On the Effect of the Hard-sphere Term on the Statistical Associating Fluid Theory Equation of State

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The hard-sphere system is the reference fluid for most versions of the statistical associating fluid theory (SAFT) equation of state (EoS). In the SAFT-type equations of state, the hard-sphere equation directly affects the reference term and through the radial distribution function, indirectly affects the chain and association terms. Although there are various EoSs for describing the thermodynamic behavior of the hard-sphere fluid, the Carnahan-Starling EoS has traditionally been used to express the hard-sphere contribution in SAFT-type models. In this work, we integrated eight hard-sphere EoS in the simplified SAFT EoS and parameterized the resulting EoS with pressure-density-temperature data. Then, using modified versions of the simplified SAFT (SSAFT), we calculated the thermodynamic properties including pressure, density, temperature, saturated vapor-pressure, isochoric heat capacity, isobaric heat capacity, and speed of sound, for ethane, butane, hexane, and hexatriacontane, and compared the results. In general, the results of calculations show that although the modified Carnahan-Starling, Kolafa, and Carnahan-Starling EoSs have had the best results, considering the simplicity and straightforwardness of the Carnahan-Starling EoS, this EoS is a reasonable choice for developing SAFT-type equations of state.

Keywords: Hard-sphere fluid, Radial distribution function, Thermodynamic modeling, Statistical Associating Fluid Theory (SAFT), Equation of state

INTRODUCTION

Molecularly-based EoSs have become increasingly popular tools for thermodynamic modeling [1-4]. SAFT equation of state (EoS) is a molecular-based model, based on the perturbation theory of Wertheim (TPT1) [5-8]. The SAFT EoS was formulated and parameterized in the late 1980s and early 1990s, first by Chapman *et al*. [9-11] and then by Huang and Radosz [12,13]. Since then, various modifications of the SAFT EoS have been developed. Recent progress in developing and implementing SAFT-type EoSs has already been summarized through several extensive reviews [14-16]. In general, SAFT EoS is expressed as follows:

$$A^{res} = A - A^{ideal} = A^{hs} + A^{disp} + A^{chain} + A^{as} \tag{1}$$

where A, A^{ideal}, A^{res}, A^{hs}, A^{disp}, A^{chain} and A^{assoc} are total, ideal, residual, hard-sphere, dispersion, chain, and association Helmholtz energy, respectively. In addition, the polar, electrolyte, and other terms also can be added to SAFT EoS [14,15]. However, for non-polar and non-associating fluids, the SAFT is expressed as the sum of the hard-sphere, dispersion, chain terms.

All expressions used in the development of the SAFT EoS for pure fluids are a function of temperature and density by using several pure-component parameters. Experimental data is used to estimate these adjustable parameters, which are theoretically linked to size, shape, and molecular interactions. [17]. Typically, the SAFT-type EoSs have three and five parameters for non-associating and associating fluids, respectively. The traditional method to determine SAFT-type EoSs parameters is to use saturated vapor pressure and liquid phase density data, but there are other alternative methods such as using pressure-density-

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temperature data [18] and critical constants [19].

In most widely used versions of the SAFT EoS such as SAFT-HR [12], PC-SAFT [20], and SAFT-VR-Mie [21], the hard-sphere is considered as the reference fluid. The reason for this choice lies in the results of molecular simulation, which shows that the hard-sphere fluid can be a good reference for approximating soft repulsive interactions [22]. Despite the simplicity of the hard-sphere system, it has played a fundamental role in the advancement of various fields of science, including EoSs [23]. In the definition of a hard-sphere fluid, as its name suggests, molecules are considered to be perfectly spherical with no attraction interactions. Accordingly, the hard-sphere potential is defined as follows:

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \qquad (2)$$

where r and σ are the intermolecular distance and sphere diameter, respectively. This simple potential has been used for many years as a basis for calculating the thermodynamic behavior of various fluids, and many studies have been done on it. Generally, in analytical expressions for the hard-sphere EoS, the compressibility factor (Z) is expressed as a function of the packing fraction (η). In the theory, the maximum value of the packing fraction (η_c) is equal to 0.74048 so the compressibility factor should have a pole at η_c [23].

Various forms of formulation for the hard-sphere (HS) EoS have been developed in the literature, but the virial equation is a unique equation of state that can be calculated precisely in statistical thermodynamics and can be systematically improved by adding new terms. However, only the first to fourth virial coefficients for the hard-sphere can be calculated analytically, and subsequent coefficients must be determined numerically [23]. The fifth to sixteenth virial coefficients are available in the literature [24,25]. Unfortunately, the convergence of the calculated virial coefficients is very slow, so approximations are needed to develop the hard-sphere EoS. The use of approximations such as Pade and fitting molecular simulation data are alternatives to the development of the hard-sphere EoS [23].

The simplest hard-sphere equation is presented by Van der Waals (VDW):

$$Z = \frac{1}{1 - 4\eta} \qquad (3)$$

Since then, many analytical expressions have been proposed for hard-sphere EoS [23]. Undoubtedly, the most famous and widely used version of the HS EoS is the Carnahan-Starling (CS) equation of state [26].

