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A Hard Convex Core Yukawa Equation of State for Nonassociated Chain Molecules

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The compressibility factor of nonassociated chain molecules composed of hard convex core Yukawa segments was derived with SAFT-VR and an extension of the Barker-Henderson perturbation theory for convex bodies. The temperature-dependent chain and dispersion compressibility factors were derived using the Yukawa potential. The effects of temperature, packing fraction, and segment number on the compressibility factor were investigated for chains of the prolate sphereocylinder segments. A comparison of hard core Yukawa chain compressibility factor values and hard chain compressibility factor values showed that the type of interaction potential has more effect on those chain molecules with higher segment numbers. The results demonstrated that in reduced temperatures 1.4 and 2.4, the Yukawa chain of the compressibility factor is insensitive to temperature, while the dispersion term of the compressibility factor changes remarkably with the temperature. The derived equation of state can fairly predict the SAFT-VR results of the hard sphere core chain molecules in the limit of $\alpha = 1$.

Keywords: Convex body, Chain molecule, Perturbation theory, SAFT-VR, Yukawa potential

INTRODUCTION

The thermodynamic properties of chain-like molecules, such as proteins and polymers, are of industrial and scientific interest [1-5]. The equilibrium properties of fluids are related mainly to the structure of the constitutive components of fluids and their mutual interaction. The equations of state describing such systems have great importance both experimentally and theoretically.

Numerous equations of state have been developed for accurately determining the thermodynamic properties and phase equilibria of complex fluids at the molecular level [6-10]. The thermodynamic perturbation theory (TPT) of Wertheim [11,12] in 1984 introduced the statistical associating fluid theory (SAFT) that, because of its predictive accuracy and firm molecular foundation, rapidly superseded well-established chemical engineering equations of state. The SAFT approach describes the fluid phase equilibria of a wide variety of non-polar and polar fluids and their mixtures [13]. Many extensions of the SAFT are presented; among them, the SAFT-VR is a general version for chain molecules formed from hard core monomers with an arbitrary potential of variable range (VR) [14]. In the general form of the SAFT equation of state, the reduced residual Helmholtz energy, A^{res} is usually defined as a series of terms approximating different free energies resulting from molecular interaction as,

$$\frac{A^{res}}{NkT} = \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \qquad (1)$$

The superscripts on the right hand side of Eq. (1) refer to the monomer, the chain, and the association contributions of the Helmholtz free energy, respectively.

According to the first order Barker-Henderson perturbation theory [15], the monomer Helmholtz free energy can be presented as,

$$A^{mono} = A^{HS} + \beta A_1 \qquad (2)$$

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*Corresponding author. E-mail: nfarzi@sci.ui.ac.ir where A^{HS} is the hard sphere Helmholtz free energy and A_1 is the perturbed Helmholtz free energy due to the dispersion interactions.

The chain Helmholtz free energy is calculated by [16],

$$\frac{A^{chain}}{NkT} = -(m-1)\ln y^M(\sigma) \tag{3}$$

where m is the number of monomers per chain and $y^M(\sigma)$ is the monomer-monomer background correlation function evaluated at the hard-core contact. The background correlation function is related to the pair correlation function as,

$$y^M(\sigma) = e^{\beta U^M(\sigma)} g^M(\sigma) \tag{4}$$

where $g^M(\sigma)$ and $U^M(\sigma)$ are the monomer pair correlation function and the monomer intermolecular potential at the hard-core contact, respectively.

Since the structure of the hard sphere reference system is well-known, and the structure of a fluid is mainly related to repulsive interactions, the monomer background correlation function at hard-core contact is usually obtained by its hard sphere value,

$$y^M(\sigma) = y^{HS}(\sigma) \tag{5}$$

The analytical expression for $y^{HS}(\sigma)$ is obtained by the hard sphere pair correlation function at contact, $g^{HS}(\sigma)$, by the similar relation as Eq. (4).

The compressibility factor of the nonassociated chain molecules is obtained using Eq. (1) as,

$$Z = 1 + Z^{HS} + Z^{chain} + Z^{Disp} \tag{6}$$

where Z^{HS}, Z^{chain} and Z^{Disp} are the hard sphere, the chain, and the dispersion compressibility factors, respectively. The compressibility factor of the chain molecules of the m-hard sphere segments, Z^{HSC}, can be evaluated by Z^{HS} and Z^{chain} as,

$$Z^{HSC} = mZ^{HS} - (m-1)\left(1 + \eta\frac{\partial \ln g^{HS}(\sigma)}{\partial \eta}\right) \tag{7}$$

The hard sphere term of the compressibility factor for the *m*-segment chain molecules, Z^{HS}, is usually given by the Carnahan-Starling equation of state as,

$$Z^{HS} = m\frac{4\eta - 2\eta^2}{(1-\eta)^3} \tag{8}$$

where $\eta = m\pi\rho\sigma^3/6$ is the packing fraction.

The second term in the right hand side of Eq. (7) is the chain contribution of the compressibility factor, Z^{chain}.

In spite of the extensive application of the hard sphere model in theoretical studies of fluids, most real molecules are neither spherical nor spherically symmetric. Therefore, the equations of state reflecting this anisotropy are of interest. The equations of state derived by T. Boublik [17-19] and M. J. Maeso *et al.* [20] are examples of such equations. In their works, a nonspherical geometry parameter was used to account for the better representation of the geometry of many real molecules.

