

Modeling Chain Stiffness and Attractive Interaction for Polymeric Systems in the NPT Ensemble

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Abstract

Theoretically based equations of state (EOS) serve as practical tools for obtaining equilibrium properties of polymers. Most of the theoretically based EOS in current use are pressure-explicit. However, chemical engineering operations are usually carried out at constant temperature and pressure thereby making volume-explicit EOS more practically relevant.

Significant fractions of engineering polymers are made up of non-flexible chains and yet the EOS for polymeric systems in current use do not explicitly take account of chain stiffness. In this work, we present a model for polymeric systems which include the effect of chain stiffness and attractive contributions based on a simple volume-explicit hard chains EOS. Chain stiffness is modeled based on non-additive size interactions. We used approximations based on a known exact solution for one-dimensional square well fluid to model the attractive contributions in three-dimensional polymeric system.

Introduction

Development of equations of state (EOS) for predicting the pressure-volume-temperature (PVT) behavior of polymeric systems is an important activity in view of its relevance to process design and material development. There are various EOS, both theoretical and empirical, given in the literature for modeling the PVT behavior of polymers. Excellent reviews on the subject are presented by Rodgers (1993) and Lambert et al (2000).

Polymer systems because of their large molecular size exhibit quite different PVT and phase-behavior from non-polymeric systems. One of the most striking features of polymers is their non-volatility and hence vapor-phase volume is non-physical for such systems. Despite this fact, existing theoretically-based polymer EOS are pressure-explicit and mostly cubic in volume. Moreover, in chemical engineering most operations are carried out at constant temperature and pressure and the use of pressure explicit equations with multiple-volume roots is inconvenient due to the added numerical procedure of finding the correct volume. This is what makes volume-explicit EOS for polymers such as the Tait equation (Danner and High, 1993) to have wide acceptability among researchers. However, the empirical nature of the Tait equation limits its extension to polymer mixtures and copolymers. Thus, there is need to develop a volume-explicit EOS for polymer systems with sound theoretical basis.

In a previous study Hamad (1997) has developed a volume-explicit EOS for hard spheres and mixtures of hard spheres based on a summation of the pressure virial expansion. He later extended the equation to hard chains of tangent spheres and their mixtures (Hamad,1998) through utilization of contact pair correlation functions in the isothermal-isobaric ensemble, NPT, to form a chain out of individual monomers. The main purpose of this paper is to present our current effort in further extending the equation to real polymers. We intend to achieve this by using non-additive size interactions to model chain stiffness and by adding a term to account for the effect of attractive interactions in the EOS.

Model Development

Repulsive Contribution. It is theoretically known that at high pressure, when the average separation between molecules is small, fluid structure is predominantly shaped by repulsive forces. For this reason, EOS are usually built around accurate repulsive equations for small molecules.

In this work, we consider the following hard-chain equation to represent the repulsive part of our EOS:

$$Z_{HC} = 1 + 4mp + \frac{3}{16}(1 - m + 4mp) \ln \left[\frac{3 + p}{3 + 25p} \right] \quad (1)$$

where m is the number of segments, $p = \pi\sigma^3 P / 6kT$ is the dimensionless pressure, P is the pressure, T is the temperature and σ is the diameter of the hard sphere. It is important to note that the above equation is volume-explicit and its derivation is given elsewhere (Hamad, 1998). The equation is simple and satisfies fundamental boundary conditions required of a theoretical EOS.

