

An Efficient Equation of State for Screening Polymer Melts and Solutions

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$$Z = m \left(1 + \frac{4\eta + 5.3696\eta^2}{1 - 1.453\eta} \right) - (m - 1) \left(1 + \frac{1.3424\eta}{1 + 1.3424\eta} + \frac{1.453\eta}{1 - 1.453\eta} \right) - \left(\frac{m}{2} - 1 \right) (1 + 4.482\eta) - \frac{a}{RTV}$$

Introduction

Equations of state (EOS) are mathematical relationships that intertwine the state properties of bulk matter. State properties are measurable variables such as pressure, temperature, and volume. They allow scientists to predict some of these properties for chemicals in certain conditions/settings without having to actually perform the experiment or obtain pre-existing data from literature.

This project aimed to further develop a cubic EOS for fluids (gases and liquids) that is molecularly-based and requires only the chemical structure of the fluid(s) being looked at. However, this phase of research focused on polymeric and chain fluids.

Polymers are extremely large chain molecules, and are of utmost industrial significance (for example, the plastic industry is completely comprised of polymers). As such, it is very important to be able to model their physical behavior/characteristics. An original, structurally-based EOS has resulted from this research, and must now be developed further.

Methodology

Athermal Chains

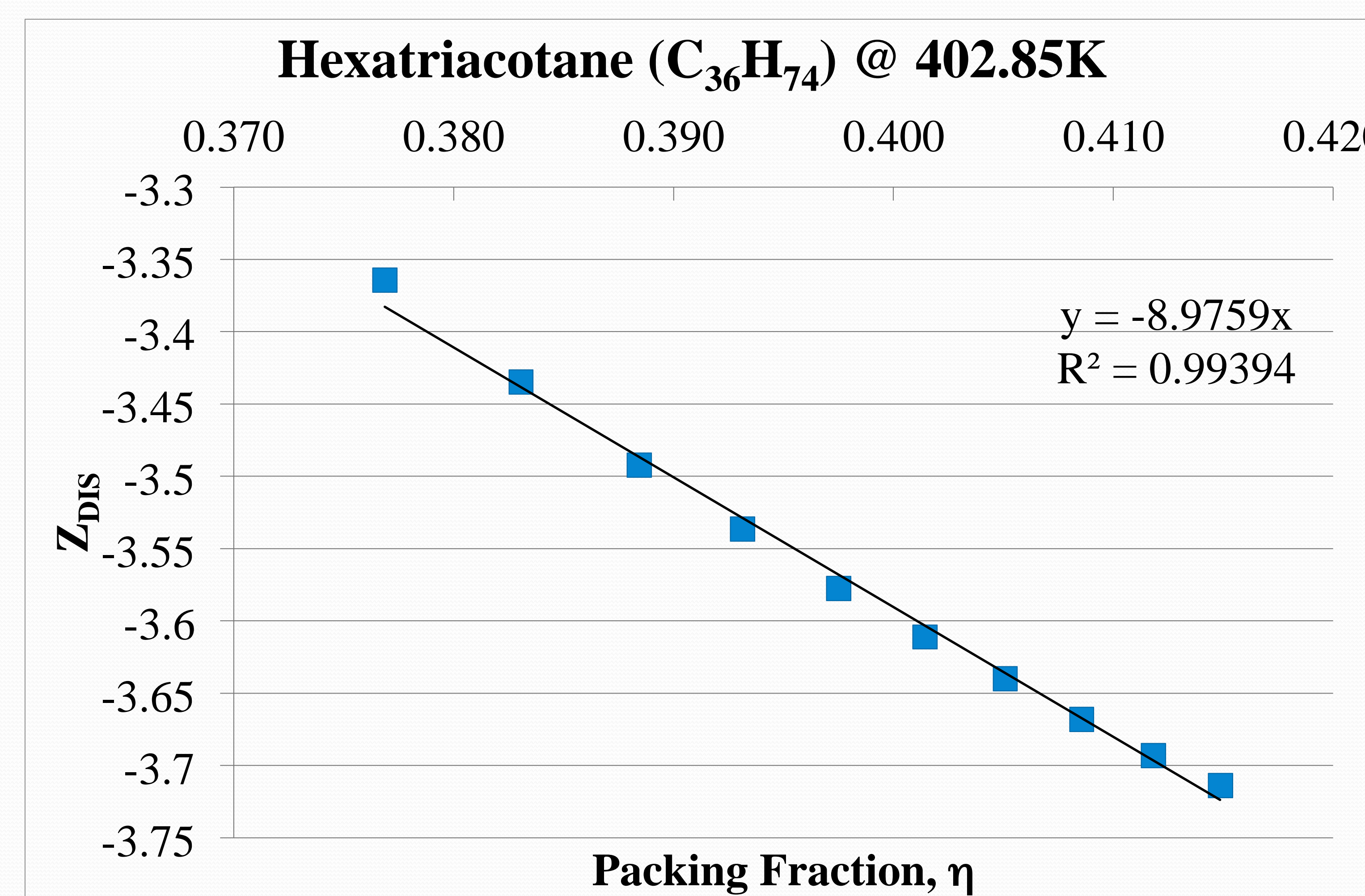
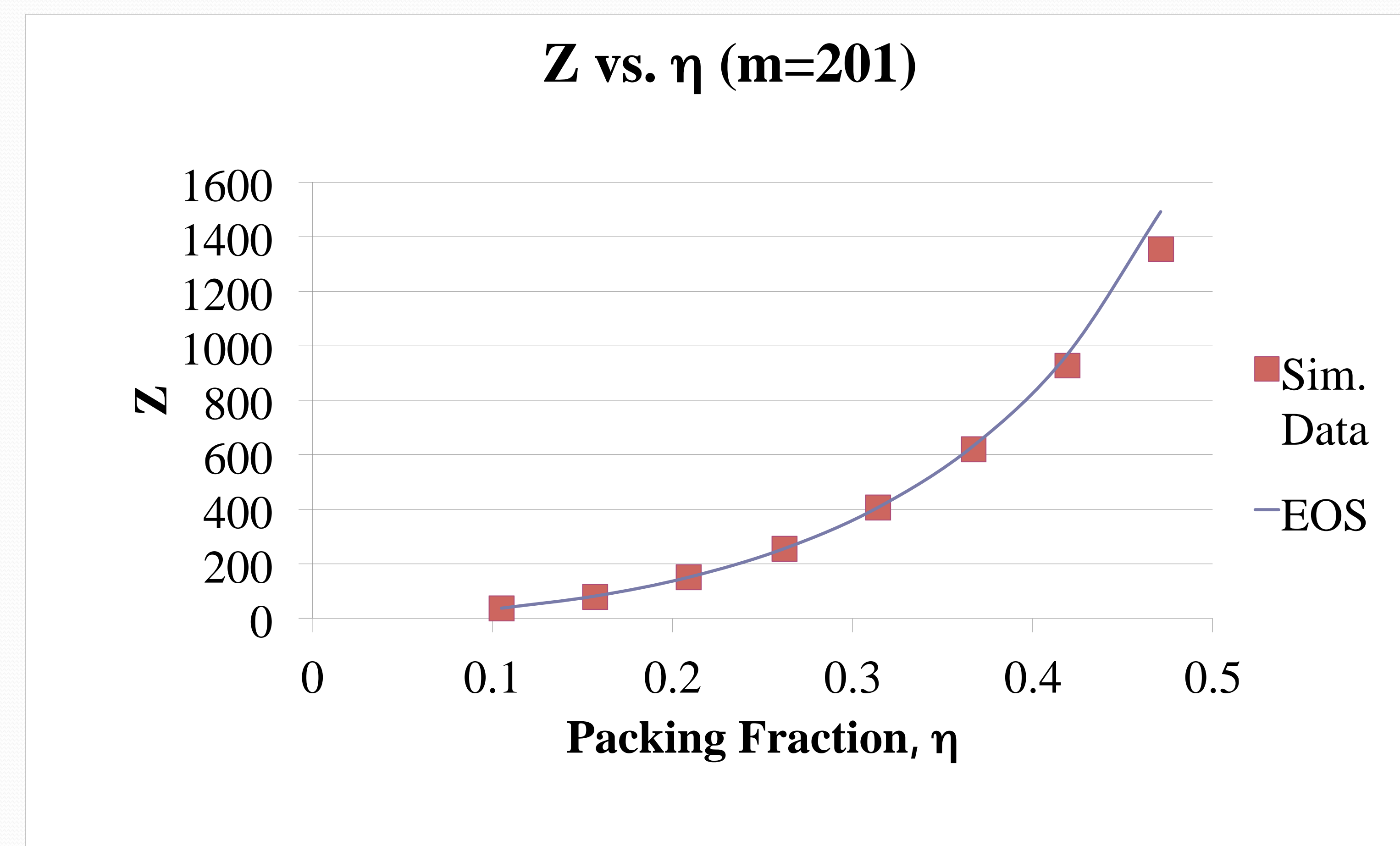
A variety of thermodynamic bonding terms for molecular equations of state were paired with different hard-sphere repulsive terms and analyzed. Some original terms were even created by direct fits of simulation data. The results of each combination were compared to computer simulation data for athermal hard-sphere chains from literature. The equation that most closely matched the simulation data was chosen to have the new dispersive term added on.