Sadus [21] formulated a hard convex body chain (HCBC) compressibility factor using the Boublik hard convex body (HCB) compressibility factor [18]. According to this formulation, the compressibility factor of a chain molecule composed of *m* hard convex body (HCB) segments, Z^{HCBC}, can be written similarly to Eq. (7), using the HCB compressibility factor, Z^{HCB} and the HCB site-site correlation function at contact, $g^{HCB}(\sigma)$, namely:

$$Z^{HCBC} = mZ^{HCB} - (m-1)\left(1 + \eta\frac{\partial \ln g^{HCB}(\sigma)}{\partial \eta}\right) \tag{9}$$

where the HCB site-site correlation function at contact, $g^{HCB}(\sigma)$, is given by [22],

$$g^{HCB} = 1 + S_R\left(\frac{1-\eta/2}{(1-\eta)^3} - 1\right) \tag{10}$$

where S_R is the ratio of the actual surface area of HCB, S^{HCB}, to the surface area of the equivalent hard spheres, S^{EHS}, which occupy the same volume as the HCB,

$$S_R = \frac{S^{HCB}}{S^{EHS}} \tag{11}$$

Equation (10) is converted to the Percus-Yuvick relation for the hard sphere pair correlation function at contact by $S_R = 1$.

The HCB compressibility factor, Z^{HCB}, can be accurately obtained from the Boublik equation of state as [17],

$$Z^{HCB} = \frac{1+(3\alpha-2)\eta+(3\alpha^2-3\alpha+1)\eta^2-\alpha^2\eta^3}{(1-\eta)^3} \tag{12}$$

where α is a parameter for deviation from spherical geometry and given by,

$$\alpha = \frac{RS}{3V} \tag{13}$$

where R, S and V are the mean radius, surface area, and volume of a convex body, respectively. The value of α for the hard sphere is equal to one.

In Ref. [21], the chain molecules were considered completely hard and composed of HCB monomers, while in real fluids monomers have only hard cores which can interact with each other through an appropriate dispersion force. Therefore, in this work, the compressibility factor of nonassociated chain molecules composed of hard convex core Yukawa segments has been derived with the SAFT-VR description using an extension of the Barker-Henderson perturbation theory for convex bodies. It was considered that monomers have hard convex cores and can interact with each other through the dispersion potential of variation range as a perturbed interaction potential. Therefore, the monomer Helmholtz free energy term is derived for the hard convex core Yukawa segments using a perturbation theory for convex bodies [23]. The chain Helmholtz free energy term is calculated. The resulting equation of state is investigated in different temperatures, segment numbers, and packing fractions and finally, the role of dispersion term for prolate spherocylinder segments is investigated.

MONOMER TERM

According to the SAFT-VR, the monomer segments Helmholtz free energy, A^{mono}, is given by,

$$\frac{A^{mono}}{NkT} = m\left(\frac{A^{HS}}{NkT}+\beta A_1+\beta^2 A_2\right) \tag{14}$$

where $\beta = 1/kT$ and A_1 and A_2 are the first two perturbation terms associated with the attractive well.

In this study, it was assumed that the chain molecules had been composed of the convex segments interacting by the hard core Yukawa potential. The monomer Helmholtz free energy of the convex monomer segments, $A^{HCBmono}$, can be written by the first perturbation term as in Eq. (14) as,

$$\frac{A^{HCBmono}}{NkT} = m\left(\frac{A^{HCB}}{NkT}+\beta A_1\right) \tag{15}$$

where A^{HCB} is the HCB Helmholtz free energy of the hard core convex monomers and A_1 is the perturbed Helmholtz free energy due to the dispersion forces between the monomers.

The dispersion Helmholtz free energy can be calculated from the first order perturbation theory of Barker-Henderson as,

$$\frac{A_1}{NkT} = 2\pi\rho\int_0^\infty U(r)g(r)r^2dr \tag{16}$$

Equation (16) was rewritten for the convex bodies by Boublik [23] as,

$$\frac{A_1}{NkT} = \frac{\rho}{2kT}\int_\sigma^\infty U(s)\,g^{HCB}(s)S_{i+s+i}\,ds \tag{17}$$

where s denotes the distance between surfaces of the convex bodies of interacting molecules, $U(s)$ is the dispersion potential between two convex bodies in the distance s, and $g^{HCB}(s)$ is the pair correlation function of the convex body at distance s. The mean surface area S_{i+s+i} of a pair of molecules is given by the motion of the center of gravity of one convex molecule around the second one keeping a constant surface-to-surface distance s. The mean surface area with a surface distance s can be expressed in terms of the reduced parameters $R' = R/\sigma$, $S' = S/\sigma^2$, and the reduced distance $z = s/\sigma$ as, R/σ

$$S_{i+s+i} = 4\pi\sigma^2\left[z^2+4R'z+2(S/4\pi+R'^2)\right] \tag{18}$$

Among the analytically solvable models, the hard core Yukawa potential is very useful in theoretical studies [24]. Because of its analytical solution, the hard core Yukawa potential along with the mean spherical approximation has been used in many applications [25,26]. The different properties of the chain molecules, such as proteins and polymers, have been frequently investigated by the Yukawa potential [27-30]. It is expected that the application of the hard core Yukawa potential, as a dispersion potential to the chains composed of nonspherical segments, will be a proper choice and will give logical results. Thus, to calculate the dispersion term of the Helmholtz free energy, the hard core Yukawa potential was used. The hard core Yukawa potential is given as,

$$U(s)=\begin{cases}\infty & s\le\sigma \\ -\dfrac{\varepsilon\sigma}{s}\exp\left[-\lambda\left(\dfrac{s}{\sigma}-1\right)\right] & s>\sigma\end{cases} \tag{19}$$

where ε is the depth of the potential minimum, σ is the distance that the potential is zero, and λ is a quantity that determines the range of potential.

