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ORIGINAL PAPER

A simplified equation of state for polymer melts from perturbed Yukawa hard-sphere chain

S. M. Hosseini · M. M. Papari · J. Moghadasi

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Abstract This paper addresses the modeling of the pressure–volume–temperature (PVT) properties of 14 polymer melts using simplified Yukawa hard-sphere-chain equation of sate (EOS) plus first-order perturbation theory. Three pure-component parameters appeared in the EOS have been determined via the volumetric data. These parameters reflect the segment number, non-bonded segment–segment interaction energy, and segment size. Likewise, this study considered chains that interact through a range-parameter of Yukawa potential with 1.8. The reliability of the proposed model has been assessed by comparing the results with 1,315 experimental data points over a broad range of pressures and temperatures for which, their measured values were available in the literature. Our calculations on the specific volume of studied liquid polymers reproduce very accurately the experimental PVT data. The overall average absolute deviation of the calculated specific volumes from literature data was found to be 0.89 %.

Keywords Equation of state · Polymer melts · PVT

Abbreviations

PEO	Poly(ethylene oxide)
PES	Poly(ether sulfone)
PE	Poly(ethylene)
PB	Poly(1-butene)
PO	Poly(1-octene)
PMPS	Poly(methyl phenyl siloxane)

S. M. Hosseini (✉) · J. Moghadasi
Department of Chemistry, Shiraz University, 71454 Shiraz, Iran
e-mail: seied_mostafa_hosseini@yahoo.com

M. M. Papari
Department of Chemistry, Shiraz University of Technology, 71555-313 Shiraz, Iran

PDMS	Poly(dimethyl siloxane)
PVME	Poly(vinyl methyl ether)
PVC	Poly(vinyl chloride)
PVF	Poly(vinylidene fluoride)
PS	Poly(styrene)
PAMS	Poly(α-methyl styrene) Polyesters
PPG	Poly(propylene glycol)
PEG	Poly(ethylene glycol)

List of symbols

a_{i}	Values of coefficients in Eq. (5) for the case of $\lambda = 1.8$
AAD	Average absolute deviation (%)
K	Boltzmann's constant (J K^{-1})
NP	Number of data points
P	Pressure (Pa)
T	Absolute temperature (K)
V	Specific molar volume (m^3 mol^{-1})
$\mathrm{M}M_W$	Monomer molecular weight (g mol^{-1})
m	Segment number
R	Universal gas constant (J mol^{-1} K^{-1})

Greek letters

η	Yukawa Hard-sphere-chain packing fraction
ρ	Segment density (mol m^{-3})
σ	Segment diameter (nm)
ε	Non-bonded segment–segment interaction energy (J)
λ	Range parameter of attractive forces

Superscripts

HSC	Hard-sphere-chain reference system
pert	Perturbed system

Superscripts

f	Freezing point

Introduction

Knowledge of the thermophysical properties of polymers is a prerequisite for the design and optimization of their production plants. They are widely used for industrial and residential purposes. The first synthetic cyclic polymers that were prepared and characterized are the poly(dimethylsiloxanes) (PDMS), which were reported in 1977 [1]. Polystyrene (PS) is one of the most widely used plastics, having applications in multiple industries for packaging, appliances, construction, automobiles, electronics, furniture, toys, house wares, and luggage. The major applications of polyethylene oxide (PEO) are related to textiles, cosmetics, antifoaming agents, and others (chemical inter-mediates, ink, and dye solvents, demulsifiers, plasticizers, etc.) [2, 3]. Poly(ethylene glycol) (PEG), along with PEO, belongs to a family of polymers that exhibit very different thermodynamic properties according to the molecular weight. PEG is well-known for its hydrophilicity, water solubility, lack of toxicity, and excellent biocompatibility. It has been combined physically or chemically with many therapeutic polymeric systems, either proteins and particles or implants, to make them stealthy with respect to natural body defences [4–6]. High viscous and adhesion of poly(vinyl methyl ether) (PVME) has made it applicable for coatings; aqueous tackifier; adhesion promoter of non-adhering materials to glass, metal, and plastics; copolymers used in pharmaceuticals; and lens arrays for optical device (as thermographic copying material).