Attractive Contribution. Due to the weak nature of attractive forces on fluid structure, perturbation methods are usually employed to describe the contribution of attractive interaction to the EOS of real molecules. There are various expressions used for attractive contribution in pressure-explicit EOS. The simplest among them is the van der Waals attractive form and it is the form used in the perturbed hard-sphere chain EOS developed by Song et al (1994). The attractive term in the SAFT EOS is based on the power series initially fitted by Alder et al. (1972) to molecular dynamics data for square-well sphere. This was subsequently modified by Chen and Kreglowsky (1977) to model attraction between segments. Other works employing square-well as attractive term are the perturbed hard sphere chain from square-well coordination number EOS (Peng and Wang, 1999), the EOS for square-well chain fluids (Gross and Sadowski,2000) and Paredes et al.'s (2001) EOS for polymers using square-well potential with variable width. We are not aware of any volume-explicit attractive term for real systems (i.e. three-dimensional bodies). Perhaps, this is because theoretically-based polymer equations of state are traditionally based on

pressure-explicit repulsive terms. But fortunately, in contrast to the canonical ensemble, exact analytical solution for equation of state of one dimensional fluids interacting with various potential models can be found in the isothermal-isobaric ensemble (Thompson, 1972). Our approach, therefore, is to use exact results for one-dimensional fluid interacting via square-well attractive potential as a means for analyzing and obtaining approximate form for the attractive contribution in three-dimensional fluids.

For a one-dimensional fluid in which nearest neighbors interact via the square-well potential:

$$u(|x|) = \begin{cases} \infty, & |x| < a \\ -\varepsilon, & a \leq |x| \leq \lambda a \\ 0, & |x| > \lambda a \end{cases} \quad (2)$$

where ε is the energy depth of the square well, a is length of the hard rod and λ is a characteristic well width parameter. The thermodynamic limit of the compressibility factor in isothermal-isobaric ensemble for a system of N one-dimensional molecules interacting via the potential given in equation 2 is found (Kihara, 1987) to be given by

$$Z_{sw} = 1 + p - \frac{(\lambda - 1) p q \exp\{-p(\lambda - 1)\}}{1 - q \exp\{-p(\lambda - 1)\}} \quad (3)$$

where $p = \beta P a$ is the dimensionless pressure for the one-dimensional fluid and $q = 1 - \exp(-\beta\varepsilon)$. The first two terms on the right hand side give exactly the expression for compressibility factor of hard-rod. The third term represents the attractive contribution (Z_{att}) due to cohesiveness of the rods.

The attractive part can be rearranged to give

$$\frac{p}{Z_{att}} = \frac{1}{(\lambda - 1)} - \frac{1}{(\lambda - 1)q} \exp\{p(\lambda - 1)\} \quad (4)$$

The above equation, which is for a one-dimensional fluid, is plotted in figure 1 for $\lambda = 1.5$ at different values of reduced temperature, $T^* = kT/\varepsilon = 1/\beta\varepsilon$. We also present a plot of p/Z_{att} against $\exp(p(\lambda - 1))$ for spherical square-well molecules in figure 2. The Z_{att} values used in figure 2 are obtained by subtracting the contribution due to repulsive forces from the overall compressibility factor of square-well simulation data given by Tavares et al (1995). Comparison of the two figures shows that the three-dimensional square-

well fluid qualitatively obeys the same functional relationship to the one-dimensional fluid except at low temperatures and low pressures where slight deviation from linearity is observed. This suggests that the attractive contribution of square-well fluids in the NPT ensemble may be approximated by the following relation:

$$Z_{att} = \frac{\alpha_1 \alpha_2 p e^{-\alpha_1 p}}{1 - \alpha_2 + \alpha_2 e^{-\alpha_1 p}} \quad (5)$$

where α_1 and α_2 are constants. While α_2 is considered to be temperature dependent the other constant α_1 is assumed to be a function of the well-width parameter (λ) only and therefore temperature independent. The two constants

