Prediction of volumetric properties of polymer melts using new perturbed hard-chain equation of state

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ARTICLE INFO

ABSTRACT

A perturbed hard-sphere equation of state (PHS EOS) has been previously employed for modeling the volumetric properties of some molten metals and ionic liquids (S.M. Hosseini, M.M. Papari, F. Fadaei-Nobandegani, J. Moghadasi, J. Non-Cryst. Solids 358 (2012) 1753–1758). In this work, the chained version of our previous PHS EOS has been developed for predicting the volumetric properties of 19 polymer melts including homopolymers and copolymers. The performance of the proposed EOS has been checked by comparing the results with 2273 literature data points for the specific volumes over wide temperature and pressure range, the overall average absolute relative deviation (AARD) was found to be 0.33%. Uncertainty of specific volume calculations was of the order of $\pm 2.0\%$. Isothermal compressibility coefficient (κ_T), of studied polymer melts has also been estimated and compared with those obtained by the use of Tait equation; from 1349 data points examined, the AARD was found to be 3.91%.

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1. Introduction

Thermophysical property investigations represent an underappreciated area of polymer science and engineering due to their promising applications in prediction of polymer–polymer miscibility, evaluation of start and progress of chemical reactions in polymer melts in cases when volume effects accompany the reaction and so on.

This work is the continuation of our studies on the modeling of the thermophysical properties of chained fluids (i.e., polymeric systems) using equation of state (EOS) method. Although some experimental data for thermophysical properties of polymer melts exist, prediction of these properties is still an important task considering polymeric liquids have been in focus as materials offering many highly promising applications [1–5]. Under this circumstance, the development of modern EOSs for predicting the thermophysical properties of homopolymers and copolymers can be considerably useful to decide whether the use of these fluids

could be extended from the laboratory level to large-scale industrial applications. The specific volume and isothermal compressibility of homopolymer and copolymer melts are important issues with relevancy in many applications where these liquids are considered as fluid design.

Physically based EOSs, derived by applying principles of statistical mechanics, have continuously been developed and improved upon over the past 4 decades. Modern equations of state aim at highly non-ideal systems, such as polymers and associating compounds [6,7]. Since the hard-sphere concept cannot be used successfully for equations of state of highly non-ideal systems (from size point of view e.g., polymers); the prediction of the properties of these fluids requires a more sophisticated method exemplified by the simplified perturbed hard-chain theory (SPHCT) [8] and some approaches based on the statistical associating fluid theory (SAFT) [9] including statistical associating fluid theory-variable range (SAFT-VR) equation [10], the soft-SAFT equation [11], the truncated perturbed chain polar SAFT (tPC-PSAFT) equation [12] and the square-well for chain fluids (SWCFs) equation [13].
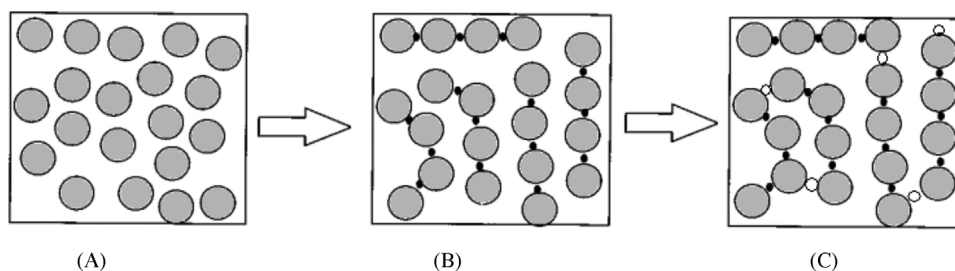
A literature survey of some previous efforts on the application of equations of state for polymeric systems can be discussed herein based on the various approaches over a wide range of pressures and temperatures with the works of Kontogeorgis et al. [14], Sato et al. [15], and Liu and Hu [16] to the very recent works by Hosseini et al. [17,18].

Kontogeorgis et al. [14] used the van der Waals equation of state to correlate vapour-liquid equilibrium data of polymer solutions. They proposed a method to calculate the interaction parameter a

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Fig. 1. Schematic representation of the physical basis of the new PHC model for polymer melts. The reference fluid consists of hard-spheres (A step) that form chains (e.g., tetramers) through covalent bonds (B step). The last step is to account for the weak dispersion forces between hard-chains (C step).

and co-volume b in the equation of state for polymers from two volumetric datasets at low pressure.