Therefore, accurate knowledge of thermophysical properties of polymeric materials is valuable as it is required to decide whether the use of these fluids could be extended from the laboratory level to large-scale industrial applications. To improve the above-mentioned processes based on liquid polymers, the thermophysical properties of these liquids must be exactly characterized. In other words, the design of industrial processes and new products based on polymer melts can only be achieved when their thermophysical properties are exactly known. Under this circumstance, the development of equation of states (EOSs) and methods for modeling their thermophysical properties such as PVT properties can be considerably useful.

Physically based equations of state, derived by applying principles of statistical mechanics, have continuously been developed and improved upon over the past four decades. Modern equations of state aim at highly nonideal systems, such as polymers or associating compounds [7, 8].

Yukawa hard-sphere-chain (YHSC) model have been widely used to theoretically model a broad range of fluids in liquid state physics [9]. It has found success in modeling the thermodynamics of simple liquids, colloidal suspensions, electrolytes, and molten salts. This model involves hard-sphere repulsion as well as a long-range attraction and that it describes many physical phenomena involving screened interactions, for example, strong electrolytes and polymer solutions. On the other hand, by varying a single parameter λ, the range of attractive forces can be easily adjusted with different interactions encountered in many physical systems. It should be noted that the local structure of the YHSCs is strongly affected by the range parameter of the potential [10]. With 1.8, the model has been well-found to approximate the tail of the Lennard-Jones potential. In the perturbative scheme studied in this study, the segments are already connected. The hard-sphere chains are chosen as the reference system and the reference system will be perturbed by a potential.

In this study, three pure-component parameters appeared n the perturbed hard-sphere chain (PHSC) EOS must be determined by regressing vapor pressures or liquid densities as well-established approach for compounds of low molecular weight. However, the first approach cannot be hold for macromolecules: Neither vapor-pressure data nor heats of vaporization are accessible for polymers. Moreover, caloric data (liquid heat capacity data) cannot be used for parameter regression, because the ideal gas contribution to the heat capacity can only be estimated with considerable uncertainty. In this regard we aim to utilize the liquid density data for the determination of three pure-component parameters of the proposed model. The major point of this study is that; there is no requirement to macroscopic pure-component constants due to fact that their values rarely available in the literature (e.g., freezing and glass transition data). To other word, knowing of only three adjustable pure-component constants is sufficient to present an accurate EOS for liquid polymers.

Theory

In the framework of the first-order perturbation theory, the compression factor of perturbed Yukawa hard-sphere chain (PYHSC) may be written as [10, 11]:

$$Z_{PYHSC} = \frac{P}{\rho kT} = Z^{HSC} + Z^{Pert.} \tag{1}$$

where P is the pressure, ρ is the number density of segments, and kT is the thermal energy per segment. The first- and second-term of the right hand of Eq. (1) represent contributions to the compressibility factor from the reference HSC potential (Z^{HSC}) and the attractive perturbation potential ($Z^{\mathrm{Pert.}}$), respectively.

Regarding the polymer melts, we aim to combine the YHSC model as the reference system by the contribution from the attractive Yukawa tails as the perturbation part. The HSC compression factor for the reference model is that of statistical associating fluid theory (SAFT) equation previously developed by Chapman et al. [12] which is given below:

$$Z_{\mathrm{SAFT}}^{\mathrm{HSC}} = m\frac{(1+\eta+\eta^2-\eta^3)}{(1-\eta^3)} - (m-1)\frac{(1+\eta-\eta^2/2)}{(1-\eta)(1-\eta^2/2)} \tag{2}$$

and

$$Z^{Pert.} = -\frac{12m\eta}{T_r} I(\eta, m; \lambda) \tag{3}$$

where m is the segment number and η is the segment packing fraction of Yukawa hard-spheres, defined as:

$$\eta = {}^{\pi\rho\sigma^3}\!/_{6} \tag{4}$$

Here, ρ is the number density of Yukawa segments with diameter σ.