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \qquad (4)$$

Although the CS EoS is simple and relatively accurate, CS EoS, like VDW EoS, has an error in accurately predicting the expected pole at η_c. The maximum packing fraction of VDW EoS ($\eta_{Pole} = 0.25$) is much less than the theoretical value and the maximum packing fraction of the CS EoS ($\eta_{Pole} = 1$) is higher than η_c. Therefore, CS EoS in packing fractions higher than η_c has no physical meaning [27].

The Carnahan-Starling EoS has traditionally been used to represent the hard-sphere contribution in most versions of SAFT-type EoSs, including original SAFT [11], SAFT-HR [12], SSAFT [28], PC-SAFT [20], and SAFT-VR-Mie [21]. Most of the modifications applied to SAFT EoS have focused on the dispersion term [15,20,21] and the parameterization method [18,19]. However, in the structure of some versions of the SAFT EoS, such as GV-SSAFT [29], other hard-sphere EoSs have also been applied. Although more than eighty different EoSs for the HS fluid have been reported in the literature [23], the use of another HS equation instead of Carnahan-Starling EoS in the development of the SAFT-type EoSs has been very limited in the literature. On the other hand, to the best of our knowledge, no comprehensive study has been done on the role of the hard-sphere expression in the SAFT-type equations of state. However, hard-sphere, as the reference fluid in the SAFT-type models, has a direct effect on its results.

In this work, we compare the calculated results of seven thermodynamic properties including pressure (P), density (ρ), temperature (T), saturated vapor-pressure (P^{sat}), isochoric heat capacity (C_V), isobaric heat capacity (C_P), and speed of sound (u) with the modified SSAFT EoS [28] for four sample systems, including ethane, butane, hexane, and hexatriacontane by replacing the CS EoS with seven other

HS equations of state.

THEORY AND METHOD

Hard-sphere Equations of State

Among the numerous HS equations of state in the literature [23], seven EoSs including scaled-particle theory (SPT) [30], Kolafa (K) [31], modified CS (MCS) [27], Yelash and Kraska (YK) [32], de Rand *et al.* (RNSK) [33], Sun *et al.* (SCWJ) [34], and Liu (L) [35] have been selected to study the effect of the hard-sphere term on the results of the SAFT-type EoSs. In the selection procedure, the accuracy of the results, the simplicity of the relations, and the feasibility of using them in the SAFT-type EoSs are considered. Also, the HS EoSs have been selected to cover a wide period so that the effect of the development of equations and the improvement of molecular simulation results in recent years can be analyzed in the results. Figure 1 shows the plot of the compressibility factor (Z^{hs}) as a function of the packing fraction (η) for studied hard-sphere EoSs (see Table 1). As shown in Fig. 1, despite the differences in the method of development and expression of hard-sphere equations of state, their behavior at low densities is very similar. The main differences between these equations are how to characterize the behavior of Z^{hs} at high densities and the location of the pole. Three hard-sphere EoSs, including MCS, YK, and RNSK have poles at η_c and the rest do not converge at η_c.

As mentioned earlier, hard-sphere EoSs are often developed based on the compressibility factor (Z^{hs}), while SAFT-type EoSs are developed based on Helmholtz energy (A^{hs}). Therefore, to replace the hard-sphere term in the SAFT-type EoSs, the hard-sphere equations must be rewritten in the Helmholtz energy form. The expression of the HS EoS in Helmholtz energy form can be obtained as follows [36]:

$$\frac{A^{hs}}{RT} = \int_0^\eta \frac{Z^{hs}-1}{\eta} d\eta \tag{5}$$

where T and R are the temperature and universal gas constant, respectively. The hard-sphere EoSs in the compressibility factor and Helmholtz energy forms are listed in Table 1. As can be seen, the Helmholtz energy
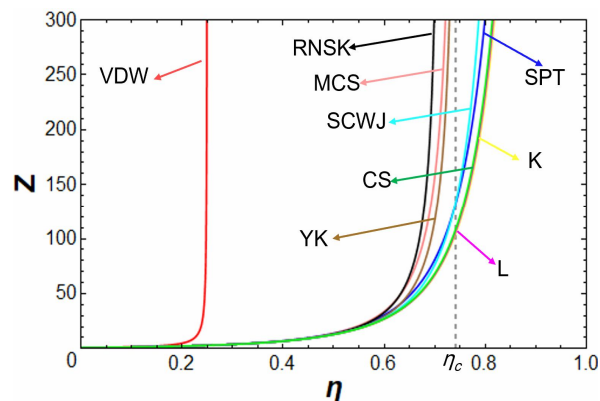

Fig. 1. Hard-sphere compressibility factor (Z) as a function of the packing fraction (η). Red, blue, green, yellow, pink, brown, black, cyan, and purple solid lines are scaled-particle theory (SPT) [30], Kolafa (K) [31], modified CS (MCS) [27], Yelash and Kraska (YK) [32], de Rand *et al.* (RNSK) [33], Sun *et al.* (SCWJ) [34], and Liu (L) [35] EoSs, respectively. The vertical dashed line represents η_C.

form of CS EoS is very simple and straightforward, while other HS EoSs are more complex and have a logarithmic part. This simplicity can be considered as a motivation to apply the CS EoS in most versions of the SAFT EoS [17].