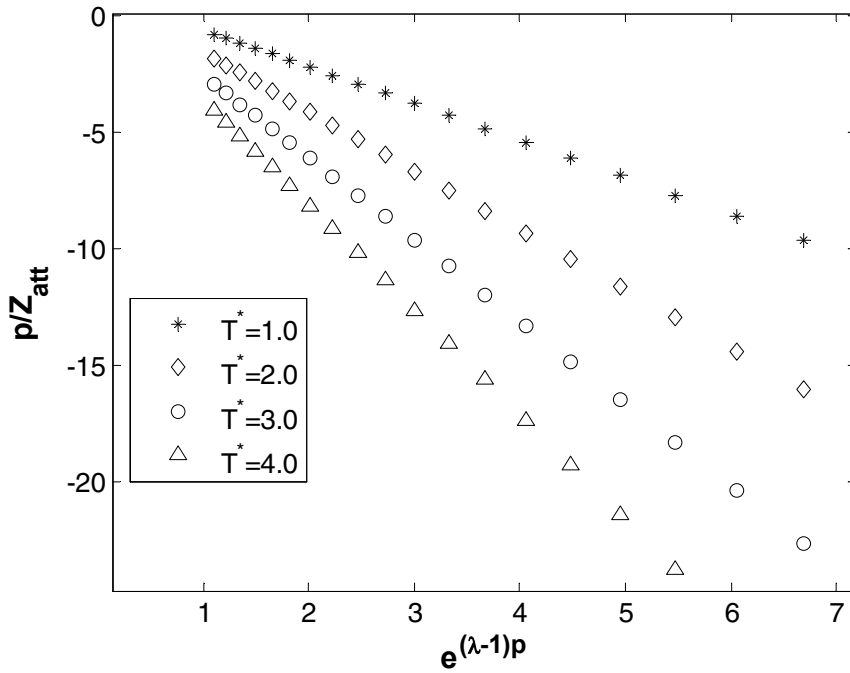


Figure 1. Plot of equation 4 with $\lambda = 1.5$ at 4 different reduced temperatures.

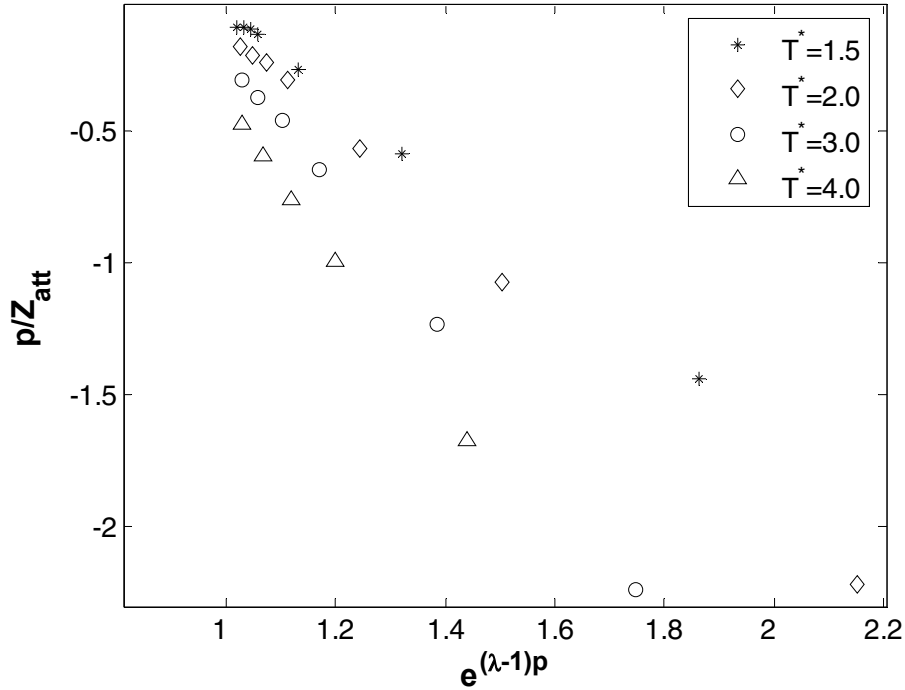


Figure 2. p/Z_{att} vs $\exp((\lambda-1)p)$ for three-dimensional square-well fluid. Points are deduced from simulation data of Taveras et al (1995) with $\lambda=1.5$.

