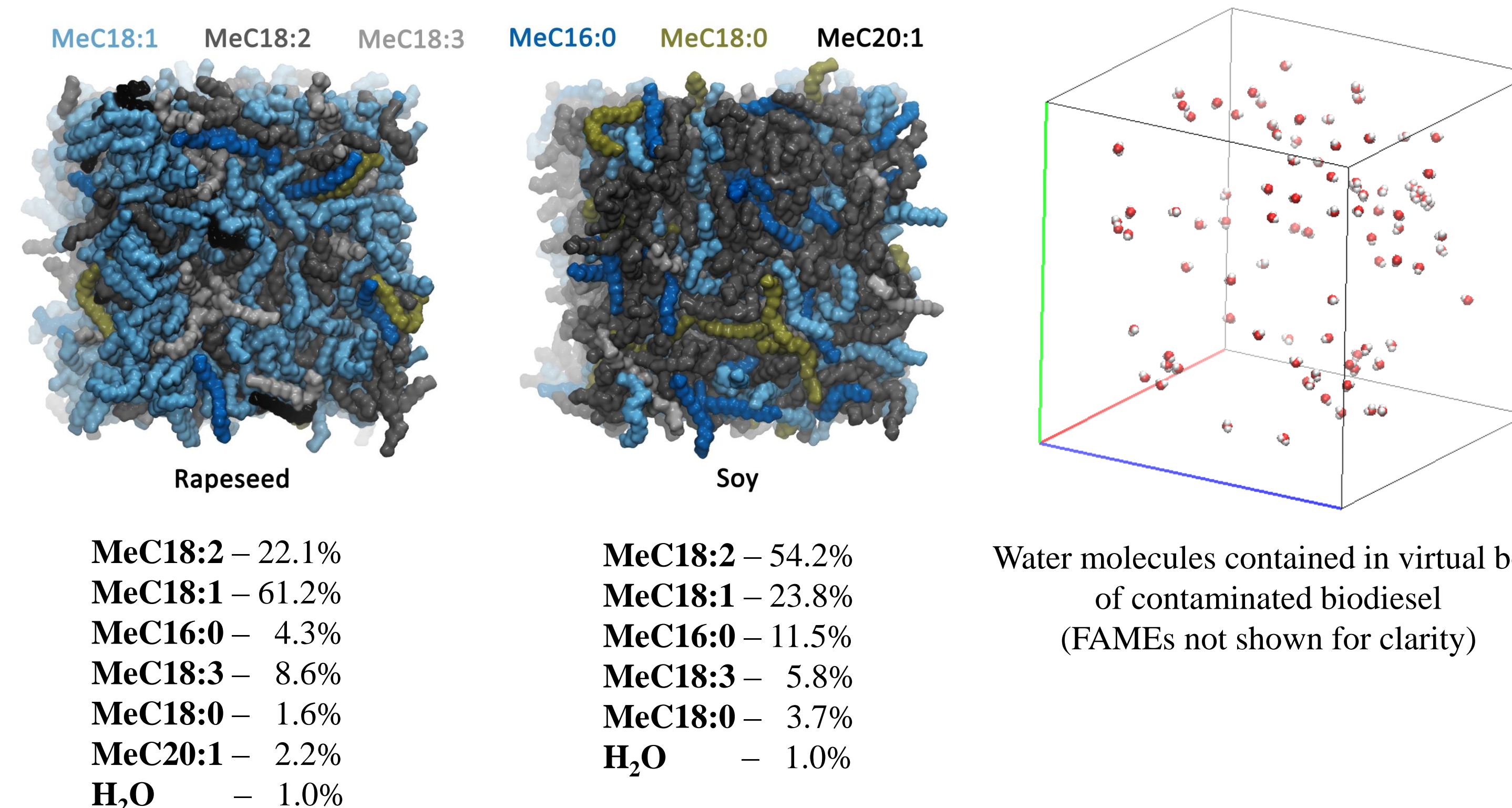
$$V(r^N) = \sum_{\text{Bonds}} k_b (l - l_0)^2 + \sum_{\text{Angles}} k_a (\theta - \theta_0)^2 + \sum_{\text{Torsions}} \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)] \quad F = -\nabla V$$

$$+ \sum_{j=1}^{N-1} \sum_{i=j+1}^N \left\{ \epsilon_{i,j} \left[\left(\frac{r_{ij}}{r_{ij}^0} \right)^{12} - 2 \left(\frac{r_{ij}}{r_{ij}^0} \right)^6 \right] + \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} \right\} \quad F = ma = m \frac{d^2 r}{dt^2}$$

van der Waals electrostatic

| FAME | Short Name | Optimized Structure |
|---------------------|------------|---------------------|
| Methyl palmitate | C16:0 | |
| Methyl palmitoleate | C16:1 | |
| Methyl gondoate | C20:1 | |
| Methyl laurate | C12:0 | |
| Methyl stearate | C18:0 | |
| Methyl oleate | C18:1 | |
| Methyl linoleate | C18:2 | |
| Methyl linolenate | C18:3 | |