The modification of the reference fluid in the SAFT-type EoSs is not limited to the HS part of the model. The expression of the chain contribution is also based on the radial distribution function (RDF) of the reference fluid. By changing the hard-sphere EoS, the expression of the RDF (g^{hs}) also changes. Therefore, before applying the hard-sphere equations in SAFT-type EoSs, the expression of RDF for all HS equations must be calculated. One of the simplest methods for calculating the RDF is to use the following equation [23]:

$$Z^{hs} = 1 + 4\eta g^{hs} \tag{6}$$

The RDF for all hard-sphere EoSs in Table 1 can be calculated from Eq. (6). Figure 2 shows the plot of the calculated RDFs for all studied HS EoSs.

SSAFT EoS

After calculating the Helmholtz energy form of the HS

Table 1. List of Selected HS EoSs and their Compressibility Factor (Z^{hS}) and Helmholtz Energy (A^{hS}) Expressions

| EoS	Year	Z^{hS}	A^{hS}	Ref.
SPT	1963	$Z^{SPT} = \dfrac{1 + \eta + \eta^2}{(1-\eta)^3}$	$A^{SPT} = \dfrac{3}{2}\left[\dfrac{1}{(1-\eta)^2} - 1\right] - \ln(1-\eta)$	[30]
CS	1969	$Z^{CS} = \dfrac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}$	$A^{CS} = \dfrac{4\eta - 3\eta^2}{(1-\eta)^2}$	[26]
K	1986	$Z^{K} = \dfrac{1 + \eta + \eta^2 - \frac{2}{3}\eta^3(1-\eta)}{(1-\eta)^3}$	$A^{K} = \dfrac{5}{3}\ln(1-\eta) + \dfrac{\eta(34 - 33\eta + 4\eta^2)}{6(1-\eta)^2}$	[31]
MCS	1999	$Z^{YMCS} = \dfrac{3 + 5\eta + 6\eta^2}{(1-\eta)(3-4\eta)}$	$A^{MCS} = -\dfrac{27}{2}\ln(1 - \dfrac{4\eta}{3}) + 14\ln(1-\eta)$	[27]
YK	2001	$Z^{YK} = \dfrac{3 + 8\eta + 14\eta^2 + 14\eta^3 + (\frac{40}{30})\eta^4}{(3-4\eta)}$	$A^{YK} = -8\eta - 3\eta^2 - \dfrac{10\eta^3}{9} + 9\ln(\dfrac{9}{9-12\eta})$	[32]
RNSK	2012	$Z^{RNSK} = \dfrac{1 + 2.601\eta + 4.4038\eta^2 + 5.3635\eta^3}{1 - 1.399\eta}$	$A^{RNSK} = -2.373 - \eta(5.888 + 1.917\eta) - 7.068\ln(0.714 - \eta)$	[33]
SCWJ	2013	$Z^{YK} = 1 + \dfrac{4\eta}{1 - 1.126\eta} + \dfrac{5.696\eta^2}{(1 - 1.126\eta)^2}$	$A^{SCWJ} = -4.381 + \dfrac{3.990}{0.888 - \eta} + 0.940\ln(0.888 - \eta)$	[34]
L	2021	$Z^{L} = \dfrac{1 + \eta + \eta^2 - \frac{8}{13}\eta^3 - \eta^4 + \frac{1}{2}\eta^5}{(1-\eta)^3}$	$A^{L} = \dfrac{1}{52}[\dfrac{\eta(188 - 126\eta - 13\eta^2)}{(1-\eta)^2} - 20\ln(1-\eta)]$	[35]
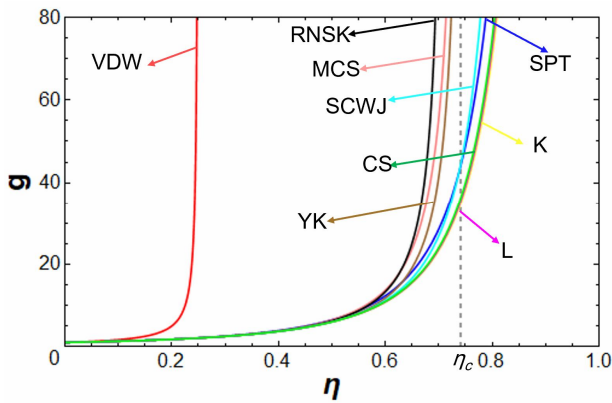
Fig. 2. Hard-sphere radial distribution function (g) as a function of the packing fraction (η). Red, blue, green, yellow, pink, brown, black, cyan, and purple solid lines are scaled-particle theory (SPT) [30], Kolafa (K) [31], modified CS (MCS) [27], Yelash and Kraska (YK) [32], de Rand *et al.* (RNSK) [33], Sun *et al.* (SCWJ) [34], and Liu (L) [35] EoSs, respectively. The vertical dashed line represents η_C.