are related to the known exact second virial coefficient for square-wells by the relation

$$B_{att} = \alpha_1 \alpha_2 \quad (6)$$

where

$$B_{att} = -\frac{2\pi}{3} \sigma^3 (\lambda^3 - 1) (e^{\beta\epsilon} - 1) \quad (7)$$

Contrary to our expectation, the above formulation was found to be unable to accurately represent available simulation data. Although it is qualitatively okay and satisfies low pressure and high pressure limits correctly, it fails to quantitatively fit the simulation data. An extension of the 1-D form is therefore proposed as follows:

$$Z_{att} = \frac{p(\alpha_1 \alpha_2 e^{-\alpha_1 p} + \alpha_3 \alpha_4 e^{-\alpha_3 p})}{1 - \alpha_2 - \alpha_4 + \alpha_2 e^{-\alpha_1 p} + \alpha_4 e^{-\alpha_3 p}} \quad (8)$$

This equation contains four parameters and it reduces to the 1-D form when $\alpha_3 = 0$ and $\alpha_4 = 0$. The parameters, α_2 and α_4 , are related to the other

parameters and the second and third virial coefficients of square-well fluid through the following equations:

$$\alpha_2 = -\frac{\alpha_3 B_{att} + C_{att} - B_{att}^2}{\alpha_1(\alpha_1 - \alpha_3)} \quad (9)$$

$$\alpha_4 = \frac{C_{att} + \alpha_1 B_{att} - B_{att}^2}{\alpha_3(\alpha_1 - \alpha_3)} \quad (10)$$

where $B_{att} = B - B_{HS}$ and $C_{att} = C - C_{HS}$. The expression for B_{att} is already given in equation 7. Similar to the second virial coefficient, the third virial coefficient of square-well fluid is also known exactly (Kihara, 1953). In the density form, the exact third virial coefficient for $1.5 \leq \lambda \leq 2.0$ is given by

$$C' = \left(\frac{2\pi}{3} \sigma^3 \right)^2 (1 - C_1 \Delta - C_2 \Delta^2 - C_3 \Delta^3) \quad (11)$$

where $\Delta = e^{\beta\epsilon} - 1$ and

$$C_1 = \frac{1}{5} (\lambda^6 - 18\lambda^4 + 32\lambda^3 - 15) \quad (12)$$

$$C_2 = \frac{2}{5} (\lambda^6 - 18\lambda^4 + 16\lambda^3 + 9\lambda^2 - 8) \quad (13)$$

$$C_3 = \frac{1}{5} (6\lambda^6 - 18\lambda^4 + 18\lambda^2 - 6) \quad (14)$$

The pressure virial coefficient can be calculated from the density virial coefficient by using the equation $C = (C' - B'^2) / RT$. The other parameters, α_1 and α_2 , are determined using simulation data and found to be $\alpha_1 = 0.5$ and $\alpha_3 = 6$ for the case of $\lambda = 1.5$.

Figure 3 shows a comparison of equation 8 to Zatt data deduced from simulation results of Tavares et al. (1995). The equation performs well at high reduced temperatures but deteriorates at low reduced temperatures.