Replacing the Yukawa potential in Eq. (17) results in:

$$\frac{A_1}{NkT}=-\frac{2\pi\rho\sigma^3}{T^*}\int_{\frac{1}{c}}^{\infty}\frac{e^{-\lambda(ct-1)}}{t}g^{HCB}(c\sigma t)\left[(ct)^2+4R'(ct)+2\left(\frac{S'}{4\pi}+R'\right)\right]dt \tag{20}$$

where $T^* = kT/\varepsilon$ is the reduced temperature, t is a new variable which is defined as $t = z/c$, and c is a dimensionless quantity defined as the ratio of thickness (ζ) to $\sigma/2$. To calculate the integral in Eq. (19), it is necessary to know the pair correlation function of convex body, g^{HCB} ($c\sigma t$). To determine g^{HCB} ($c\sigma t$), the definition of the total correlation function of convex body, h^{HCB} ($c\sigma t$), was used as,

$$h^{HCB}(c\sigma t) = g^{HCB}(c\sigma t) - 1 \tag{21}$$

The total correlation function of a convex body is given with a good approximation [23] by,

$$h^{HCB}(c\sigma t)=\frac{S^{HCB}}{S^{EHS}}h^{EHS}(x) \tag{22}$$

According to this approximation, the total correlation function of a convex body, h^{HCB} ($c\sigma t$), can be approximated by the correlation function of an equivalent hard sphere, h^{EHS} (x), which can be calculated by the Percus-Yuvick relation for the total correlation function, h^{PY} (x),

$$h^{EHS}(x)=\frac{h^{EHS}(1)}{h^{PY}(1)}h^{PY}(x) \tag{23}$$

where h^{EHS} (1) and h^{PY} (1) are their values at contact and x is:

$$x = 1 + ft \tag{24}$$

that f has been defined as:

$$f=\frac{\alpha}{1+2R} \tag{25}$$

It has been shown that this approximation works well for prolate and oblate spherocylinders [23]. Replacing Eq. (23) into Eq. (22) and the result into Eq. (21) gives,

$$g^{HCB}(c\sigma t)=S_R\frac{h^{EHS}(1)}{h^{PY}(1)}\left(g^{PY}(x)-1\right)+1 \tag{26}$$

Therefore, using g^{HCB} ($c\sigma t$), given in Eq. (26), the dispersion Helmholtz free energy, Eq. (20), becomes:

$$\frac{A_1}{NkT}=-\frac{2\pi\rho\sigma^3}{T^*}\int_{\frac{1}{c}}^{\infty}\frac{e^{-\lambda(ct-1)}}{t}\left[S_R\frac{h^{EHS}(1)}{h^{PY}(1)}\left(g^{PY}(x)-1\right)+1\right]\left[(ct)^2+4R'(ct)+2\left(\frac{S'}{4\pi}+R'\right)\right]dt \tag{27}$$

where x is related to t by Eq. (24).

In this study, c was taken as equal to unit for simplicity; in other words $\zeta = \sigma/2$. The mean-value theorem (MVT) from the theory of calculus [31] was used to evaluate the integral in Eq. (27). The MVT states that if $f(x)$ and $h(x)$ are continuous functions in the interval $I = [a,b]$, and $h(x) > 0$, then there is a value $\zeta \in [a,b]$, such that

$$\int_a^b f(x)h(x)dx = f(\xi)\int_a^b h(x)dx \tag{28}$$

According to MVT, since $e^{-\lambda(ct-1)}/t$ and g^{PY} (x) are the continuous functions in the interval $[1,\infty]$, we can obtain the following relation after changing the variable t to x:

$$\frac{A_1}{NkT} = -\frac{2\pi\rho\sigma^3}{T^*}\left[S_R \frac{h^{EHS}(1)}{h^{PY}(1)}\left(g^{PY}(\xi,\eta)-1\right)+1\right] \times\left[\frac{1}{\lambda}+\frac{1}{\lambda^2}+\frac{4R'}{\lambda}+e^{\lambda\left(\frac{c}{f}+1\right)}\left(2\left(\frac{S'}{4\pi}+R'^2\right)\int_{1+\frac{f}{c}}^{\infty}\frac{e^{-\frac{\lambda cx}{f}}}{(x-1)}dx\right)\right] \tag{29}$$

With a good approximation in the SAFT-VR description, the function g^{PY} (ζ,η) can be represented by its contact value, but evaluated at an effective packing fraction, η_{eff}, such that,

$$g^{PY}(\xi,\eta) = g^{PY}(1,\eta_{eff}) \tag{30}$$

This is justified, since g^{HS} (x) is a decreasing function in the interval of values of the mean-value theorem distances ζ, even for long-range interactions and for the whole range of liquid densities [32]. Thus it can be written as,

$$g^{PY}(1,\eta_{eff}) = \frac{1-\eta_{eff}/2}{(1-\eta_{eff})^3} \tag{31}$$

Gil-Villegas *et al.* [32] obtained the dependency of the effective packing fraction η_{eff} on the actual value of η and the Yukawa potential range parameter, λ, as:

$$\eta_{eff} = C_1\eta + C_2\eta^2 \tag{32}$$

where $C_1$and C_2 are calculated using the Yukawa potential range parameter by,

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} 0.900678 & -1.50051 & 0.776577 \\ -0.314300 & 0.257101 & -0.0431566 \end{bmatrix}\begin{bmatrix} 1 \\ \lambda^{-1} \\ \lambda^{-2} \end{bmatrix} \tag{33}$$

Therefore, according to the above-mentioned method, the dispersion contribution of the monomer Helmholtz free energy can be evaluated from Eqs. (29)-(33), and in turn, the corresponding compressibility factor from,

$$Z^{Disp} = \frac{\eta}{NkT}\left(\frac{\partial A_1}{\partial\eta}\right) \tag{34}$$

Finally, the dispersion compressibility factor, Eq. (34), along with the hard convex body compressibility factor, Eq. (12), gives the monomer compressibility factor.