EoSs and the corresponding expression for the RDF, the only remaining challenge is to select the appropriate version of the SAFT EoS. In some versions of the SAFT EoS such as SAFT-HR [12] and PC-SAFT [20], the universal parameters of the dispersion term have been obtained by applying the CS equation of state as the reference fluid. However, there are some versions of SAFT EoS in which the dispersion term is independent of the hard-sphere term. The SSAFT EoS [28] is one of these versions. The general form of the SSAFT EoS is similar to Eq. (1) and for non-associating fluids is as follows:

$$A^{res} = A^{hs} + A^{disp} + A^{chain} \qquad (7)$$

In the SSAFT EoS, A^{disp} is

$$\frac{A^{disp}}{RT} = Z_M \ln\left(\frac{V_S}{V_S + V^*Y}\right) \qquad (7)$$

with

$$Y = \exp\left(\frac{u}{2KT}\right) - 1 \tag{9}$$

where Z_M, V_S, V^*, u, and k are maximum coordination number ($Z_M = 36$), molar volume, close-packed molar volume, depth of the square-well potential, and Boltzmann constant, respectively.

The chain contribution in SSAFT EoS is also calculated as follows:

$$\frac{A^{chain}}{RT} = (1-m)\ln(g^{hs}) \tag{10}$$

where m is the number of segments. Finally, the packing fraction is

$$\eta = \frac{\pi N_{av}}{6} m\rho d^3 \tag{11}$$

where N_{av}, ρ, and d are Avogadro constant, molar density, and the effective hard-sphere diameter, respectively [28].

Sample Fluids and Parameterization

In this work, we have analyzed the results of modifying the SSAFT EoS reference hard-sphere fluid for four pure fluids, including ethane, butane, hexane, and hexatriacontane. The reason for choosing these fluids is the possibility of analyzing the effect of hard-sphere and chain contributions on the SSAFT EoS results. The chain length of the ethane molecule is very short, so the effect of the HS term is predominant. While the chain length of butane and hexane molecules is longer and the effect of the chain expression increases. hexatriacontane is also analyzed as a high molecular weight with a long carbon chain to examine the generalizability of the results.

Similar to the original SSAFT EoS, derived equations of state have three adjustable parameters for non-associating fluids that are estimated using experimental data. In this contribution, we have used a new general parameterization method that can be applied to estimate the parameters of any EoS with any number of parameters, including the SAFT-type EoSs. This method is based on using global and local optimization methods along with hyperparameter. A full description of this method is given elsewhere [18]. The

experimental data used to estimate the parameters were pressure-density-volume (PρT) data. The following objective function (OF) was minimized to obtain the parameters of the equations of state:

$$OF = \frac{1}{N_P}\left[\left(\sum_{i=1}^{N_P}\left|\frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}}\right|\right) + \left(\sum_{i=1}^{N_P}\left|\frac{\rho_i^{cal} - \rho_i^{exp}}{\rho_i^{exp}}\right|\right) + \left(\sum_{i=1}^{N_P}\left|\frac{T_i^{cal} - T_i^{exp}}{T_i^{exp}}\right|\right)\right] \tag{12}$$

where N_P, *cal,* and *exp* are the number of data points, calculated and experimental, respectively. The modified SSAFT EoSs pure-compound parameters for ethane, butane, hexane, and hexatriacontane, which are obtained using a new general method, are listed in Table 2.

RESULTS AND DISCUSSION

In this section, we first compare the results of the modified versions of the PρT-SSAFT EoS to predict the thermodynamic properties for ethane, butane, and hexane. The studied thermodynamic properties are pressure (P), density (ρ), temperature (T), saturated vapor pressure (P^{sat}), isochoric heat capacity (C_V), isobaric heat capacity (C_P), and speed of sound (u). Then, to generalize the results to fluids with higher chain lengths and molecular mass, we compare the results of the modified versions of the PρT-SSAFT EoS in predicting heat capacity, and sound velocity of hexatriacontane.

Pressure (P), isochoric heat capacity (C_V), isobaric heat capacity (C_P), and speed of sound (u) can be calculated from Helmholtz energy [18]:

$$P = \rho^2\left(\frac{\partial A}{\partial \rho}\right) \tag{13}$$

$$C_V = C_V^{ideal} - T\left(\frac{\partial^2 A^{res}}{\partial T^2}\right) \tag{14}$$

$$C_P = C_V + \frac{T}{\rho^2}\frac{\left(\frac{\partial P}{\partial T}\right)_\rho^2}{\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{15}$$

$$u = \sqrt{\left(\frac{C_P}{C_V M}\right)\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{16}$$