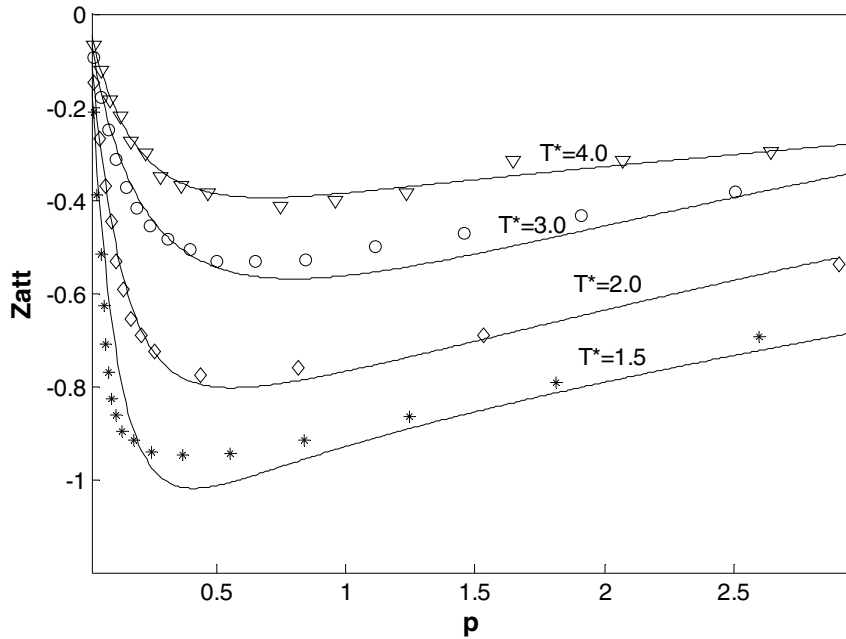


Figure 3. Attractive contribution to compressibility factor as a function of reduced pressure. The points are deduced from simulation data while the curves are drawn using Eq. 8.

Equation of State

The overall compressibility factor for a square-well chain molecule of m segments can be represented as

$$Z = Z_{HC} + mZ_{att} \quad (15)$$

Combining equations 1 and 8 according to the above equation yields the following:

$$Z = 1 + 4mp + \frac{3}{16}(1 - m + 4mp) \ln \left[\frac{3 + p}{3 + 25p} \right] + \frac{mp(\alpha_1\alpha_2e^{-\alpha_1p} + \alpha_3\alpha_4e^{-\alpha_3p})}{1 - \alpha_2 - \alpha_4 + \alpha_2e^{-\alpha_1p} + \alpha_4e^{-\alpha_3p}} \quad (16)$$

For square well spheres ($m=1$, $\lambda=1.5$) equation 16 compares favorably with simulation data of Tavares et al(1995) as can be seen in Figure 4.

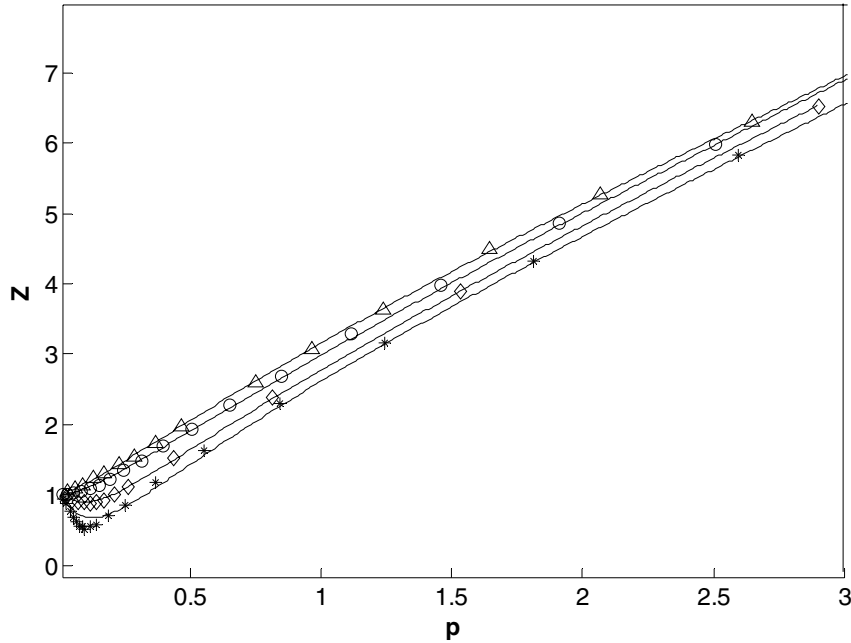


Figure 4. Compressibility factor as a function of reduced pressure. The points are simulation data while the curves are drawn using equation 15 with $\lambda=1.5$. Symbols have the same meaning as in Figure 3.