CHAIN TERM

The chain term of the compressibility factor is usually calculated by the pair correlation function at contact of the hard segments as:

$$Z^{HSchain} = -(m-1)\left(1+\eta\frac{\partial \ln g^{HS}(\sigma)}{\partial\eta}\right) \tag{35}$$

Where $Z^{HSchain}$ is the hard segment chain compressibility factor. Similarly, the hard convex segment chain compressibility factor, $Z^{HCSchain}$, can be written using the pair correlation function of the HCB as [21],

$$Z^{HCSchain} = -(m-1)\left(1+\eta\frac{\partial \ln g^{HCB}(\sigma)}{\partial\eta}\right) \tag{36}$$

The $Z^{HCSchain}$ can be obtained using the HCB pair correlation function, which is given in Eq. (10) as,

$$Z^{HCSchain} = -(m-1)\left[1+\frac{2.5S_R\eta - S_R\eta^2}{(1-\eta)\left(1-(3-2.5S_R)\eta+(3-3S_R)\eta^2-(1-S_R)\eta^3\right)}\right] \tag{37}$$

This relation is applicable for the chain molecules of convex segments that are completely hard. However, for hard core convex segments interacting through the dispersion force, another relation has to be obtained. Then, to find a suitable expression for the pair correlation function of the hard convex core segments, a high-temperature expansion for the monomer pair correlation function, g^M (r), was used as,

$$g^M(r) = g^{HCB}(r) + \beta\varepsilon g_1(r) + (\beta\varepsilon)^2 g_2(r) + \ldots \tag{38}$$

where g_1 (r) and g_2 (r) are the correction terms to account for the contribution of the dispersion force, and ε is the potential energy parameter.

In this work, just the first correction term, *i.e.* g_1 (r), was considered in the calculation of g^M (r).

A closed expression was derived for g_1 (σ) based on a self consistent method for the pressure P from the Clausius Virial theorem and the density derivative of the Helmholtz free energy as,

$$g_1(\sigma) = \frac{1}{4\varepsilon}\frac{\partial A_1}{\partial \eta} - \int_1^{\infty} x^3 \frac{\partial U}{\partial x} g^{HS}(x)dx \qquad (39)$$

For extension of Eq. (39) to the HCB, the pair correlation functions of HCB were used instead of the hard sphere pair correlation function.

The following expression was obtained for the monomer pair correlation function at contact by replacing the Yukawa potential in Eq. (39) and the results into Eq. (38),

$$g^{Y}(\sigma^{+}) = g^{HCB}(\sigma^{+}) + \frac{1}{4}\beta\left[\frac{\partial A_1^Y}{\partial \eta} + \frac{\lambda}{3\eta}\frac{\partial A_1^Y}{\partial \lambda} - \frac{(1+\lambda)}{3\eta}A_1^Y\right] \qquad (40)$$

The superscript Y denotes the Yukawa potential. Eq. (40) is used to calculate the pair correlation function of the hard convex core Yukawa bodies by replacing A_1 from Eq. (29). The chain contribution of the compressibility factor of the hard convex core Yukawa body chain molecule was calculated using Eqs. (40) and (36). The resulting relation is significantly long; therefore, only the final results are presented in the next section.

It is worthy to note that the final expression for the compressibility factor of the chain molecules of hard core Yukawa segments, which was calculated using Eq. (6), is a temperature-dependent expression. The ability to predict the temperature-dependent properties of a fluid is a significant advantage for an equation of state.

RESULTS AND DISCUSSION

In the present work, the compressibility factor of nonassociated chain molecules, $Z^{(1)}$, composed of hard convex core Yukawa segments was derived using the SAFT-VR and an extension of the Barker-Henderson perturbation theory for convex bodies. The derived convex body SAFT-VR (CB-SAFT-VR) equation of state for the nonassociated chain molecules is given by:

$$Z^{(1)} = 1 + Z^{HCB} + Z^{HCYSchain} + Z^{Disp} \qquad (41)$$

where Z^{HCB} is the hard convex body compressibility factor, Eq. (12), $Z^{HCYSchain}$ is the compressibility factor of the hard convex core Yukawa segment chain which can be calculated using Eqs. (40), (4) and (3), and Z^{Disp} is the dispersion compressibility factor term obtained by Eqs. (34) and (29). It should be noted that the nonspherical character of segments was considered in the hard convex body, the dispersion and chain compressibility factor terms of $Z^{(1)}$.

The derived compressibility factor of the chain molecules composed of the hard convex core Yukawa bodies, $Z^{(1)}$, depends on the molecular shape α, Yukawa parameter λ, packing fraction η, segment number m, and the ratio of the actual surface area of HCB to the hard sphere one, S_R. The values of R, S, V, α, η and S_R in terms of the ratio of maximum length to breath, γ, are given in Table 1 for sphere and prolate sphereocylinder bodies [21].

The compressibility factors of the hard convex core Yukawa chain molecules of prolate sphereocylinder segments, $Z^{(1)}$, in different segment numbers, m, are plotted versus the packing fraction in Figs. 1a and 1b for the reduced temperatures 1.4 and 2.4, respectively. It is observable from Figs. 1a and 1b that, for each segment number, m, the isotherms of the compressibility factor increase with the packing fraction and decrease with temperature.

The compressibility factors of the prolate sphereocylinder segment chain molecules with different lengths in the constant segment number and the reduced temperature 1.4 are plotted in Fig. 2. It can be seen that the compressibility factor increases as chain length increases.