Table 2. The Modified PρT-SSAFT EoSs Pure-compound Parameters for Ethane, Butane, Hexane, and Hexatriacontane

| PρT-SSAFT HS term | Compound (Data source) | T range (K) | P range (MPa) | Parameters | | | AAD% | | | |
				m	$\frac{u^{\circ}}{k}$ (K)	V^0 (m^3 mol^{-1})	P	T	ρ	Total (No. of data)
SPT	Ethane ([37])	180-600	0.1-60	1.9776	99.999	16.7575	44.72	0.78	0.773	46.27 (271)
	Butane ([37])	200-600	0.1-70	3.2494	98.666	17.3250	64.68	0.87	0.854	66.40 (247)
	Hexane ([37])	200-600	0.1-100	5.0360	97.748	16.1592	182.03	0.89	0.869	183.79 (268)
	Hexatriacontane ([38])	363-403	0.1-152	37.3100	140.197	12.796	43.93	0.97	0.576	45.48 (64)
CS	Ethane	180-600	0.1-60	1.9939	90.002	16.4000	21.94	0.78	0.782	23.50
	Butane	200-600	0.1-70	3.3642	98.686	17.0965	64.01	0.87	0.843	65.72
	Hexane	200-600	0.1-100	5.2996	99.920	15.6776	170.27	0.92	0.893	172.08
	Hexatriacontane	363-403	0.1-152	36.0530	144.580	12.8277	50.17	0.98	0.556	51.71
K	Ethane	180-600	0.1-60	2.3917	82.684	13.9641	20.95	0.73	0.732	22.41
	Butane	200-600	0.1-70	3.3932	98.505	16.9179	65.26	0.87	0.842	66.97
	Hexane	200-600	0.1-100	5.3231	99.908	15.5746	172.29	0.92	0.894	174.1
	Hexatriacontane	363-403	0.1-152	36.8200	143.663	12.5169	52.12	0.97	0.550	53.64
MCS	Ethane	180-600	0.1-60	2.9650	74.999	11.1423	25.16	0.70	0.717	26.58
	Butane	200-600	0.1-70	3.1900	98.968	17.8264	58.49	0.88	0.860	60.23
	Hexane	200-600	0.1-100	5.0575	99.931	16.3144	166.94	0.90	0.883	168.72
	Hexatriacontane	363-403	0.1-152	32.7900	147.905	14.0962	38.20	0.99	0.598	39.79
YK	Ethane	180-600	0.1-60	1.9822	100.000	17.1105	42.83	0.79	0.784	44.40
	Butane	200-600	0.1-70	3.3743	98.815	17.0702	63.85	0.87	0.841	65.56
	Hexane	200-600	0.1-100	5.3480	99.941	15.5554	169.98	0.92	0.895	171.8
	Hexatriacontane	363-403	0.1-152	34.6443	147.844	13.3884	50.96	0.98	0.558	52.50
RNSK	Ethane	180-600	0.1-60	1.9568	99.877	17.1564	40.60	0.78	0.772	42.15
	Butane	200-600	0.1-70	3.3825	98.770	16.9064	63.77	0.87	0.843	65.48
	Hexane	200-600	0.1-100	5.3648	99.921	15.4052	171.30	0.92	0.895	173.12
	Hexatriacontane	363-403	0.1-152	32.0840	151.888	14.0819	49.57	1.00	0.989	51.56
SCWJ	Ethane	180-600	0.1-60	2.0116	100.009	16.8635	43.63	0.80	0.798	45.23
	Butane	200-600	0.1-70	3.4229	98.739	16.7997	63.44	0.87	0.839	65.15
	Hexane	200-600	0.1-100	5.4386	99.849	15.2550	168.19	0.93	0.902	170.02
	Hexatriacontane	363-403	0.1-152	34.8060	148.109	13.2897	51.61	0.98	0.554	53.14
L	Ethane	180-600	0.1-60	2.0295	98.681	16.6779	42.09	0.99	0.994	44.07
	Butane	200-600	0.1-70	3.3938	98.623	16.9196	65.49	1.00	0.991	67.48
	Hexane	200-600	0.1-100	5.3282	99.912	15.5610	172.10	1.00	0.985	174.09
	Hexatriacontane	363-403	0.1-152	36.8200	143.663	12.5169	54.39	0.97	0.551	55.91

where C_V^{ideal} is ideal isochoric heat capacity and M is molecular mass.

The average absolute percentage deviation (AAD%) has also been used to evaluate the accuracy of the predicted results and to compare modified versions of the PρT-SSAFT EoS predictions:
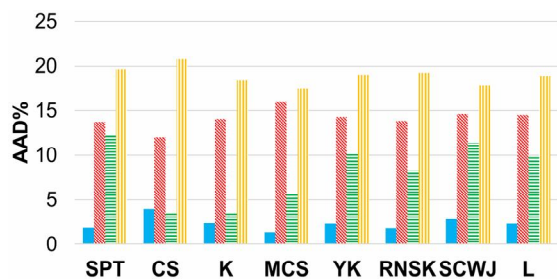
Fig. 3. A comparison of the modified versions of the SSAFT EoS AAD% for saturated vapor pressure (■), isochoric heat capacity (▨), isobaric heat capacity (≡), and speed of sound (▥) of ethane.
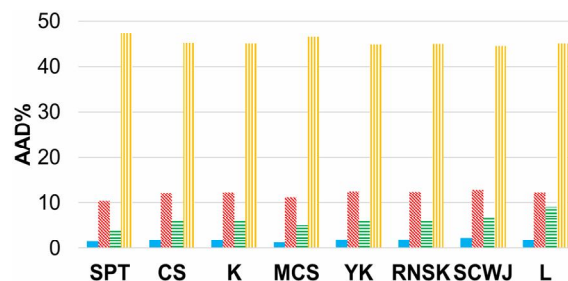

