

# An Efficient Equation of State for Screening Polymer Melts and Solutions

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## Abstract

A molecularly-based equation of state (EOS) that is quartic in molar volume was developed for long chain molecules and polymers. Different existing theoretical calculations of intermolecular forces (dispersion and bonding) were compared to computer simulation results as well as experimental data where possible, and original terms were also developed. The most accurate athermal hard-sphere chain EOS tested here uses the vdWS2-1 hard sphere compressibility contribution within the TPT-D framework (using a fit of simulation data for the radial distribution function at contact value for hard dimers), giving an AAD of 2.83% compared to athermal hard-sphere chain computer simulations. A van der Waals type dispersion term is also added into the equation to model real chain fluids, using a novel technique of obtaining the fluid-specific segment dispersive energy ( $\mu/k$ ). Typical problems with modeling polymers (i.e. polydispersity) were found and are discussed, preventing the application of this equation/method to most industrial polymers (>500 segments). Relatively short, straight-chain nonpolar polymers (~50 segments) with low polydispersity can be modeled well, however.

## Introduction

Equations of state (EOS) are of utmost importance to many chemical process engineers, big product industries, and even those in academia. An equation of state is a mathematical relationship that intertwines the measurable state variables of matter, such as pressure (P), temperature (T), and specific volume (V). This allows its users to accurately predict some unknown variable if the other conditions are known and specified, without having to actually perform an experiment. Any EOS requires experimentation/actual data to be developed initially, but it is possible to have a powerful, stand-alone equation in the end with all the required data built in. All could be found just from chemical structure.

To do this however, trends must be realized in the data analysis process when comparing species. These changes in data are no doubt due to differences occurring in the atomic level processes, so looking at this problem from a molecular point of view is required. This is where this research falls under a distinct category in equation of state research. The two main types of equations of state are molecularly-based and empirically-based. Equations of state originally were empirically based; mostly arbitrary numbers that happened to mathematically describe the phase behavior of species. But as more research in this area was performed and with a tremendously increased understanding of overall physical chemistry, we have more recently been able to look at things on the atomistic level. We can mathematically analyze and model changes caused by chemical structure, and begin to break the equations of state down into components. Not only does this give us a better real understanding of what is happening small-scale and how it effects the bulk properties, but it could ultimately allow for possible extrapolation to species that have not been experimented with, or even hypothetical ones. The first highly accurate, successful molecularly based theory for fluids was the SAFT (Statistical Associating Fluid Theory) EOS (Huang and Radosz, 1990). Unfortunately, the SAFT EOS and its modifications have many mathematical roots and correlated parameters with weak physical significance.

This work aimed to provide an equal level of molecular detail but in a more robust and efficient equation, but only for completely nonpolar species at this point in time.

This research also focused specifically on applications to polymers, an industry that is growing very quickly. Polymers are very large molecules comprised of hundreds, thousands, or even more atoms in repeated units. Most polymers can be viewed as relatively straight, long chains, but branched/dendritic polymers have been focused on more recently. This work only applies to straight chain nonpolar polymers and does not apply to these branched or dendritic species, as branching specificity is not yet included in the developed EOS. Polymers are generally processed in

## **Methods**

### *Athermal Hard-Sphere Chains*

To examine the bonding contribution to volumetric behavior, data from real fluids is not used at all. An equation must first be developed without any dispersion effects present. However,  $d$

Clearly the TPT-D based equations show much improvement over their TPT1 predecessors. This was expected, because more information about the structure of the chain is included in the additional term that is present in TPT-D. That term involves information about the radial distribution function at contact value ( $g_{HD}(\sigma)$ ) for hard dimers. More generally, TPT1 only looks at hard dimers being formed from separate hard spheres while TPT-D additionally looks at the formation of hard tetramers by those initially formed dimers.

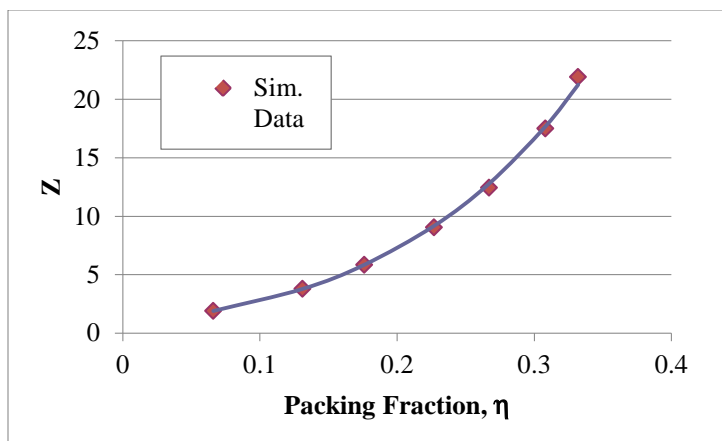
EOS Components ( $Z_{HS}/CHAIN/g_{HD}$ )	% AAD (Overall)
CS/TPT1	7.54
vdWS2-1/TPT1	9.31
CS/TPT-D/Sim	3.15
CS/TPT-D/Chiew	3.26
vdWS2-1/TPT-D/Sim	2.83
vdWS2-1/TPT-D/Chiew	8.69