Biodiesel Box Simulations

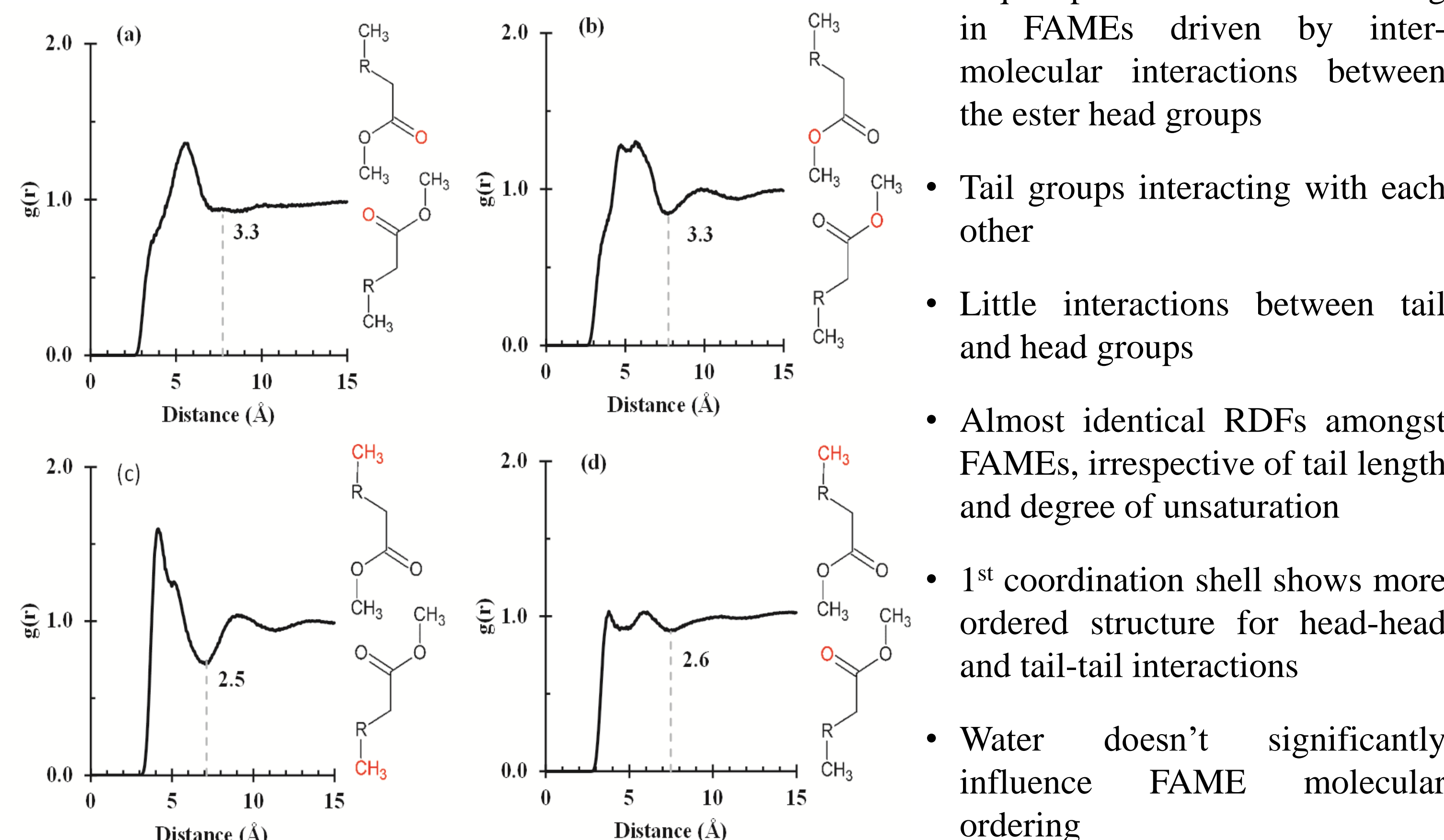


Molecular Dynamics Results

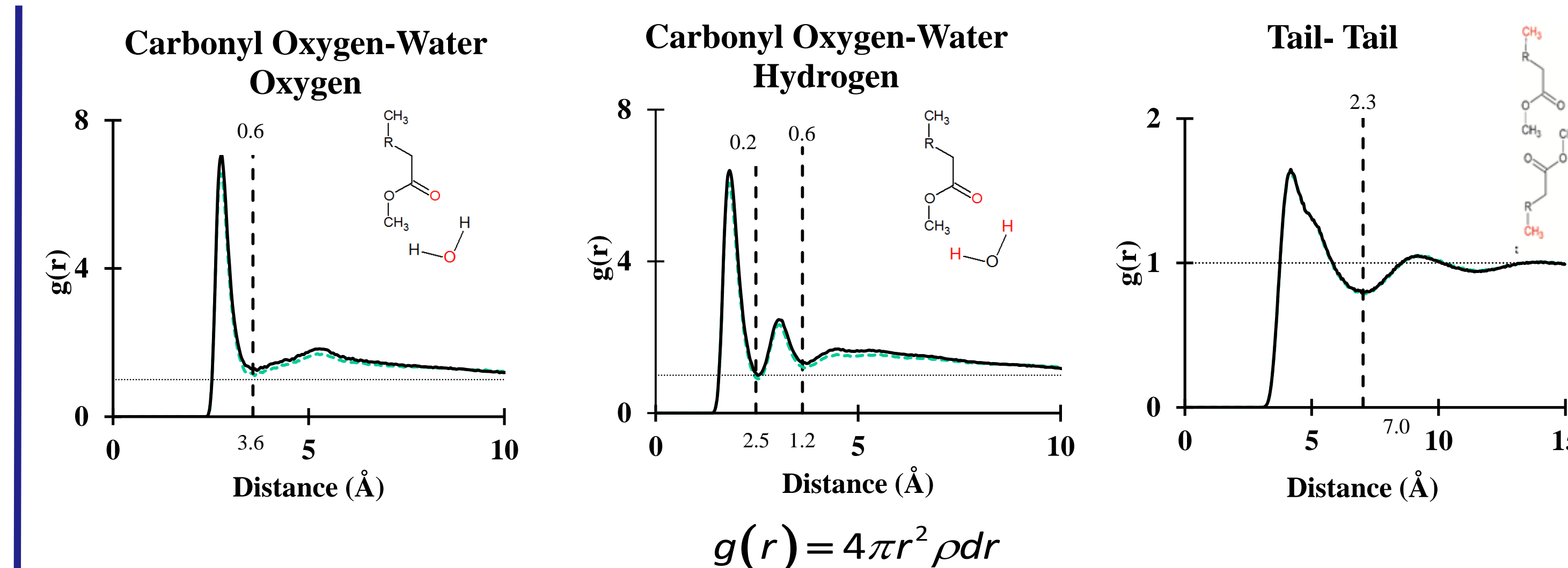
| | Radii of Gyration | | End to End Distance | | Characteristic Ratio | |
|---------|-------------------|-----------|---------------------|------------|----------------------|-----------|
| | Soy | Rapeseed | Soy | Rapeseed | Soy | Rapeseed |
| MeC16:0 | 5.8 ± 0.4 | 5.8 ± 0.4 | 16.9 ± 2.5 | 16.7 ± 2.5 | 7.0 ± 0.3 | 6.8 ± 0.3 |
| MeC18:0 | 6.4 ± 0.5 | 6.4 ± 0.5 | 18.3 ± 3.0 | 18.1 ± 3.1 | 7.3 ± 0.3 | 7.3 ± 0.3 |
| MeC18:1 | 5.6 ± 0.6 | 5.6 ± 0.6 | 15.0 ± 4.1 | 14.9 ± 4.0 | 5.2 ± 0.5 | 5.4 ± 0.5 |
| MeC18:2 | 5.4 ± 0.6 | 5.4 ± 0.6 | 14.3 ± 3.8 | 14.3 ± 3.9 | 4.8 ± 0.5 | 4.9 ± 0.5 |
| MeC18:3 | 5.4 ± 0.6 | 5.4 ± 0.6 | 13.4 ± 4.0 | 13.7 ± 3.9 | 4.5 ± 0.5 | 4.6 ± 0.5 |
| MeC20:1 | - | 6.1 ± 0.8 | - | 16.2 ± 4.6 | - | 5.6 ± 0.5 |

- Pure FAME system results for the radii of gyration, end to end distance, and characteristic ratio.
- No significant differences were found, for 1% water diluted mixture