To investigate the contribution of the dispersion term on the compressibility factor of the chain molecules, $Z^{(1)}$, the dispersion term was neglected and the Yukawa potential was considered only in the calculation of the chain term, $Z^{HCYSchain}$. In this case, the hard convex segment chain Yukawa compressibility, $Z^{(1)}$, can be obtained by,

$$Z^{(2)} = 1 + Z^{HCB} + Z^{HCYSchain} \qquad (42)$$

The plots of $Z^{(2)}$ versus the packing fraction in the reduced temperatures 1.4 and 2.4 and different segment numbers are shown in Figs. 3a and 3b, respectively. It can be found from Figs. 3a and 3b that the compressibility factor in each segment number, m, has not changed with

Table 1. The Values of Mean Radius, *R*, Surface Area, *S*, Volume, *V*, Nonspherical Parameter, α, and the Ratio of the Actual Surface Area of HCB to the Hard Sphere One, S_R, is Given for Sphere and Prolate Spherocylinders

Shape	R	S	V	α	S_R
Sphere	$\sigma/2$	$\pi\sigma^2$	$\frac{\pi\sigma^3}{6}$	1	1
Prolate	$\frac{(\gamma+1)\sigma}{4}$	$\gamma\pi\sigma^2$	$\frac{(3\gamma-1)\pi\sigma^3}{12}$	$\frac{\gamma^2+\gamma}{3\gamma+1}$	$\frac{\gamma}{(1.5\gamma-0.5)^{2/3}}$

γ is length/breath ratio.

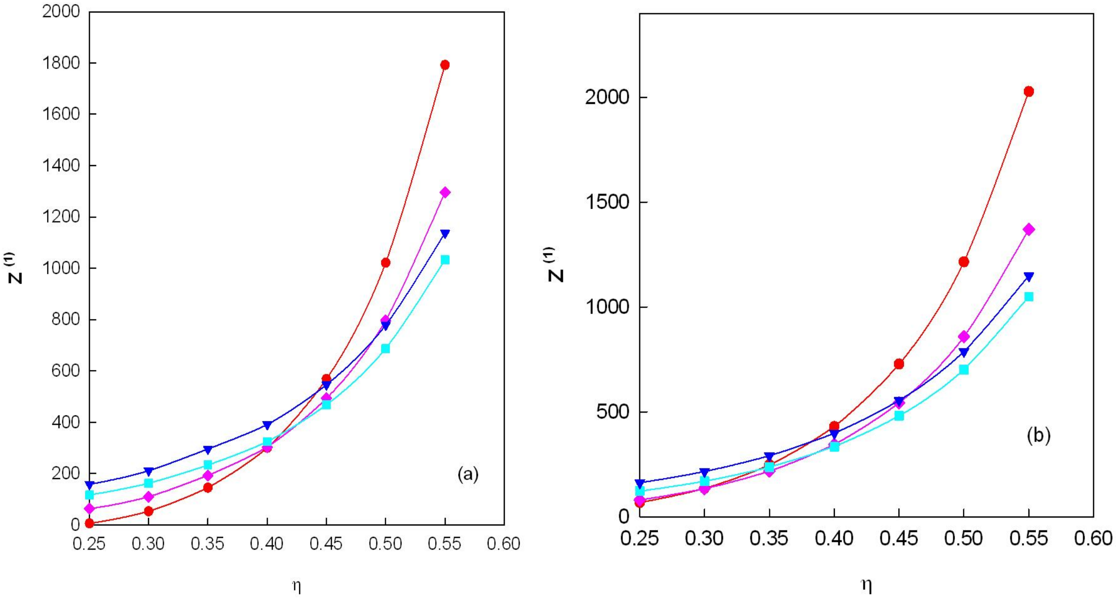

Fig. 1. $Z^{(1)}$ *vs.* η for chain molecules with a length of 100σ and various prolate sphereocylinder segment numbers: 5 (●), 10 (♦), 30 (■) and 50 (▼), in the reduced temperatures (a) 1.4 and (b) 2.4.

variations in temperature. This affirms that the affects the dispersion contribution of the compressibility factor more than the chain contribution. In other words, in Eq. (40) for g^Y, the first term is enough for the calculation of the chain contribution term compressibility factor.

Comparing Figs. 1a with 3a and 1b with 3b shows that the dispersion term in Eq. (41) reduces the compressibility factor values of $Z^{(1)}$ with respect to $Z^{(2)}$ because of the attractive character of dispersion term. In addition, the temperature variation affects only the dispersion interaction and, consequently, the dispersion compressibility factor term.

The effect of potential type on the chain term of the compressibility factor can be found from comparing the

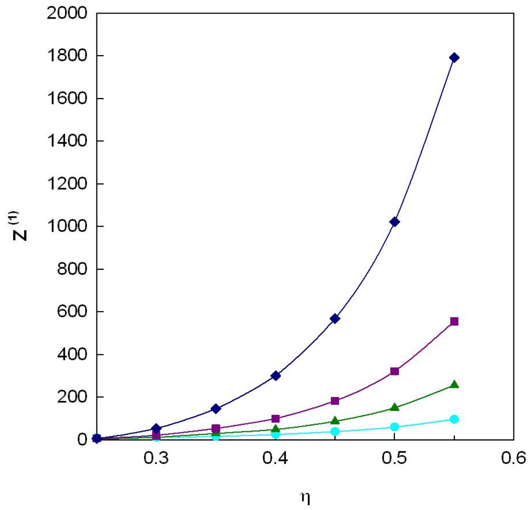

Fig. 2. $Z^{(1)}$ *vs.* η for chain molecules with *m* = 5 and different chain lengths: 10σ (●), 30σ (▲), 50σ (■) and 100σ (♦), in the reduce temperature 1.4.