$I\,(\eta,\ m;\ \lambda)$ is related to the average interchain function for HSCs in the context of the Percus–Yevick (PY) integral equation theory by Chiew [13, 14]. Using the PY numerical solution, $I\ (\eta,\ m;\ \lambda)$ has been previously evaluated in the literature [15, 16] for value of $\lambda = 1.8$ as a power series in segment packing fraction, η:

$$I(\eta, m;\ \lambda = 1.8) = \sum_{i=0}^{2} a_i\,(i+1)\,\eta^i \tag{5}$$

The values of coefficients a_i have been provided in Table 1.

Table 1 Value of coefficients in Eq. (5) for the case of $\lambda = 1.8$

I	a_{0i}	a_{1i}	a_{2i}
0	0.864000	−0.444375	−0.170239
1	0.697700	0.866242	0.713 402
2	−0.239900	−0.638078	−0.845203

Table 2 Pure-component parameters of the PYHSC EOS for polymer melts

Polymer	MM_W (g/mol)	ε/k (K)	σ (nm)	(m/MM_W)
PEO	44.00	778.77	0.5005	0.026319
PES	232.25	567.97	0.4060	0.007042
PE	28.00	482.97	0.2993	0.04435
PMPS	136.08	456.70	0.4999	0.011008
PEG	60.00	349.96	0.38974	0.024111
PDMS	74.08	591.82	0.42900	0.021598
PVME	58.00	573.26	0.33007	0.025348
PVC	62.50	540.90	0.3979	0.018257
PVF	64.00	576.10	0.3240	0.018048
PS	104.00	749.00	0.4477	0.011961
PPG	74.00	660.00	0.4823	0.015541
PB	56.00	526.51	0.3267	0.020911
PO	112.00	597.20	0.50999	0.014563
PAMS	118	577.70	0.42299	0.015518

MM_W represents the monomer molecular weight

Results and discussion

To utilize the proposed EOS three pure-component parameters of liquid polymers must be characterized. In this regard, Table 2 has been presented to provide the required pure-component parameters (m, σ, ε/k) for studied systems as well as their monomer molecular weight. The pure-component parameters have been adjusted over the appropriate temperature and pressure range covered by the available PVT data.

Figure 1 has been presented to illustrate the correlation of freezing temperature and the non-bonded interaction energy between two Yukawa segments, ε to accept the values of ε/k reported in this study. As a matter of fact, Fig. 1 shows the degree of correlation of T_f values with ε/k in dimensionless form.

To show the distinctive feature of this study, a typical plot for the calculated values of $P/\rho RT$ using Eq. (1) versus temperature for poly(1-octene), PO has been exemplified in Fig. 2. As it is impressive from Fig. 2, the data at constant T will be nearly proportional to P. Since the variable on the vertical axis is $P/\rho RT$, this proportionality would imply ρ to be independent of P, which means incompressibility of liquid polymers. So, the Eq. (1) could successfully describe a liquid state which apparently is not far from incompressibility. The only way we can see is that, according to the fitted parameters, the Yukawa hard-sphere packing fraction, η comes out to be slightly close to unity.