Fig. 5. A comparison of the modified versions of the SSAFT EoS AAD% for saturated vapor pressure (■), isochoric heat capacity (▨), isobaric heat capacity (≡), and speed of sound (▥) of hexane.
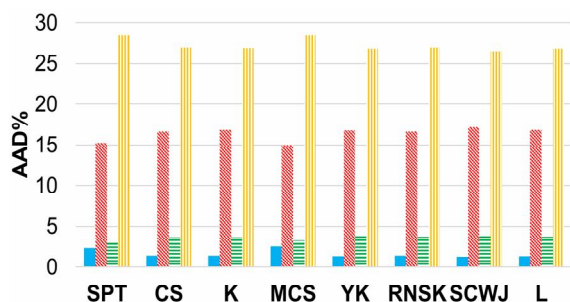

Fig. 4. A comparison of the modified versions of the SSAFT EoS AAD% for saturated vapor pressure (■), isochoric heat capacity (▨), isobaric heat capacity (≡), and speed of sound (▥) of butane.
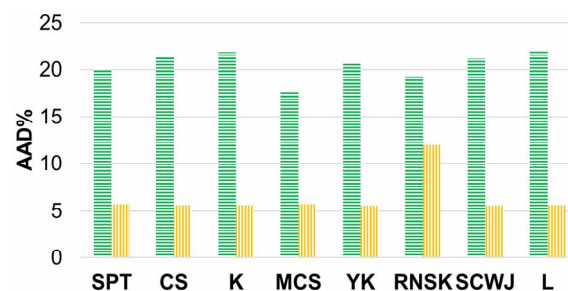

Fig. 6. A comparison of the modified versions of the SSAFT EoS AAD% for isobaric heat capacity (≡) and speed of sound (▥) of hexatriacontane.

$$AAD\% = \frac{100}{N_P} \left(\sum_{i=1}^{N_P} \left| \frac{Y_i^{cal} - Y_i^{exp}}{Y_i^{exp}} \right| \right) \qquad (17)$$

where Y^{cal} is calculated thermodynamic properties and Y^{exp} is experimental thermodynamic properties.

Figures 3 to 5 show the predicted results of the saturated vapor pressure, isochoric heat capacity, isobaric heat capacity, and speed of sound for ethane, butane, and hexane using the eight modified versions of the PρT-SSAFT EoS. As can be seen, the modification of the hard-sphere reference fluid expression in the PρT-SSAFT EoS has not led to any significant improvement and the results of all modified EoSs are similar. Either in the results for ethane, where the role of the chain term is minimal or in the results for butane and hexane, where the role of the chain term is increased, there is no considerable difference between the

results of the modified versions of the PρT-SSAFT EoS. Also, the results of hexatriacontane, which is a long-chain alkane with thirty-six carbons, are similar to the results of ethane, butane, and hexane. As can be seen in Fig. 6, modifying the reference fluid of the PρT-SSAFT EoS did not lead to a noteworthy improvement in hexatriacontane results, and the prediction of isobaric heat capacity and sound velocity for all modified equations of state (except C_P with the RNSK) are similar. The results are also listed in Table 3. A similar trend is observed in pressure (P), density (ρ), and temperature (T) calculations and the results of all modified versions of the PρT-SSAFT EoS for sample fluids are close (see Table 2).

For a more detailed analysis on the effect of modifying the reference fluid expression in the PρT-SSAFT EoS, the contribution of the hard-sphere, dispersion, and chain terms in calculating the saturated vapor pressure and sound

Table 3. The Average Absolute Percentage Deviation (AAD%) of Saturated Vapor Pressure (P^{sat}), Isochoric Heat Capacity (C_V), Isobaric Heat Capacity (C_P), and Speed of Sound (u) with Modified Versions of the PρT-SSAFT EoS