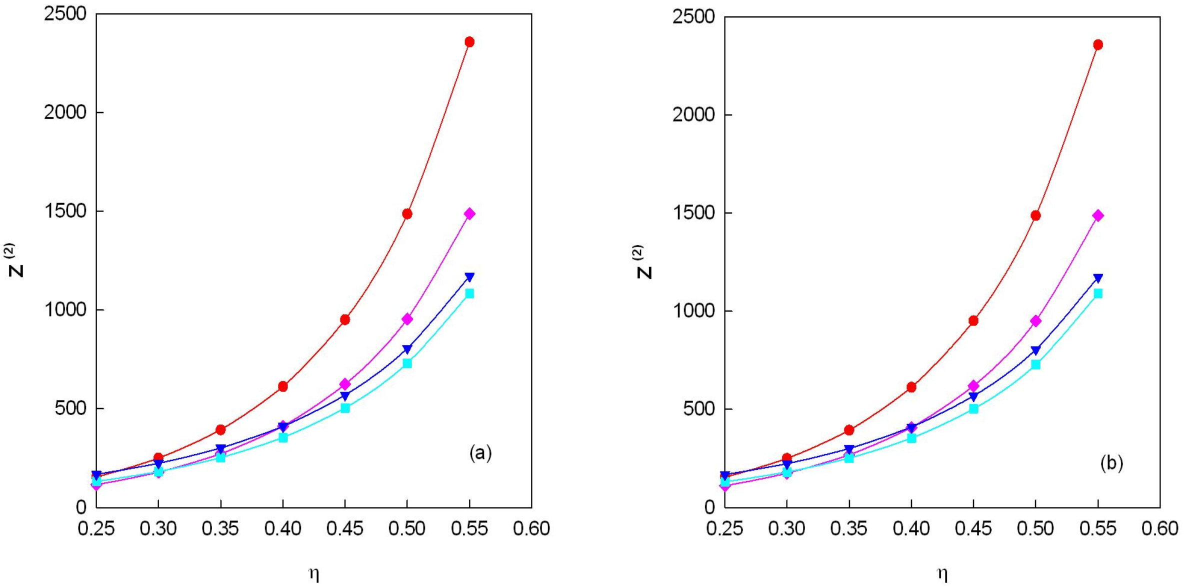

Fig. 3. $Z^{(2)}$ *vs.* η for chain molecules with a length of 100σ and various prolate sphereocylinder segment numbers: 5 (●), 10 (♦), 30 (■) and 50 (▼), in the reduced temperatures (a) 1.4 and (b) 2.4.

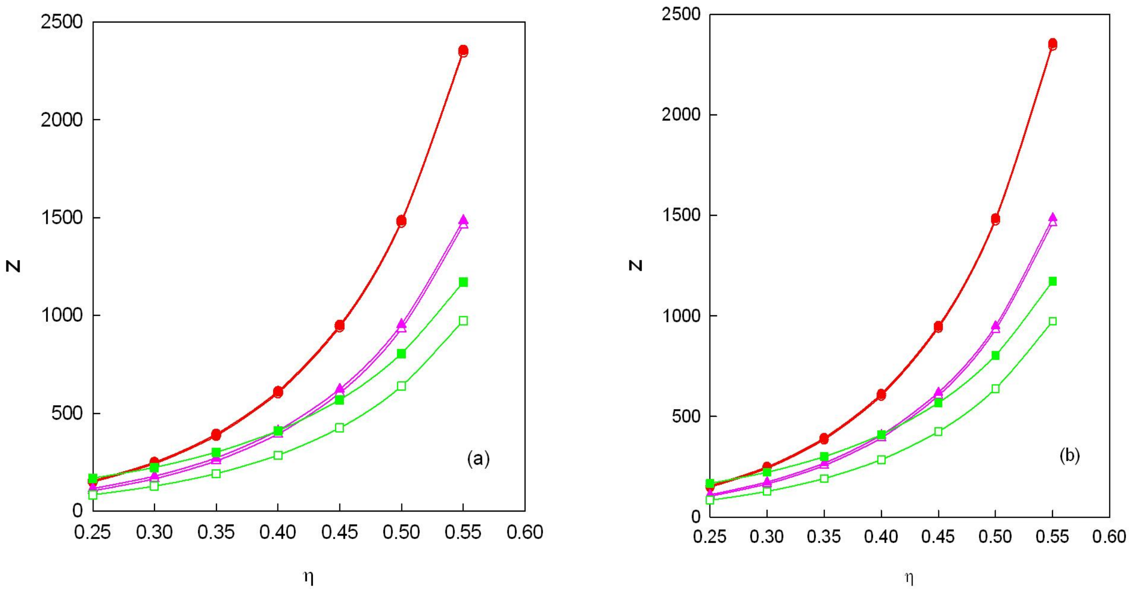

Fig. 4. The compressibility factor of chain molecules of prolate sphereocylinder segments using the hard chain term, Eq. (9), (bold symbol) and the Yukawa chain term, $Z^{(2)}$, (no bold symbol) in the segment numbers: 5 (circle), 10 (triangle), and 50 (square), and the reduced temperatures (a) 1.4 and (b) 2.4.

compressibility factor values [21] of Eq. (9) with Eq. (42), $Z^{(2)}$. In the former equation, the chain segments are considered hard, however, in the latter the chain segments had a hard core with an attractive interaction which is defined with the Yukawa potential. The compressibility factor of chain molecules of prolate spherocylinder segments according to Eqs. (9) and (42) are plotted in Figs. 4a and 4b for $T^* = 1.4$ and 2.4 and different *m*, respectively. It must be noted that Eq. (9) was compared with Eq. (42), since in Eq. (42) the dispersion term is absent as in Eq. (9).

It can be seen that the difference between the compressibility factors of two models increases as the segment numbers increase, but increasing temperature had no effect on the difference of the compressibility factors of the two models. In other words, the type of potential interaction affects more the dispersion term of the compressibility factor and also the chain term just in the high segment numbers.

Since the equation of state, $Z^{(1)}$, is too long, it is hard to fit with the experimental data, but it can be tested in the limiting value of $\alpha = 1$. In this limit, the derived equation of state must be converted to an equation of state for the hard segment chain molecule of variable range potential which has been given by Gil-Villegas *et al.* Figure 5 comprises our results in the $\alpha = 1$ limit with the results of Gil-Villegas *et al*. [32]. As seen, in this limit two equations of state are completely coincidental. Thus, the derived equation of state is well able to predict the behavior of the chain of the hard sphere segments.

