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 (μ/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 the fluid phase, or in solution, so an EOS that models the data well while remaining theoretically/physically sound and efficient in computational nature is highly sought after. However, molecularly-based EOS generally have trouble modeling polymers because of their extremely long lengths and the inherent polydispersity factor associated with the synthetic processes. With a solid EOS backbone, extrapolation to other polymer species would be fairly simple, as many polymers differ only in functional groups.

The most important contributions to the phase behavior of nonpolar polymer species are bonding and dispersion. These two components are very separate in nature, so most of the research can be categorized into these two distinct sections. The combination of these two components should provide a good EOS for straight chain polymer species that follows the general form in Equation 1:

$$Z = Z_{CHAIN} + mZ_{DIS} \quad (1)$$

where Z is the overall compressibility factor (a measure of the non-ideal behavior of fluids), m is the segment number (number of segments/atoms in the molecule), and Z_{CHAIN} and Z_{DIS} are the athermal hard-sphere chain and dispersive contributions to the overall compressibility factor. Keep in mind that Z_{CHAIN} includes the effects of hard sphere repulsion and bonding, and is represented by the overall athermal hard-sphere chain EOS.

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, dispersion is a degree of mutual, electrostatic attraction found in all real molecules. So in order to exclusively examine the effects of bonding, computer simulation tests that specifically remove the effects of dispersion must be performed on hard sphere chains (representative of molecules). The athermal chain equation is obtained from the results of these simulations. Multiple bonding models exist in thermodynamic literature, but Wertheim's thermodynamic perturbation theory (TPT) seems most promising and are therefore focused on in this work. TPT is based off of the hard-sphere compressibility factor term (Z_{HS}) that is chosen. This work compares different combinations of the most accurate Z_{HS} terms found in literature with both the first order thermodynamic perturbation theory (TPT1) and its dimer counterpart (TPT-D). Different models of the derivative of the natural log of the radial distribution function at contact value for dimers ($g_{HD}(\sigma)$) with respect to packing fraction (η) were also compared, one of them being an original term based on a direct fit of simulation data (shown in Figure 1) (Chang and Sandler, 1994). The results of these combinations were compared to the computer simulation data for chains to find the best combination of components for the athermal chain EOS.

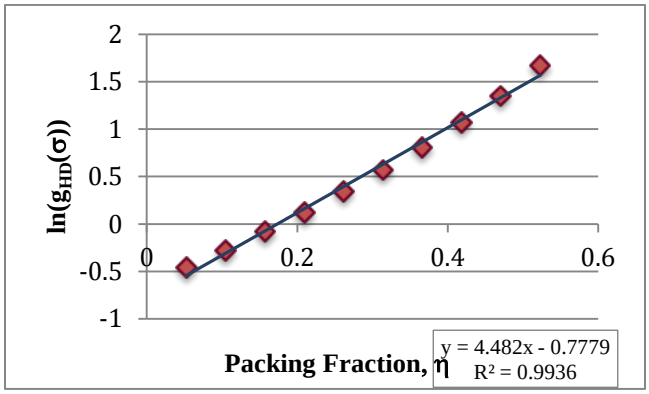

Figure 1. Computer simulation results for the natural log of the radial distribution function (at contact value) of hard dimers at various packing fractions (Chang and Sandler, 1994), along with a linear fit of the data.

Dispersion

Nearby molecules distort one another's electron clouds, creating a relatively weak mutual attraction. However, these effects have to be accounted for in order to accurately predict the volumetric behavior of fluids. Therefore dispersion forces must be added to the athermal chain EOS, as they are the only remaining aspect to be accounted for in order to model real fluids. Calculating the overall compressibility factor Z in Equation 1 using experimental data from literature (Walsch and Zoller, 1995) and Z_{CHAIN} by the vdWS2-1/TPT-D/Sim EOS, the compressibility factor of dispersion for a real fluid can be solved for.

Z_{DIS} was then plotted against η for a chosen fluid, and the hard-sphere diameter was varied until the slope (*a'*) for each isotherm was as linear as possible (shown mathematically in Equation 2). This novel method is a reliable way to obtain consistent hard-sphere diameters, which is an issue for other models. The fluid-specific parameter *a* in the original van der Waals attraction term can be obtained easily if desired.

$$Z_{DIS} = -a'\eta = -\frac{a\eta}{RTc} \qquad (2)$$

where *a* is the temperature-dependent, fluid-specific parameter in the van der Waals attractive term, *R* is the universal gas constant, and *c* is a known temperature-dependent value (because it includes the hard-sphere segment diameter, which varies with temperature). Clearly, this is much simpler in form and more efficient than some other models found in literature, such as the following:

CK SAFT EOS Model (Chen and Kreglewski, 1977)

$$Z_{DIS} = \sum_{i=1}^{4}\sum_{j=4}^{9} j\, D_{ij}\left(\frac{u}{kT}\right)^i\left(\frac{\eta}{\tau}\right)^j \qquad (3)$$