**Table 1.** Results of athermal chain EOS compared with computer simulation data.

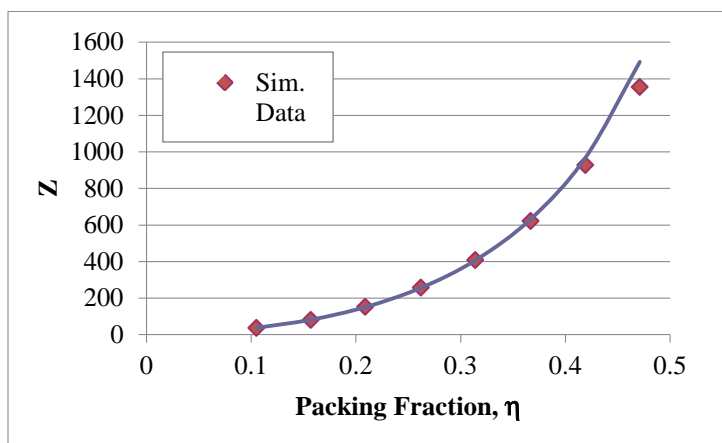
Because of its superior performance, vdWS2-1/TPT-D/Sim athermal EOS was chosen to be developed further for real fluids. Figures 2 and 3 below show the performance of this EOS for chains of lengths  $m=8$  and  $m=201$  respectively. Any bonding model tends to degrade with increasingly long chain lengths, so at extremely high lengths the bonding term is no longer modeling the actual behavior of the chains and becomes useless. However, Table 2 shows that the vdWS2-1/TPT-D/Sim athermal EOS works well even for a chain length of  $m=201$ , with an AAD of 2.69%. Computer simulation data for higher chain lengths could not be found.

m	% AAD
2	1.7
3	1.85
4	2.31
8	1.25
16	4.22
32	3.49
51	3.46
201	2.69

**Table 2.** Deviation of the vdWS2-1/TPT-D/Sim athermal chain EOS from computer simulation results at various chain lengths.



**Figure 2.** Computer simulation results for the compressibility factor of a hard octomer ( $m=8$ ) compared with the predicted results from the new EOS. The deviation is 1.25%.



**Figure 3.** Computer simulation results for the compressibility factor of a chain of length 201 ( $m=201$ ) compared with the predicted results from the new EOS. The deviation is only 2.69%.

Table 3 below shows the results of using this novel method of finding the dispersive parameters for relatively short chain polymers. The results follow the pattern expected, as dispersion (even per segment) should increase with the length of the chain due to a larger and more polarizable electron cloud.

Fluid	$\mu/k$ (K)
n-Hexane ( $m=6$ )	669.93
n-Undecane ( $m=11$ )	856.92
n-Tetracosane ( $m=24$ )	979.93
n-Hexatriacotane ( $m=36$ )	1042.06
n-Tetratetracotane ( $m=44$ )	1057.73

**Table 3.** Fluid-specific segment dispersive energies derived using the outlined method.

However, this method did not work for very long chain polymers, such as polyethylene. The hard-sphere diameters that were calculated for polyethylene using the method presented were unrealistically low, so further analysis of these extremely long chain molecules was avoided. There are reasons that fully explain this issue

however; most important is the polydispersity of a sample. Any very long polymer sample is always going to consist as a variety of chains of different lengths, as exact control is nearly impossible in synthesizing these compounds. The EOS developed in this work does not take this into consideration, so the values obtained using the new method are not truly physically representative. Another contribution to the error is the fact that the chain term is likely breaking down at such long lengths. The error due to this should be far less than that caused by the issue of polydispersity.

### Conclusions

The vdWS2-1/TPT-D/Sim athermal chain EOS coupled with a simple van der Waals-type dispersive term is the form of the final EOS developed, which works well for relatively short non-polar species/polymers ( $m < 50$ ). Additionally, the novel method of finding the dispersive

0.076 12(e)4(1)7( )-12(m)13(e)4J-q( )4( b0 Tc14( t)3(3(t)-9( c 0.0 Tc14(pe)4(d,)3( w)10(pu us)9(/)7(podC /TT(e)-3(r)-17