VOLUMETRIC PROPERTIES OF CHAIN MOLECULES

The volumetric behavior of gases (vapors), liquids, and solids must be known to calculate; for example, the operation of heat engines, industrial chemical processes, the action of an explosion, and aerodynamic and hydrodynamic effects observed during motion at high velocities. Isothermal compressibility, K_T, and thermal expansion coefficient, α, are two known volumetric properties which are often measured and calculated for different fluids.

Isothermal compressibility, K_T, is the fractional change in volume of a system as the pressure changes at constant

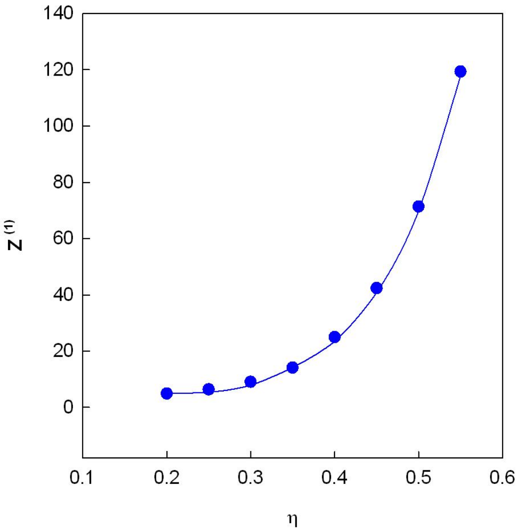

Fig. 5. Comparison of the compressibility factor of chain molecules calculated in this work (line) in the $\alpha = 1$ limit and $m = 10$ with the results of Gil-Villegas *et al*. [32] (●) in the reduced temperature 1.4.

temperature. The isothermal compressibility of a fluid is defined in term of fluid density, as follows:

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{43}$$

Isothermal compressibility is also the reciprocal of the bulk modulus, *B*, of elasticity [33]. The experimental data show B increases by increasing density at constant temperature. The reduced bulk modulus, B_r, is defined as:

$$B_r = \frac{1}{RT}\left(\frac{\partial P}{\partial \rho}\right)_T \tag{44}$$

The reduced bulk modulus can be given in terms of the compressibility factor and the packing fraction as:

$$B_r = Z + \eta\frac{\partial Z}{\partial \eta} \tag{45}$$

Thermal expansion coefficient, α, is the fractional change in the volume of a system with temperature at constant pressure [34]. Temperature is a monotonic function of the average molecular kinetic energy of a substance. The kinetic energy of its molecules increases, when a substance is heated. Thus, the molecules begin moving more and usually maintain in a greater average separation. Thermal expansion coefficient is given in terms of density as,

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{46}$$

The subscript *p* indicates that the pressure is held constant during the expansion. The reduced thermal expansion coefficient can be given in terms of the compressibility factor and the packing fraction as:

$$\alpha_r = \frac{\left(Z + T\frac{\partial Z}{\partial T}\right)_\eta}{B_r} \tag{47}$$

If an equation of state is available, it can be used to predict the thermal expansion coefficient and the reduced bulk modulus values at all the required temperatures and pressures.

Therefore, in this study, the reduced bulk modulus and the reduced thermal expansion coefficient of the nonassociated chain molecules composed of hard convex

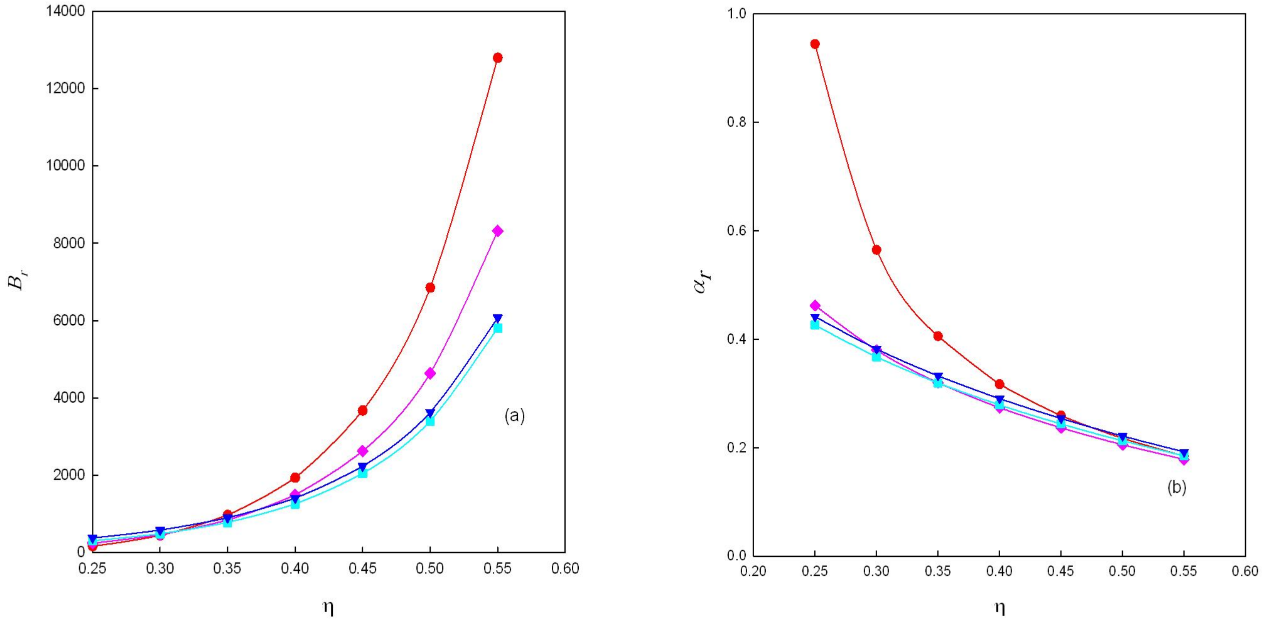

Fig. 6. The reduced bulk modulus (a), B_r, and the reduced thermal expansion coefficient, α_r, (b) *vs.* η for chain molecules with a length of 100σ and various prolate sphereocylinder segment numbers, *m*: 5 (●), 10 (♦), 30 (■) and 50 (▼), in the reduced temperature 1.4.

core Yukawa segments have been calculated by using $Z^{(1)}$. Figures 6a and 6b show the plots of the reduced bulk modulus and the reduced thermal expansion coefficient of the nonassociated chain molecules versus the packing fraction in different segment numbers, respectively.