(Fu and Sandler, 1995)

$$Z_{DIS} = -0.36mRTIn\{1+\frac{\eta}{0.74048}\left[\exp\left(\frac{\left(\frac{u}{k}\right)}{2T}\right)-1\right]\} \quad (4)$$

The segment dispersive energies (μ/k) are a measure of the dispersive strength of each segment on a molecule. These energies are related to the fluid-specific parameters and are more physically meaningful on the molecular level. They are also defined as being temperature-independent, so these are much easier to generally compare between fluids than the temperature-dependent equations for *a* and *a'*. This energy value can be obtained using the relationship in Equation 5, which can be derived from equations given in this paper.

$$a' = \frac{4\mu}{kT} \qquad (5)$$

where *k* is the Boltzmann constant. In order to utilize this relationship though, the *a'* values for each isotherm of a fluid must first be plotted against 1/*T*. The linear slope (passing through origin) is then equal to 4μ/k.

Results

The final, resultant equation of state is shown below in Equation 6:

$$Z = m\left(1+\frac{4\eta+5.3696\eta^2}{1-1.453\eta}\right)-(m-1)\left(1+\frac{1.3424\eta}{1+1.3424\eta}+\frac{1.453\eta}{1-1.453\eta}\right)-\left(\frac{m}{2}-1\right)(1+4.482\eta)-\frac{a\eta}{RTc} \qquad (6)$$

Table 1 below shows the results of the athermal chain EOS compared with computer simulation data (Chiew, 1990) for a variety of different chain lengths.

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.

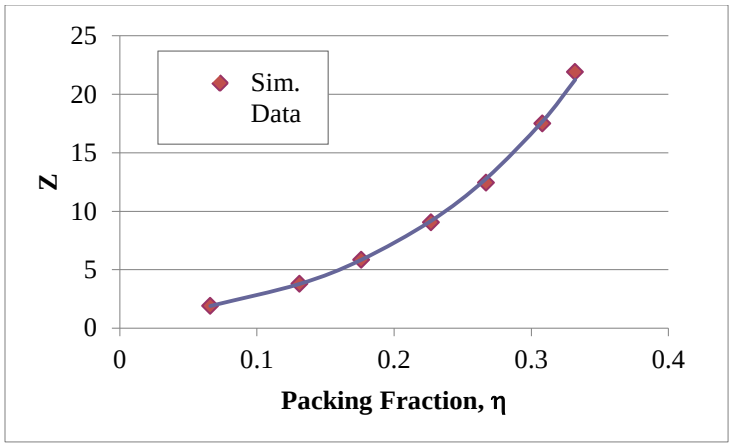

Figure 2. Computer simulation results for the compressibility factor of a hard octomer (m=8) compared with the predicted results from the new EOS. The deviation is 1.25%.

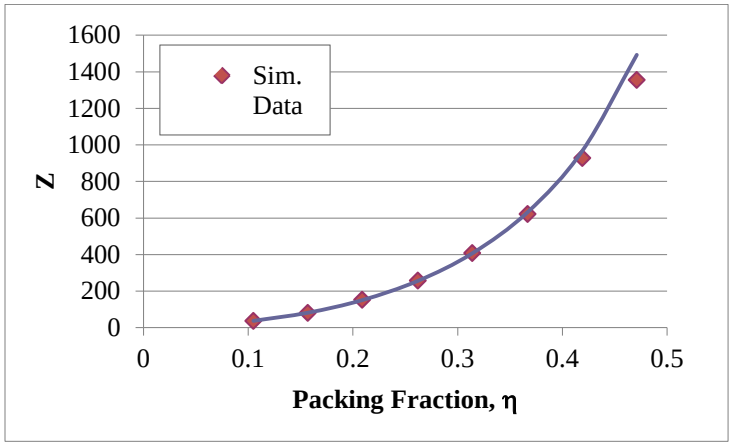

Figure 3. Computer simulation results for the compressibility factor of a chain of length 201 (m=201) compared with the predicted results from the new EOS. The deviation is only 2.69%.

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	μ/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 parameters is very reliable and simple. Unfortunately however, application to industrial and common polymers is still restricted at this time. A model that includes a polydisperse length distribution must be created in order to utilize most of the experimental data, so this would likely be the next step in application of the EOS to polymer fluids. Also, terms for hydrogen-bonding (associating), dipolar, and quadrupolar species must be developed/added in the future so that the equation is not limited to modeling non-polar fluids.

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Biographies

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Anna O'Malley is a Senior Chemistry and Forensic Science Major from Rochelle, Illinois. She is on track to graduate this coming May 2015. She plans to attend graduate school studying in the field of Chemistry. Prebiotic Chemistry is a major field of interest to her, and she hopes to more explore it through a graduate degree in Biochemistry. Researching in the field of thermodynamics has been a great experience and eye opener into the world of professional research for her.

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