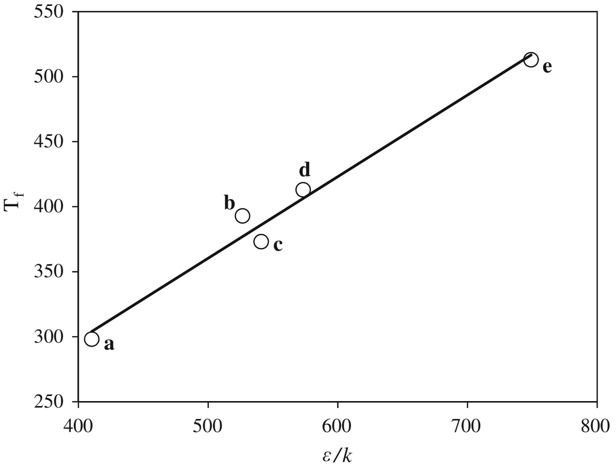

Fig. 1 Correlation of ε/k values with T_f for some examples of studied polymer melts. The *open circles* represent our calculations in this study and (*continuous line*) indicates the straight-line passing through the points. PEG (*a*), PB (*b*), PVC (*c*), PVME (*d*), and PS (*e*)

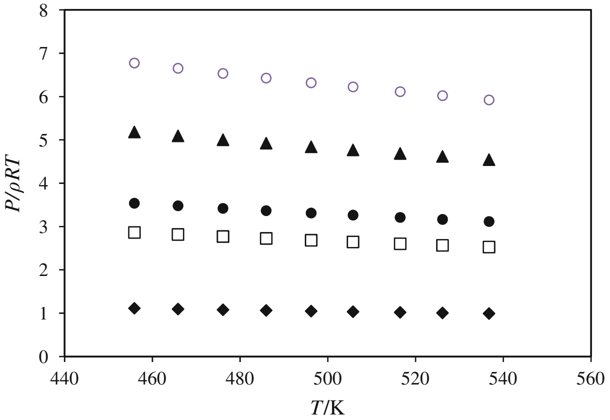

Fig. 2 A typical plot for the calculated ($P/\rho RT$) using the proposed EOS (Eq. (1)) versus temperature for PO at 30 MPa (*filled diamond*), 80 MPa (*open square*), 100 MPa (*filled circle*), 150 MPa (*filled triangle*), and 200 MPa (*open circle*)

At first, we examine the predictive power of PYHSC EOS for the prediction of the specific volume of studied polymer melts. For this purpose, 14 liquid polymers from various classes have been chosen, for which their measured values were available in the literature [17]. Our calculation results were summarized as average absolute deviation percent (AAD %) from literature data [17] in Table 3. As the Table 2 shows from 1,315 data points examined for studied polymers over a broad pressure ranging from 0.1 to 200 MPa and the temperature ranging from 293 to 557 K, AAD was found to be 0.89 %. It should be mentioned that, the uncertainty

Table 3 Average absolute deviation (AAD in %) of the predicted specific volume of the liquid polymers studied in this work using the proposed model, compared with the measurement [17]

Polymer	ΔP (MPa)	ΔT (K)	NP[a]	AAD[b] (%)	MD[c] (%)
PEO	0.1–40	353–393	045	0.45	−1.02
PES	0.1–100	497–569	081	1.42	2.46
PE	0.1–200	452–472	063	0.55	−1.39
PMPS	10–100	339–397	090	0.98	1.85
PEG	0.1–40	298–328	040	0.65	−1.17
PDMS	0.1–202	291–423	095	1.02	2.16
PVME	0.1–120	311–415	080	1.20	2.07
PVC	0–200	373–423	085	0.39	0.98
PVF	0.1–120	453–493	045	0.78	1.98
PS	0.1–200	391–557	185	1.42	2.88
PPG	0.1–100	293–373	099	0.61	−1.74
PB	0.1–200	454–534	166	1.30	−2.41
PO	0.1–200	454–537	189	0.62	−1.52
PAMS	0.1–160	481–522	063	0.53	−1.64
Overall			1,315	0.89	

[a] NP represents the number of data points examined

[b] $\mathrm{AAD} = 100/\mathrm{NP}\sum_{i=1}^{\mathrm{NP}} \left|V_{\mathrm{i,Cal.}} - V_{\mathrm{i,Exp.}}\right|/V_{\mathrm{i,Exp.}}$

[c] MD represents the maximum deviation percent of the estimated specific volumes, V