Radial Distribution Function (RDF) Analysis

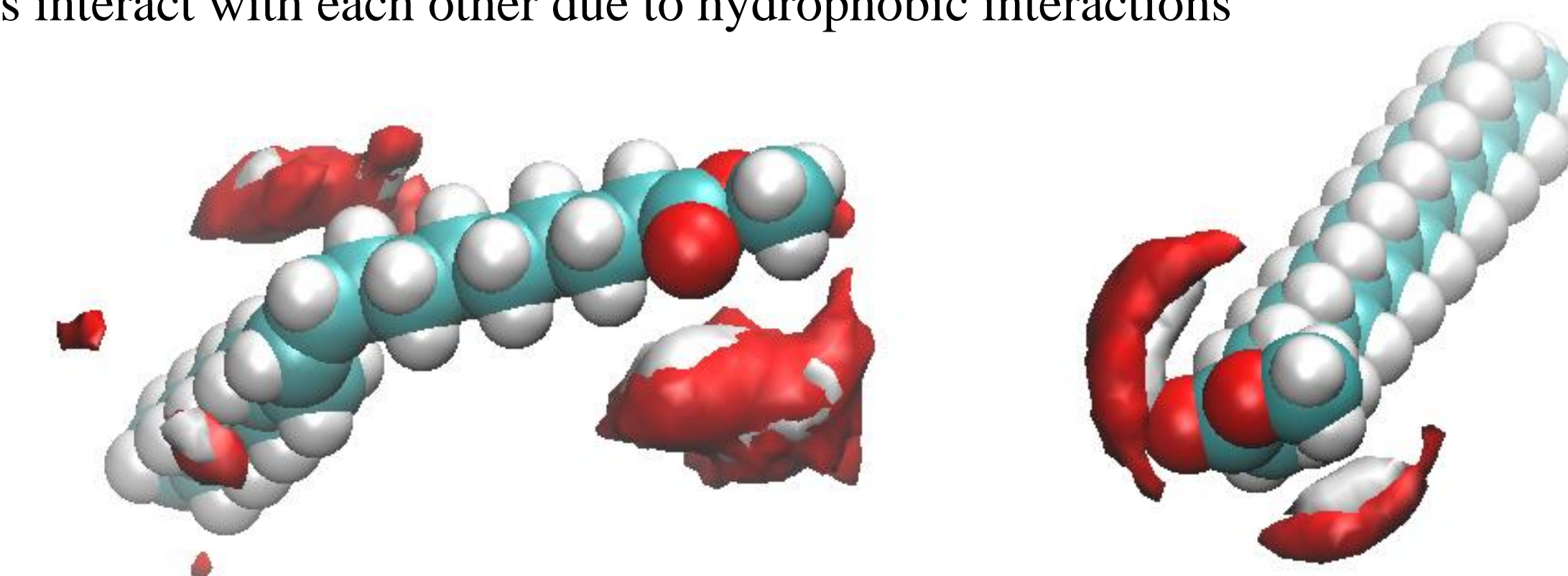


Radial Distribution Function Continued



RDFs of water interactions with FAMES. Analyzed hydrophobic (Tail) and hydrophilic (O1) interactions with water oxygen and hydrogen.

- Solvating water interacts with carbonyl oxygen
- Water is a hydrogen bond donor while carbonyl oxygen is the hydrogen bond acceptor
- Tails interact with each other due to hydrophobic interactions



Volume map of water interactions with rapeseed molecule MeC18:0 and MeC18:1. Water hydrogen interactions (white), water oxygen interactions (red).

- Indicates close proximity of hydrogens to carbonyl oxygen
- Water hydrogen bonds (donor) with carbonyl oxygen (acceptor)

Conclusions

- Water molecules orient around molecule head groups
- Water molecules tend to wedge between the head groups of two molecules
- Small water dilution amount causes minimal changes in radii of gyration, end to end distance, and characteristic ratio

Future Work

- Continue same analysis process with different water dilution amounts to compare results
- Look further into how the water cause the molecules to order what characteristics of those molecules attract water molecules
- Observe how the water causes the viscosity to change resulting in flow issues

References

- Water Content in Biodiesel, Diesel, and Biodiesel-Diesel Blends**
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M. B. Oliveira, F. R. Varanda, I. M. Marrucho, A. J. Queimada, and J. A. P. Coutinho *Industrial & Engineering Chemistry Research* **2008** 47 (12), 4278-4285
- Molecular Simulations of Fatty Acid Methyl Esters and Representative Biodiesel Mixtures**
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