Chain Stiffness

In this section, we present the modeling of chain stiffness using the concept of non-additive size interactions. For spherical segments, non-additive size interactions are given by

$$\sigma_{ij} = (1 + \Delta_{ij}) \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad \Delta_{ij} \geq -1 \quad (18)$$

where Δ_{ij} is the nonadditivity parameter.

To model chain stiffness we need at least three units. Figure 5 shows the behavior of tangent spheres with additive interactions. The three spheres can move over a large angle. To restrict this movement (make the chain stiff) we introduce non-additive interactions between sphere 1 and sphere 3 as shown in figure 6. The size interaction between these spheres is now $(1 + \Delta_{ij})\sigma \geq \sigma$. Beyond a certain bending angle an overlap between the non-additive spheres 1 and 3 will prevent further bending. The maximum allowable bending angle can be controlled by the value of Δ_{ij} . Clearly for $(1 + \Delta_{ij})\sigma = 2\sigma$ no bending is possible. The extension of this idea to chains with many units is obvious. One can in fact have different stiffness in different segments of the same chain. Again every

sphere has to be considered a different species in order to get a stiff size-additive chain.

Applying the above procedure will require the pair correlation function for non-additive spheres. Hamad (1999) has tested the above model by performing molecular dynamic simulation of non-additive spheres. We are presently trying to develop analytical models for the pair correlation function of non-additive spheres in the NPT ensemble.

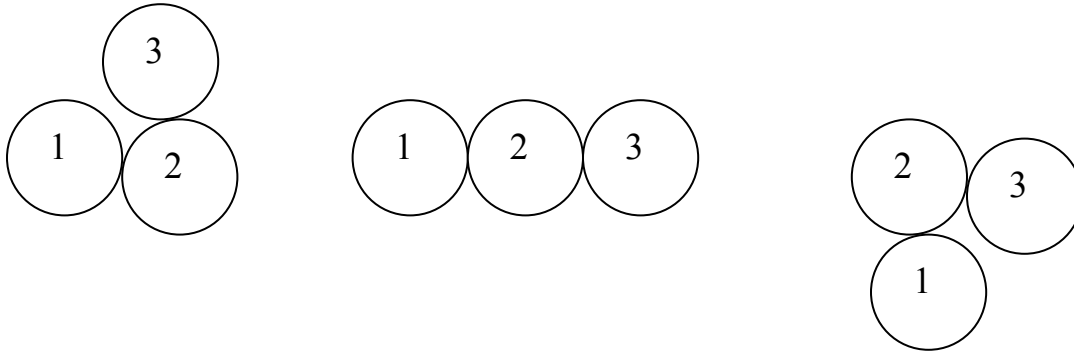


Figure 5: Chain flexibility in tangent additive hard spheres

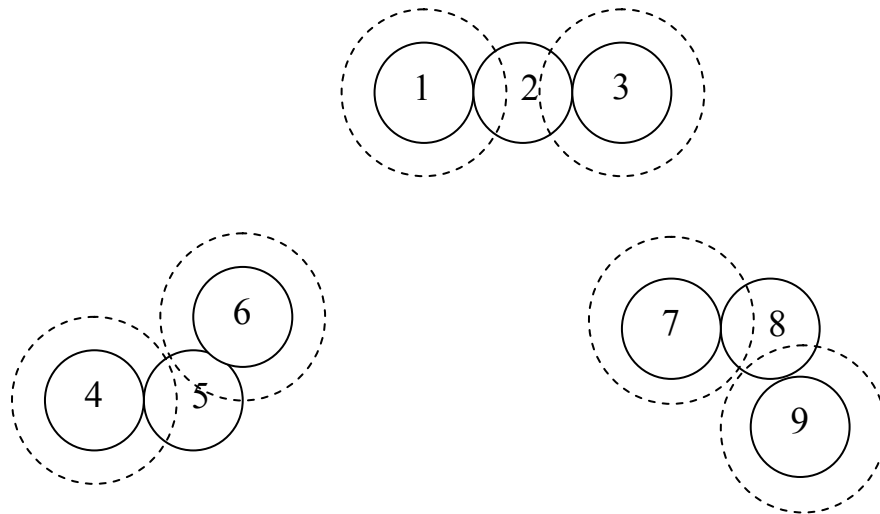


Figure 6: Limited chain flexibility in the presence of non-additive interactions (dashed lines) between every other segment.