PρT-SSAFT HS term	Compound (Data source)	T range (K)	P range (MPa)	AAD% (No. of data points)			
				P^{sat}	C_v	C_P	u
SPT	Ethane ([37])	180-600	0.1-60	1.88 (71)	13.75 (271)	12.40 (271)	19.64 (271)
	Butane ([37])	200-600	0.1-70	2.36 (110)	15.22 (256)	3.02 (256)	28.44 (256)
	Hexane ([37])	200-600	0.1-100	1.42 (126)	10.34 (276)	3.91 (276)	47.22 (276)
	Hexatriacontane ([38-40])	363-403	0.1-152	-	-	20.06 (58)	5.75 (64)
CS	Ethane	180-600	0.1-60	3.95	12.01	3.63	20.76
	Butane	200-600	0.1-70	1.42	16.65	3.68	27.00
	Hexane	200-600	0.1-100	1.76	12.27	6.03	45.14
	Hexatriacontane	363-403	0.1-152	-	-	21.29	5.62
K	Ethane	180-600	0.1-60	2.37	14.06	3.52	18.34
	Butane	200-600	0.1-70	1.38	16.81	3.68	26.91
	Hexane	200-600	0.1-100	1.81	12.31	6.01	45.08
	Hexatriacontane	363-403	0.1-152	-	-	21.83	5.60
MCS	Ethane	180-600	0.1-60	1.35	16.02	5.70	17.45
	Butane	200-600	0.1-70	2.53	14.99	3.25	28.42
	Hexane	200-600	0.1-100	1.24	11.16	5.08	46.53
	Hexatriacontane	363-403	0.1-152	-	-	17.72	5.74
YK	Ethane	180-600	0.1-60	2.33	14.29	10.18	19.00
	Butane	200-600	0.1-70	1.35	16.79	3.80	26.84
	Hexane	200-600	0.1-100	1.93	12.51	6.29	44.88
	Hexatriacontane	363-403	0.1-152	-	-	20.74	5.57
RNSK	Ethane	180-600	0.1-60	1.80	13.86	8.24	19.27
	Butane	200-600	0.1-70	1.40	16.67	3.73	26.99
	Hexane	200-600	0.1-100	1.95	12.45	6.12	44.95
	Hexatriacontane	363-403	0.1-152	-	-	19.33	11.93
SCWJ	Ethane	180-600	0.1-60	2.82	14.63	11.41	17.79
	Butane	200-600	0.1-70	1.24	17.17	3.97	26.52
	Hexane	200-600	0.1-100	2.30	12.84	6.65	44.49
	Hexatriacontane	363-403	0.1-152	-	-	21.11	5.56
L	Ethane	180-600	0.1-60	2.33	14.49	9.86	18.90
	Butane	200-600	0.1-70	1.36	16.85	3.72	26.87
	Hexane	200-600	0.1-100	1.83	12.34	9.04	45.05
	Hexatriacontane	363-403	0.1-152	-	-	21.87	5.64

velocity of hexane are shown in Figs. 7 and 8. As can be seen in Fig. 7, the contribution of the hard-sphere, dispersion, and chain for all HS EoSs over the entire temperature range are very close, and no significant difference is observed in the saturated vapor pressure calculations. Figure 8 shows a comparison of the sound velocity results of HS, dispersion, and chain terms in the modified versions of the PρT-SSAFT equations of state for
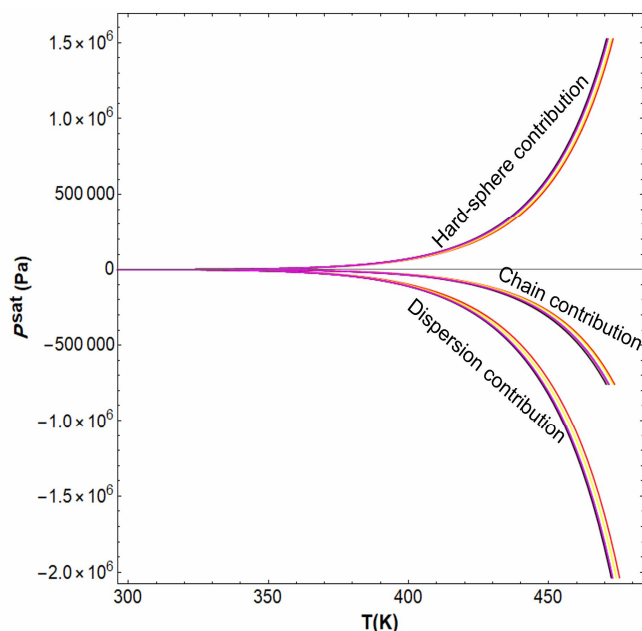
Fig. 7. A comparison of the hard-sphere, dispersion, and chain terms of the modified versions of PρT-SSAFT in calculating the saturated vapor pressure of hexane. Red, blue, green, yellow, pink, brown, black, cyan, and purple solid lines are scaled-particle theory (SPT) [30], Kolafa (K) [31], modified CS (MCS) [27], Yelash and Kraska (YK) [32], de Rand *et al.* (RNSK) [33], Sun *et al.* (SCWJ) [34], and Liu (L) [35] EoSs, respectively.
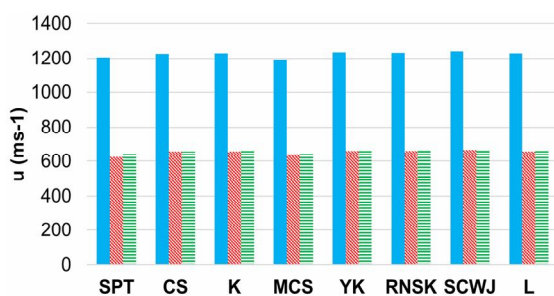

Fig. 8. A comparison of the hard-sphere (■), dispersion (▨), and chain (▤) terms of the modified versions of PρT-SSAFT in calculating the sound velocity of hexane.

hexane. This figure shows the predicted speed of sound average for each of the mentioned terms over the entire temperature and pressure range. It can be seen that

modifying the HS expression has no effect on the accuracy of the results and all of the equations of state have similar performance.