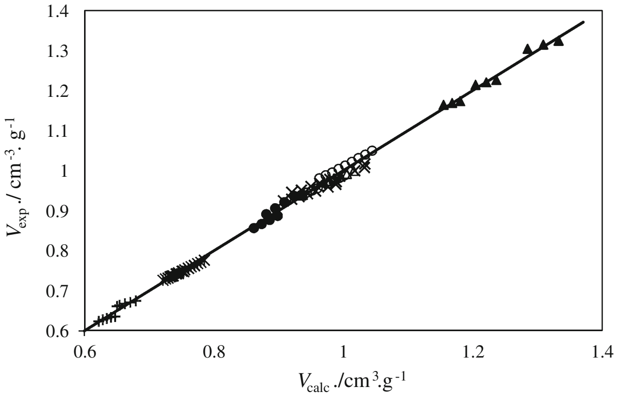

Fig. 3 The linear relationship between experimental-specific volumes (*solid straight-line*) versus calculated-specific volumes (*markers*) of liquid polymers at compressed states: PVC (*asterisk*), PVF (*plus*), PS (*times*), PEG (*filled circle*), PPG (*open circle*), PAMS (*open triangle*), and PE (*filled triangle*). The experimental data have been taken from the literature [17]

of our calculations was of the order of ±2.88 %. To show the accuracy of this study, the maximum deviations (%) of the predicted densities using Eq. (1) from the measured values for all liquid polymers studied in this work, have also been included in Table 3.

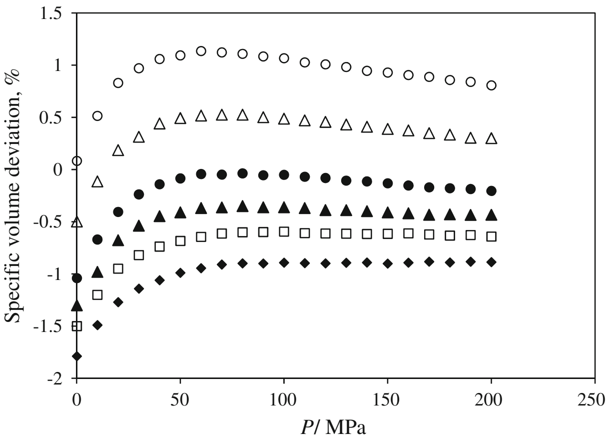

Fig. 4 Deviation plot for the estimated isothermal specific volume of liquid poly(1-octene) from zero up to the elevated pressures at 465.8 K (*filled diamond*), 476 K (*open square*), 486 K (*filled triangle*) 496.2 K, 516.5 K (*open triangle*), and 536.75 (*open circle*), compared with experiment [17]

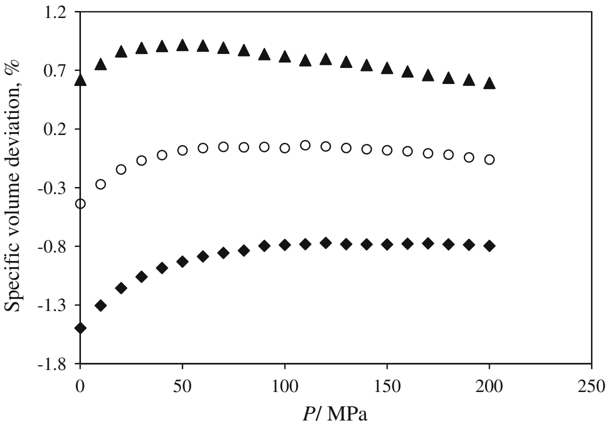

Fig. 5 Deviation plot for the estimated isothermal-specific volume of liquid poly(ethylene) from zero up to the elevated pressures at 452 K (*filled diamond*), 462.8 K (*open circle*), and 472.75 (*filled triangle*), compared with experiment [17]

Besides, it was shown in Fig. 3 that the experimental specific volumes of different classes of polymers studied in this study, displayed a very good linear relationship with those obtained by the use of the proposed EOS from low-density (LD) data to high-density (HD) ones. The data were randomly chosen from the literature [17] over the entire pressure and temperature range from 0.1–200 MPa and 293.15–557 K, respectively. The accuracy of predicted densities was impressive for a wide range of temperatures.