Conclusions

We have developed an equation to account for attractive contribution to the compressibility factor of real fluids in NPT ensemble. The model equation complements the volume-explicit equation for hard-chains developed in a previous study by one of the present authors. The equation accurately represents simulation data at high pressure. We have also discussed how to model the stiffness of chain-molecules using the concept of non-additive size interactions.

Acknowledgement

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Literature Cited

Alder, B.J., D. A. Young, and M. A. Mark, "Studies in Molecular Dynamics: X. Corrections to the Augmented van der Waals Theory of Square-Well Fluid," *J. Chem. Phys.*, **56**, 2013 (1972).

Chen, S. S., and A. Kreglewski, "Applications of the Augmented van der Waals Theory of Fluids: I. Pure Fluids," *Ber. Bunsen-Ges, Phys Chem.*, **81**, 1048 (1977).

Chiew, Y. C., "Percus-Yevick Integral-Equation Theory for Athermal Hard-Sphere Chains," *Mol. Phys.*, **70**, 129 (1990).

Danner, R. P., and M. S. High, "Handbook of polymer solution thermodynamics," *AIChE.*, New York (1993).

Feng, W., and W. Wang, "A Perturbed Hard-Sphere-Chain Equation of State for Polymer Solutions and Blends Based on the Square-Well Coordination Number Model," *Industrial & Engineering Chemistry Research*, **38**, 4966 (1999)

Gross, J., and G. Sadowski, "Application of perturbation theory to a hard-chain reference fluid: an equation of state for square-well chains," *Fluid Phase Equilib.*, **168**, 183, (2000).

Hamad, E. Z., "Volume-Explicit Equation of State for Hard Spheres, Disks and Mixtures of Hard spheres", *Ind & Eng Chem Res.*, **36**, 4385 (1997).

Hamad, E. Z., "Volume-explicit equation of state for hard chains, their mixtures, and copolymers," *AIChE J*, **44**, 2766 (1998).

Hamad, E. Z., "Modeling Chain Stiffness, Fusion and Specific Interactions Using Non-Additive Size Interactions," *J. Chem Phys.*, **111**, 2 (1999).

Kihara, T, *Intermolecular Forces*, Wiley, New York (1976).

Lambert, S. M., Y. Song, and J. M. Prausnitz, "Equations of State for Polymer Systems," In *Equations of State for Fluids and Fluid Mixtures*, Sengers, J. V., R. F Kayser, C. J. Peters, and H. J. White (Eds), IUPAC, 523, (2000).

Paredes, M.L.L., R. Nobrega, and F. W. Taveras, "An analytic equation-of-state for mixture of square-well chain fluids of variable well width," *Fluid Phase Equilib.* **179**, 231, (2001)

Rodgers, P. A., "Pressure-Volume-Temperature Relationships for Polymeric Liquids: A Riview of Equations of State and Their Characteristic Parameters for 56 polymers," *J. Applied Polymer science*, **48**, 1061 (1993).

Song, Y., S. M. Lambert, and J. M. Prausnitz, "Equation of state for mixtures of hard-sphere chains including copolymers," *Macromolecules*, **27**, 441 (1994)

Tavares, F. W., J. Chang, and S. I. Sandler, "Equation of state for the square-well fluid based on the dimer version of Werhaims's perturbation theory," *Molecular Physics*, **86**, 1451 (1995).

Thompson, C. J., "One-dimensional Models – Short Range Forces," In *Phase Transitions and Critical Phenomena*, Domb C., and M. S. Green (Eds), Academic Press, NY, Chap **5**, 184, (1972).