The total AAD% for predicting the saturated vapor pressure, isochoric heat capacity, isobaric heat capacity, and sound velocity of ethane, butane, hexane, and hexatriacontane by SPT, CS, K, MCS, YK, RNSK, SCWJ, and L versions of the PρT-SSAFT EoS are 13.24, 12.94, 12.84, 12.66, 13.32, 13.48, 13.46, and 13.58, respectively. On the other hand, the total AAD% for the correlation of pressure-density-volume (PρT) data of ethane, butane, hexane, and hexatriacontane by SPT, CS, K, MCS, YK, RNSK, SCWJ, and L versions of the PρT-SSAFT EoS are 85.48, 78.25, 79.28, 73.83, 83.56, 83.08, 83.38, and 85.39, respectively. Overall, although the performance of all equations of state was very close and competitive, the results show that the modified versions of the PρT-SSAFT EoS, whose reference fluid expression was based on the modified Carnahan-Starling [27], Kolafa [31], and Carnahan-Starling [26], equations of state, performed better in calculating the thermodynamic properties of the sample fluids. However, the results of the Carnahan-Starling EoS are very interesting. Despite the simple expression, the Carnahan-Starling EoS has well calculated the thermodynamic properties of all the studied systems.

It is worth noting that in addition to developing the theories, the parameterization method also affects the results of SAFT-type EoSs [18]. Therefore, for a more comprehensive comparison, the results of the original SSAFT EoS [28] (CS EoS and parameterized with VLE data) and PρT-SSAFT EoS (CS EoS and parameterized with PρT data) are compared. As can be seen in Table 4, the use of PρT data to estimate the SSAFT EoS parameters has led to a relative improvement in the calculation of thermodynamic properties for the systems.

Overall, it can be concluded that the Carnahan-Starling (CS) equation has an acceptable performance in predicting thermodynamic properties, at least for alkanes, and is a good choice for the development of SAFT-type equations of state. In addition, Kolafa (K) and modified Carnahan-Starling (MCS) equations had promising results for the studied fluids. However, to obtain a comprehensive analysis of the effect of the hard-sphere expression in SAFT-type EOSs, the performance of various HS equations in

Table 4. The Average Absolute Percentage Deviation (AAD%) of Saturated Vapor Pressure (P^{sat}), Isochoric Heat Capacity (C_v), Isobaric Heat Capacity (C_P), and Speed of Sound (u) with the Original CS-SSAFT and PρT-CS-SSAFT. The Number and Range of Data are Similar to Table 3

| EoS | Compound | AAD% | | | |
	(Data source)	P^{sat}	C_v	C_P	u
Original CS-SSAFT [28]	Ethane ([37])	3.19	12.4	3.95	20.49
	Butane ([37])	2.65	14.6	2.88	29.19
	Hexane ([37])	2.81	9.04	3.99	50.71
	Hexatriacontane ([38-40])	-	-	4.17	48.88
PρT-CS-SSAFT	Ethane	3.95	12.01	3.63	20.76
	Butane	1.42	16.65	3.68	27.00
	Hexane	1.76	12.27	6.03	45.14
	Hexatriacontane	-	-	21.29	5.62

thermodynamic modeling of more complex fluids such as associating and polar fluids must also be studied.

CONCLUSIONS

In most SAFT-type equations of state, HS is considered as the reference fluid. Although many expressions have been developed for the HS EoS, in most versions of the SAFT EoS, the Carnahan-Starling equation is applied for the hard-sphere term. In this work, we implemented and parameterized (with PρT data) eight hard-sphere equations of state, including scaled-particle theory (SPT) [30], Carnahan-Starling (CS) [26], Kolafa (K) [31], modified CS (MCS) [27], Yelash and Kraska (YK) [32], de Rand *et al.* (RNSK) [33], Sun *et al.* (SCWJ) [34], and Liu (L) [35] in the simplified SAFT (SSAFT) EoS. Then, we calculated the saturated vapor pressure (P^{sat}), isochoric heat capacity (C_V), isobaric heat capacity (C_P), and speed of sound (u) for the three sample fluids (ethane, butane, and hexane) and compared the results of the modified versions of the SSAFT EoS. To evaluate the generalizability of the results, heat capacity and sound speed for hexatriacontane have also been investigated.

The results of predicting (P^{sat}, C_V, C_P, and u) and correlating (P, ρ, and T) thermodynamic properties with modified versions of the SSAFT EoS show that modified Carnahan-Starling, Kolafa, and Carnahan-Starling had the

best results. Therefore, it can be concluded that for fluids in non-extreme conditions, the Carnahan-Starling equation has a good ability in predicting thermodynamic properties and is a good choice for developing SAFT-type EoSs. However, to achieve a comprehensive comparison, the effect of the hard-sphere term on calculating the thermodynamic properties of more complex fluids must also be analyzed.

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