The variation of the reduced bulk modulus and the reduced thermal expansion coefficient with the chain length in a constant segment numbers (m = 5) has been also shown in Figs. 7a and 7b, respectively.

From Figs. 6 and 7, it is found that the calculated reduced bulk modulus increases and the calculated reduced thermal expansion coefficient decreases by increasing the packing fraction. This is consistent with experience. It can be also seen that both B_r and α_r decrease as segment numbers increase in a constant chain length. It must be noticed that in spite of increasing B_r by the chain length, the variation of α_r with chain length is very small.

CONCLUSIONS

The segment type of chain molecules are usually considered spherical, but in most molecules they are neither spherical nor spherically symmetric. Therefore, finding a general equation of state that can be applied to the chain molecules of spherical or non-spherical segments has a particular importance. Though, the equation of state derived by Sadus [21] for hard convex chain molecules has such a trait, but only the repulsion interaction between the segments was considered; the attraction forces were absent.

In this work, a variable range attraction interaction and repulsion are considered in derivation of an equation of state for hard core convex chain molecules. The SAFT-VR description is extended to the hard core convex segments of chain molecules using the hard convex perturbation theory presented by Boublik for convex bodies. The derived equation of state predicts (in accordance with the experiment) that the compressibility factor of the chain molecules increase with the packing fraction and length of molecules, but it decreases with segment number and temperature. The obtained relation for the compressibility factor of chain molecules, $Z^{(1)}$, is a temperature-dependent equation. However, despite the temperature dependency of both the chain and dispersion contributions to the

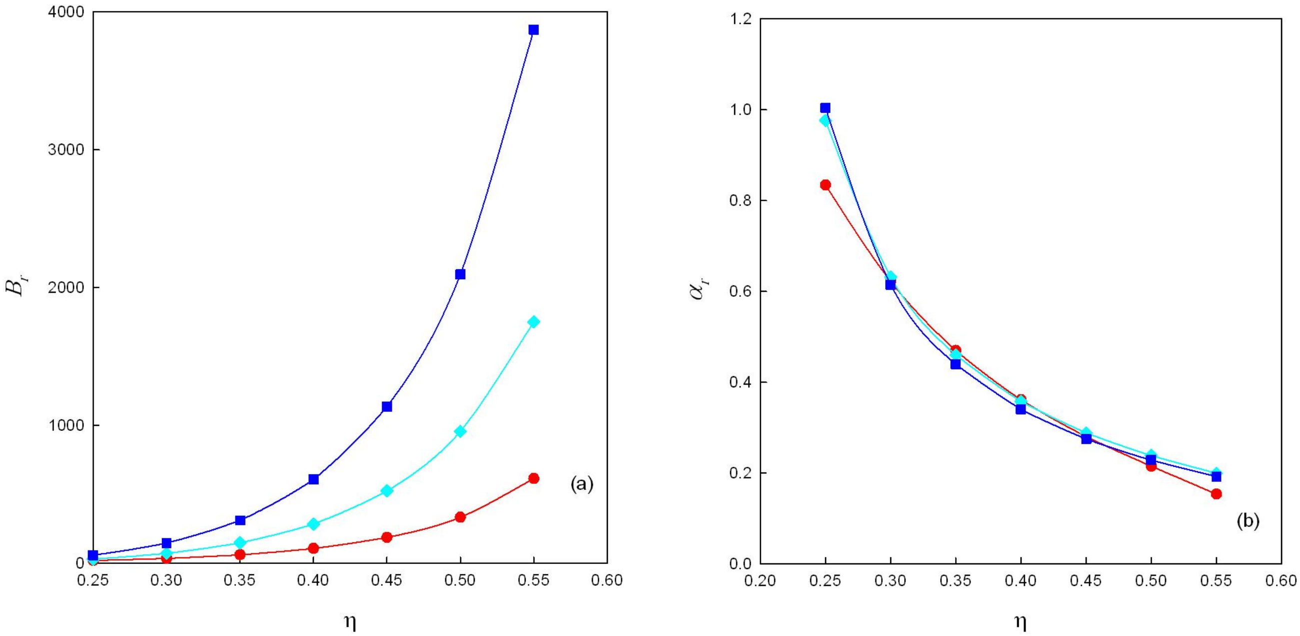

Fig. 7. The reduced bulk modulus (a), B_r, and the reduced thermal expansion coefficient, α_r, (b) *vs*. η for the chain molecules with $m = 5$ and different chain lengths: 10σ (●), 30σ (▲) and 50σ (■), in the reduce temperature 1.4.

compressibility factor, the chain compressibility factor changes very little with temperature. Comparing the results of the present work with that of Sadus revealed the important role of the dispersion force in the compressibility factor of chain molecules.

It was also shown that the derived equation of state (CB-SAFT-VR) and the Gil-Villegas *et al*. SAFT-VR equation of state are completely coincidental in the $\alpha = 1$ limit.

The reduced bulk modulus and the reduced thermal expansion coefficient were calculated by the compressibility factor of the chain molecules of hard convex body core Yukawa segments. The results show that the reduced bulk modulus increases with the packing fraction and chain length but decreases with segment number. The reduced thermal expansion coefficient decreases with the packing fraction and segment number, but its variation with chain length is very small.

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