To illustrate how the proposed model passes through the experimental points, four deviation plots for the calculated isobaric and isothermal-specific volume of

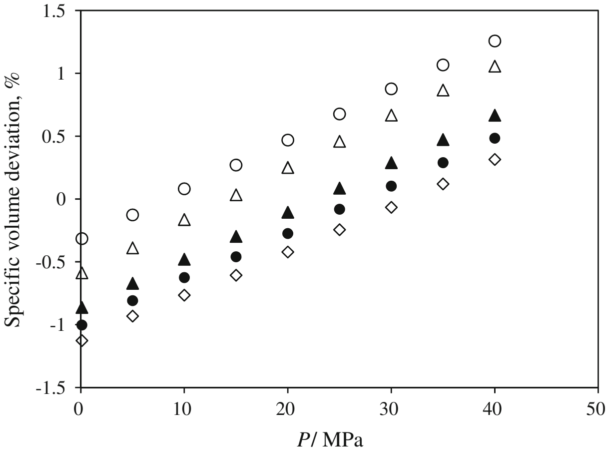

Fig. 6 Deviation plot for the estimated isothermal-specific volume of liquid poly(ethylene oxide) from zero up to the elevated pressures at 353 K (*open diamond*), 363 K (*filled circle*), 373.8 K (*filled triangle*), 388.7 K (*open circle*), and 393.4 K (*open triangle*), compared with experiment [17]

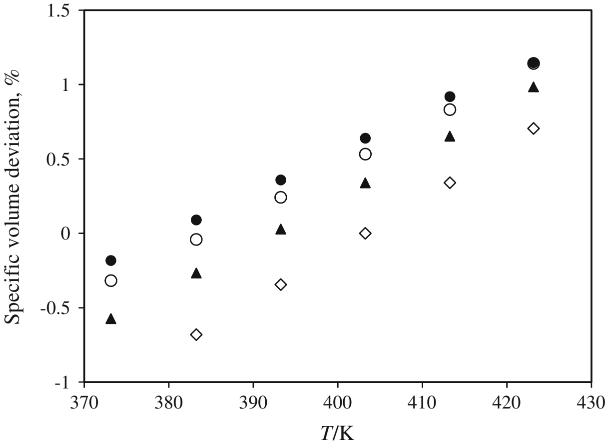

Fig. 7 Deviation plot for the estimated isobaric-specific volume of liquid poly(vinyl chloride) at several temperatures; 10 MPa (*filled circle*), 20 MPa (*open circle*), 40 MPa K (*filled triangle*), and 80 MPa (*open diamond*), compared with experiment [17]

some liquid polymers, studied in this study have been shown in Figs. 4, 5, 6, 7. As it clears from Figs. 4, 5, 6, 7 the predicted-specific volumes from PYHSC EOS were in good agreement with those obtained from the measurements [17]. This is the advantageous feature of Eq. (1) because most of the equations of state cannot describe the compressed liquid region over wide range of pressure.

Finally, we have extended PYHSC for modeling the PVT properties of liquid polymers. Knowing just two pure-component parameters, ε/k and σ, which can be readily adjusted by fitting with experimental PVT data is sufficient to predict the

PYHSC EOS. The equation-of-state works over a wide range of temperatures from under cooled melting point up to 550 K and pressures with very good accuracy.

In conclusion, the study presented here showed the entire success in describing volumetric properties of polymer melts using a simplified EOS combined from the YHSC plus the first-order perturbation theory with sufficiently few parameters. It should be mentioned that the extension of proposed EOS for modeling the volumetric properties of polymer solutions remains for a future study.

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