Dispersion

A van der Waals attractive term was integrated into the equation for athermal hard-sphere chains in order to model real, nonpolar fluids. A novel method of fitting the fluid-specific parameter 'a' to experimental data was developed that is both simple and extrapolative in nature. The segment energy, μ/k , of the fluid is calculated and then used to find the temperature dependence of 'a'.

Results

Fluid	Segment Dispersive Energy (μ/k)
n-Hexane (C_6H_{14})	669.93
n-Undecane ($C_{11}H_{24}$)	856.92
n-Tetracosane ($C_{24}H_{50}$)	979.93
n-Hexatriacotane ($C_{36}H_{74}$)	1042.06
n-Tetratetracotane ($C_{44}H_{90}$)	1057.73



Conclusions

The general form of the equation was further developed and polished during the initial stage of research. With the addition of a dispersive term, the equation is able to model simple, non-polar polymers that are relatively short (under roughly m=200) and other nonpolar fluids. The behavior of athermal chains was modeled very well by the equation, with an error of only 2.83% for all chains up to length m=201.

Issues were encountered with modeling very long chain polymers, and this is attributed mostly to their high degrees of polydispersity. This makes calculations very difficult and error can be seen when simplifications are introduced. We plan to further address this, and ultimately to be able to better predict the behavior of polymers with a higher degree of polydispersity. The temperature dependence of the variable 'a' still needs to be described, and mixing with small solvent molecules will be examined.

In the future, terms for hydrogen-bonding, dipolar, and quadrupolar molecules will also be developed so that the equation is not limited to any one type of species. But as of now, it is only useful in modeling relatively short, nonpolar fluids.

References

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