Polymeric systems have also been modeled using the SAFT-type equations of state and their modified versions in literature. For instance, Pan and Radosz [19] used the SAFT equation for copolymers to describe the fluid–liquid and solid–liquid transitions in some solutions involving polymers as well as copolymers [20]. Gross et al. [21] have also extended the perturbed chain SAFT (PC-SAFT) model [22,23] for copolymers. The authors modeled phase equilibrium for ethylene copolymer systems with random alternating chains in a wide range of compositions (including homopolymer) and with molecular weights. Tihic et al. [24,25] developed a group contribution model for simplified PC-SAFT equation to predict their pure parameters. If pure polymer parameters in SAFT-type equations are obtained only from density data, poor predictions of phase equilibrium may result. Therefore, the group contribution method for parameter estimation was developed through the adjustment of vapour pressure and density data based on a database of 400 components of low molecular weight.

Recent work by Hosseini et al. [26] led to assessment of a new perturbed hard-sphere EOS for modeling the pressure–volume–temperature (PVT) data of some molten metals and ionic liquids. They have constructed an equation of state formed by a primary hard-sphere (HS) model chosen as reference physical model and a perturbation part added to the reference system. In this respect, the hard sphere equation proposed by Malijevsky and Veverka [27] (MV) has been chosen as reference term. This term has a form of the rescaled virial series and uses the first seven virial coefficients. They have also evaluated two temperature-dependent parameters appeared in the perturbed Malijevsky–Veverka equation of state (PMV EOS) via the corresponding states correlation method.

The major point of this work is to assess the performance of chained version of previous PHS EOS [26] to present a new perturbed hard-chain (PHC) EOS for predicting some thermophysical properties of polymer melts including homopolymers and copolymers over wide range of temperatures and pressures. This issue can be regarded as the novelty of the present work. In the case of homopolymers, we also compare the results with our preceding works when predicting the specific volumes (V^S) at elevated pressures.

2. Theory

2.1. Theory of perturbed hard-chain EOS

The most promising method for the calculation of thermophysical properties of polymeric liquids today is the use of equations of state that are based on perturbation theory of liquids. This theory considers an appropriate reference system (e.g., hard-sphere) to describe the repulsive interactions of the molecules, whereas

long range attractions or the formation of hydrogen bonds are considered as perturbations of that reference system. Moreover, the chain-like structure of polymer molecules is explicitly taken into account.

In perturbation theory the Helmholtz free energy, A of the system is expanded in the inverse temperature around that of a reference system whose thermodynamic structural properties are known. The first-order expansion of the Helmholtz free energy is of the form:

$$\left(\frac{A}{Nk_BT}\right) = \left(\frac{A_0}{Nk_BT}\right) + \left(\frac{A_1}{Nk_BT}\right) \qquad (1)$$

where A_0 is the Helmholtz free energy of the hard-chain reference system and A_1 is the first-order perturbation term for the Helmholtz free energy. N is the number of molecules, k_B is the Boltzmann constant, and T is temperature. A_0 is derived from knowledge of the equation of state and the radial distribution function (RDF) of the reference fluid.

According to the perturbed hard-chain theory, the molecule is considered to be constituted by chains of freely jointed tangent hard bodies, or segments. This model takes into account the Chiew [28] equation of state for hard chains as the reference system and adds an attraction term as the perturbation. To show schematically the physical basis underlying PHC model in the development of new PHC EOS for polymer melts, Fig. 1 has been presented. The reference fluid consists of hard-spheres (A-step) that form chains (e.g., tetramers) through covalent bonds (B-step). The last step is to account for the weak dispersion forces between hard-chains (C-step). This scheme has been mathematically expressed for any PHC EOS by the following equation for the Helmholtz free energy per molecule:

$$\left(\frac{A}{Nk_BT}\right) = \left(\frac{A^{\text{HS}}}{Nk_BT} + \frac{A^{\text{chain}}}{Nk_BT}\right)_0 + \left(\frac{A^{\text{disp.}}}{Nk_BT}\right)_1 \qquad (2)$$

where subscripts 0 and 1 refer to the hard-chain reference system and the perturbation part, respectively.

The compression factor of PHC EOS may be obtained by differentiating the corresponding Helmholtz free energy term with respect to the density or packing fraction, η [28]:

$$Z^{\text{PHC}} = \frac{\eta}{Nk_BT}\left(\frac{\partial A}{\partial \eta}\right) = Z^{\text{HC}} + Z^{\text{Pert.}} \qquad (3)$$

where Z^{HC} represents the hard-chain reference system perturbed by the long-range attraction ($Z^{\text{Pert.}}$) for the representation of the attractive forces.

2.2. New perturbed hard-chain equation of state

Based on the abovementioned derivation, the general frame of the new PHC EOS can be derived in terms of the compression factor: