

Analytic Equation of State for the Square-well Plus Sutherland Fluid from Perturbation Theory

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Analytic expressions were derived for the compressibility factor and residual internal energy of the square-well plus Sutherland fluid. In this derivation, we used the second order Barker-Henderson perturbation theory based on the macroscopic compressibility approximation in combination with an analytical expression for radial distribution function of the reference hard sphere fluid. These properties are expressed in terms of density, temperature, and the potential parameters. Derived equations successfully applied to hard-core Lennard-Jones fluid. It is found that the agreement between theory and simulation is quite good for both the compressibility factor and the residual internal energy for a wide range of densities and temperature.

Keywords: Equation of state, Thermodynamic properties, Square-well plus Sutherland fluid, Radial distribution function, Pair potential

INTRODUCTION

Reliable models for the accurate correlation and prediction of thermodynamic properties of pure fluids and their mixtures are of much demand for process design and material handling in the chemical and petroleum industries [1-3]. Therefore, these properties have been widely studied by both theoretical and computer simulation methods. Helmholtz free energy is one of the most important thermodynamic properties from which any other derivative properties such as pressure, chemical potential and specific heat can be derived. An exact and easy to handle expression for the Helmholtz free energy with a wide range of validity is also very important for chemical engineering applications and theoretical tests [4]. The perturbational or variational techniques, being the only viable methods, besides the Monte Carlo and molecular dynamics simulations are of great importance [5]. The perturbation theories include those of Barker-Henderson (BH), Weeks-Chandler-Anderson (WCA), and variational approaches such as Mansoori-Canfield (MC) and Rasaiah-Stell (RS) are most

frequently used in the research of thermodynamic properties of fluids [6,7]. The main difference among these theories is the separation of the interaction potential into reference and perturbation and in the criterion for evaluation of the hard sphere diameters [7,8]. All the approaches mentioned above offer techniques for predicting the thermodynamic properties of fluids, given only the interaction potential between pairs of molecules in the system and generally employ the hard sphere potential as a reference. Robles and Haro [9] revised these approaches for Lennard-Jones fluid using the hard sphere-fluid as the reference system. Their results indicate the correlation between the isotherms in the fluid region and the location of the critical point; the second order BH scheme yields the best performance compared with the simulation data. Also, it is well known that this approach has yielded excellent results for pure liquids [10-14] and liquid mixtures [15-17] with different interaction potentials. Therefore, in this study we have preferred second order perturbation theory of BH.

Perturbation theories have been successfully applied to fluids with molecules interacting by means of a variety of potential models, especially spherical potentials with a hard repulsion and attractive tail, such as the square-well [18-22],

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triangular-well [23-26], Yukawa [27-30], or Sutherland potentials [31-33], also the soft potentials, such as the 6-12 Lennard-Jones [34-37] or exponential-six [6,38] potentials. They can also be used for nonspherical and polar molecules [39]. Paricaud [40] presented a new perturbation scheme based on the BH perturbation theory to predict the thermodynamic properties for a large variety of potential functions.

Potential functions, such as hard sphere (HS), square-well (SW), triangular-well (TW), Sutherland (S) and Lennard-Jones (LJ) are known to be empirical in nature, and that they can approximate very well the intermolecular forces in real fluids [41]. Although it is desirable that a model potential function would be able to represent intermolecular forces for various kinds of fluids as accurately as possible, in a simple mathematical form, it is difficult to satisfy these requirements simultaneously [42]. Unfortunately, in most cases this can lead to non-analytical expressions for the theoretically obtained thermodynamic properties which reduce their usefulness [23].

Nevertheless, there are a few potential functions having a form similar to the real spherically-shaped molecules, which have been suggested as alternatives to the functions mentioned above [1,42-44]. These potential functions are generally extended versions of the SW potential function, having four or more parameters. The potential function considered in this study has a similar shape with those mentioned above, but with some advantages over them, due to its fewer parameters and simplicity of the mathematical form. This potential function, which was first proposed by Pollara and Funke [43] and shown in Fig. 1, combines the advantages of both the SW and the S potentials; an adjustable bowl width, a hard repulsion, and a realistic attraction. Pollara and Funke [43] applied this potential function to neopentane for the calculation of second virial coefficient only. This potential function (SWS) is given by the following equations:

$$u(r) = \begin{cases} \infty & r \leq \sigma \\ -\varepsilon & \sigma \leq r \leq \lambda\sigma \\ -\frac{\gamma}{r^k} & r \geq \lambda\sigma \end{cases} \quad (1)$$

where σ is the hard-core diameter, ε is the depth of the well,

and λ is the reduced well width of the potential and γ is given by $\gamma = (\lambda\sigma)^k \varepsilon$. Here, k exponent practically determines the effective range of the potential. In this study, we have used the value $k = 6$ which is commonly used in the literature. This potential reduces to the Sutherland potential for $\lambda = 1$ and to the square-well potential for $\gamma = 0$. In spite of its simplicity, very little attention has been devoted to the SWS potential [45,46]. The second order BH perturbation theory was applied to SWS fluid by Boghdadi [45]. He used low density expansion form of hard sphere radial distribution function (RDF) to calculate the first four virial coefficients and compared his results with TW, SW and LJ. In addition, the coefficient of linear density in the expansion of RDF in powers of density has also been evaluated by Boghdadi in the case of SWS potential [46].

The purpose of this study is to show that any analytical calculation based on the SWS potential can be readily performed as easily as SW and S potentials and also to construct a framework which can be used in the applications of real systems. Therefore, in this study, we obtained analytical expressions for the equation of state and residual internal energy of pure SWS fluids of different widths as a function of the temperature, density and k parameter. These expressions were derived from the second order BH theory in combination with an analytic expression for the RDF of the hard sphere reference fluid which was obtained by fitting the Monte Carlo simulation data and the numerical results of the Percus-Yevick approximation for the first two coordination shells by Sun [32]. Because of the lack of any theoretical or simulation results relating to this potential, the equation of state obtained has been applied to the hard-core Lennard-Jones (HCLJ) fluid showing similar behaviour. The obtained results are in good agreement with the computer simulation data.

PERTURBATION THEORY

Perturbation theory is a very general approach devised to calculate the thermodynamic properties of fluids and solids, giving just the interaction potential between pairs of molecules in the system [47]. The basic idea of the perturbation theory is to write the pair potential energy $u(r)$ of the system as a sum of two terms

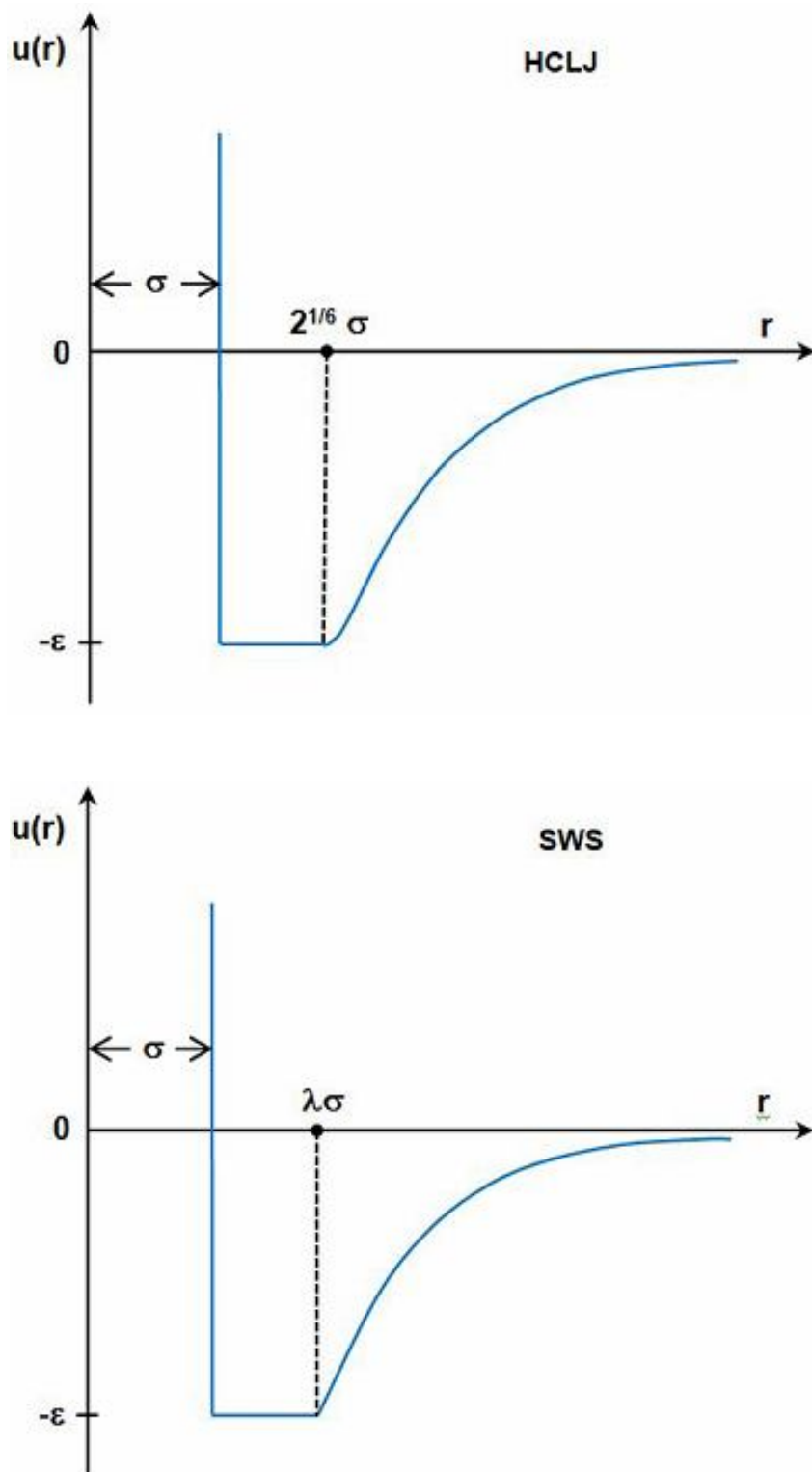


Fig. 1. Schematic representation of SWS and HCLJ potential functions.

$$u(r) = u_0(r) + u_1(r) \quad (2)$$

where $u_0(r)$ is the pair potential of the unperturbed system that includes mainly the short-range repulsive contributions to the force between the molecules, and $u_1(r)$ is the perturbation term that includes mainly the attractive contributions [48]. For nonpolar molecules, these two contributions would be

$$u_0(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \quad (3)$$

which is just the hard-sphere potential, and

$$u_1(r) = \begin{cases} 0 & r \leq \sigma \\ -\varepsilon & \sigma \leq r \leq \lambda\sigma \\ -\frac{\gamma}{r^k} & r \geq \lambda\sigma \end{cases} \quad (4)$$

respectively.

In perturbation theory of fluids, the thermodynamic properties at high densities are considered to be determined mainly by $u_0(r)$, whereas the contributions due to $u_1(r)$ are considered as a perturbation of formers. Under these circumstances, the thermodynamic properties can be expressed as a power series in the inverse of the reduced temperature, $T^* = k_B T / \varepsilon$, where k_B is the Boltzmann constant. The residual Helmholtz free energy in the Barker and Henderson perturbation theory of fluids truncated at the second order is written as [36]

$$\frac{A^{res}}{Nk_B T} = \frac{A - A^{id}}{Nk_B T} = \frac{A^{HS}}{Nk_B T} + \frac{A_1}{Nk_B T} \frac{1}{T^*} + \frac{A_2}{Nk_B T} \frac{1}{T^{*2}} \quad (5)$$

where N is the number of molecules in volume V , superscripts *id* and *HS* stand for ideal gas and hard sphere, respectively. The first order term is given by

$$\frac{A_1}{Nk_B T} = 2\pi\rho \int_0^\infty u_1^*(r) g^{HS}(r) r^2 dr \quad (6)$$

where $u_1^*(r) = u_1(r)/\varepsilon$ is the potential in units of ε .

By assuming that the space is divided into many

concentric spherical shells around a central molecule and also each spherical shell having large macroscopic volume, Barker and Henderson derived out a simple expression for the second-order term called the macroscopic compressibility (mc) approximation, which is given by [36]

$$\frac{A_2}{Nk_B T} = -\pi\rho k_B T \left(\frac{\partial \rho}{\partial p} \right)_{HS} \int_0^\infty [u_1^*(r)]^2 g^{HS}(r) r^2 dr \quad (7)$$

where $(\partial \rho / \partial p)_{HS}$ refers to the change in the number density with pressure for the reference HS fluid. From the perturbative contributions to the free energy, the relevant contributions to the residual internal energy and to the compressibility factor (*i.e.* the equation of state) can be readily obtained from the following classic thermodynamic relationships

$$\frac{U^{res}}{Nk_B T} = -T^* \frac{\partial}{\partial T^*} \left(\frac{A^{res}}{Nk_B T} \right) \quad (8)$$

and

$$Z = \frac{pV}{Nk_B T} = \eta \frac{\partial}{\partial \eta} \left(\frac{A}{Nk_B T} \right) \quad (9)$$

where $\eta = \pi\rho\sigma^3/6$ is the packing fraction and $\rho = N/V$ is the particle density. In order to obtain the thermodynamic properties of a fluid whose particles interact by means of a spherically symmetric potential, the BH theory requires knowledge of the equation of state and the RDF of a reference hard-sphere fluid. For HS fluid, a great number of equations of state are available (see extensive reviews [49-52]). Among them, the most frequently used is the Carnahan and Starling (CS) equation of state [9], which combines the simplicity and accuracy:

$$Z^{HS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (10)$$

There are several analytical expressions for the RDF of a hard sphere fluid [32,53-57]. In this study, we used the expression proposed by Sun [32] which is developed in terms of a polynomial expansion of nonlinear base function and the CS equation of state. The simplicity and precision of

his expression is superior to the well-known Pecus-Yevick expression. It is expressed in the form of

$$g^{HS}(x) = \begin{cases} 0 & x < 1 \\ 1 + \sum_{m=1}^3 \frac{\eta^m}{(1-\eta)^m} g_m(x) & 1 \leq x < 3 \\ 1 & x \geq 3 \end{cases} \quad (11)$$

where $x = r/\sigma$ is the radial coordinate reduced to the hard core diameter, and $g_m(x)$ is given by

$$g_m(x) = \begin{cases} \sum_{n=0}^3 A_{mn} (x - x^{-4})^n & 1 \leq x < 2 \\ \sum_{n=0}^3 B_{mn} (x - 256x^{-7})^n & 2 \leq x < 3 \end{cases} \quad (12)$$

The values of A_{mm} and B_{mm} coefficients are given in Ref. [32]. Sun [32], applied this expression to develop analytic equations of state for S and SW fluids using second order BH perturbation theory and showed that results are in good agreement with computer simulation data. Also, he showed that the use of the B_{mm} coefficients made only negligible differences for the S and SW potentials. Therefore, we ignore B_{mm} coefficients and consider only the first coordination shell ($1 < x < 2$).

Substituting Eqs. (4) and (11) into Eqs. (6) and (7) yields

$$\frac{A_1}{Nk_B T} = -12\eta \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} [L_m(\lambda) + \gamma L_m(k)] \quad (13)$$

$$\frac{A_2}{Nk_B T} = -6\eta Q \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} [L_m(\lambda) + \gamma L_m(2k)] \quad (14)$$

where Q is the isothermal compressibility of the reference hard sphere system and is given by

$$Q = k_B T \left(\frac{\partial \rho}{\partial p} \right)^{HS} = \frac{(1-\eta)^4}{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4} \quad (15)$$

for the CS equation of state. $L_m(\lambda)$ and $L_m(k)$ are nondimensional auxiliary coefficients introduced by Sun [32]. If we adopt the potential function as in the Eq. (4), then these coefficients are given by

$$L_0(\lambda) = \int_1^\lambda x^2 dx = \frac{1}{3}(\lambda^3 - 1) \quad (16)$$

$$L_m(\lambda) = \int_1^\lambda g_m(x) x^2 dx = \sum_{n=0}^3 \sum_{l=0}^n A_{mn} \frac{(-)^l n!}{l!(n-l)!} \frac{(\lambda^{n-5l+3} - 1)}{(n-5l+3)} \quad (17)$$

$$L_0(k) = \int_\lambda^\infty x^{2-k} dx = \frac{\lambda^{3-k}}{k-3} \quad (18)$$

$$L_m(k) = \int_\lambda^3 g_m(x) x^{2-k} dx \approx \int_\lambda^2 g_m(x) x^{2-k} dx \\ = \sum_{n=0}^3 \sum_{l=0}^n A_{mn} \frac{(-)^l n!}{l!(n-l)!} \frac{(2^{n-5l-k+3} - \lambda^{n-5l-k+3})}{(n-5l-k+3)} \quad (19)$$

The compressibility factor can be obtained from Eq. (9) in the form:

$$\frac{pV}{Nk_B T} = \left(\frac{pV}{Nk_B T} \right)^{HS} + \frac{p_1 V}{Nk_B T} \frac{1}{T^*} + \frac{p_2 V}{Nk_B T} \frac{1}{T^{*2}} \quad (20)$$

First term in the right hand side of this equation is given by Eq. (10), and

$$\frac{p_1 V}{Nk_B T} = -12\eta \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} \left(1 + \frac{m}{1-\eta} \right) [L_m(\lambda) + \gamma L_m(k)] \quad (21)$$

$$\frac{p_2 V}{Nk_B T} = -6\eta Q \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} \left(1 + \frac{m}{1-\eta} + \frac{\eta}{Q} \frac{\partial Q}{\partial \eta} \right) [L_m(\lambda) + \gamma L_m(2k)] \quad (22)$$

the residual internal energy is derived from Eq. (8) as follows:

$$\frac{U^{res}}{Nk_B T} = \frac{A_1}{Nk_B T} \frac{1}{T^*} + 2 \frac{A_2}{Nk_B T} \frac{1}{T^{*2}} \quad (23)$$

Using these equations, all other thermodynamic quantities can be evaluated analytically.

Since the expressions obtained here can be reduced readily into the equations which correspond to the S and SW potentials by taking $\lambda = 1$ and $\gamma = 1$, respectively, and these special cases are extensively treated by Sun [32], we will not give any detailed derivations here.

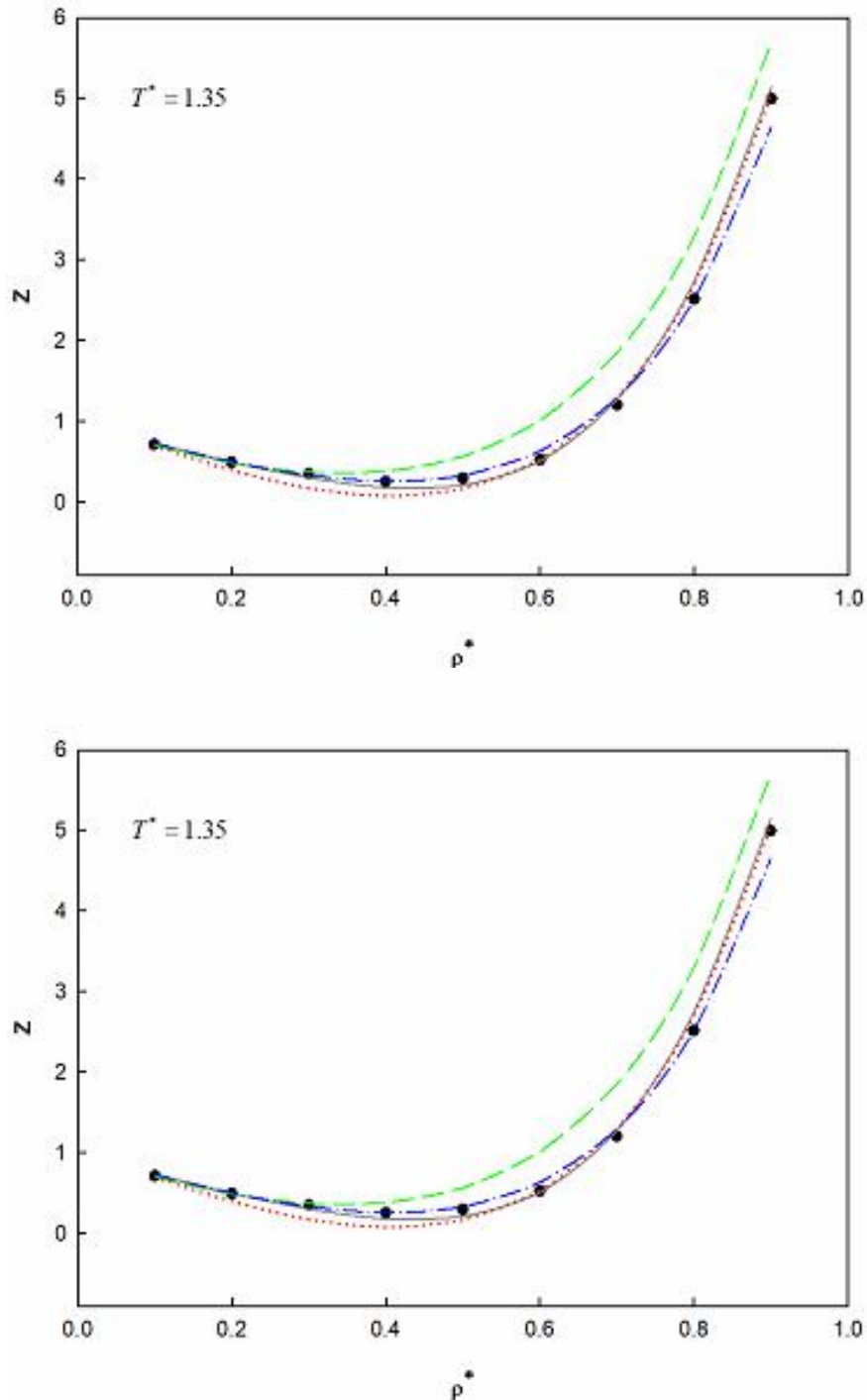


Fig. 2. Compressibility factor $Z = pV/Nk_B T$ for HCLJ fluids as a function of the reduced density $\rho^* = \rho\sigma^3$ and reduced temperature $T^* = k_B T/\varepsilon$. Points (black): simulation data from Ref. [59]; Continuous lines (grey): from Eq. (20); Dashed lines (green): from Ref. [42]; Dotted lines (red): from Ref. [1]; Dashed-dotted lines (blue): from Ref. [59].

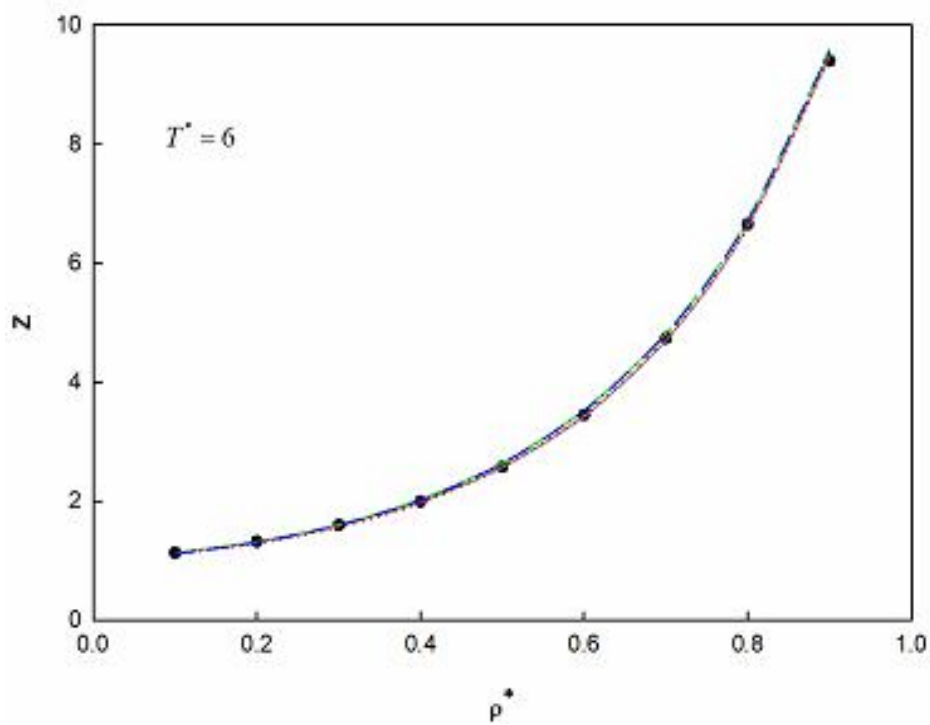
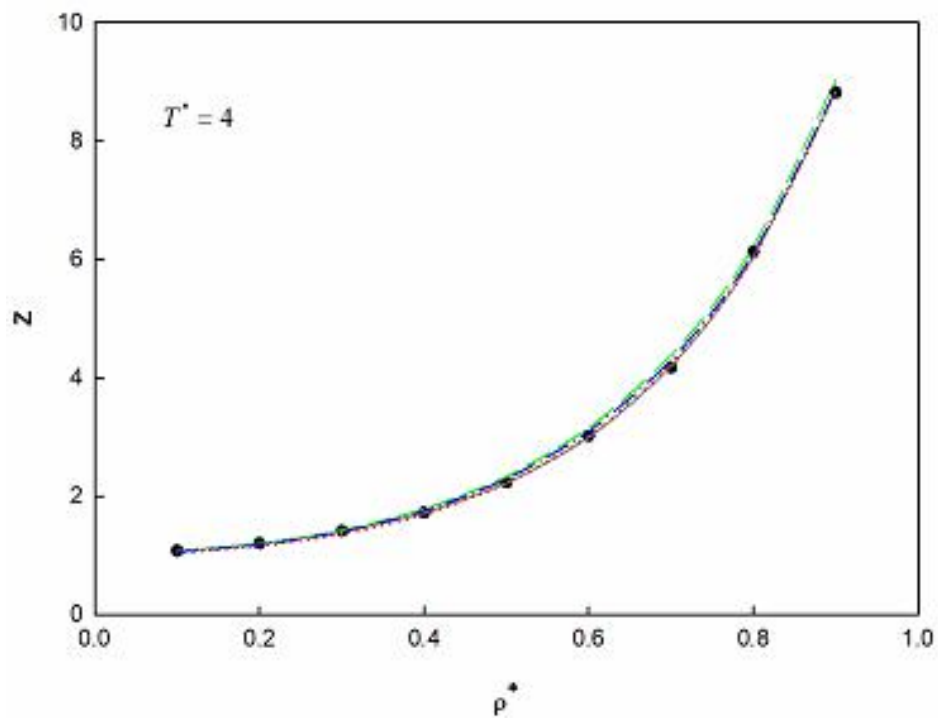


Fig. 2. Continued.

APPLICATION TO HCLJ FLUID

Since, there are not any computer simulation results reported in the literature for the SWS fluid, the equation of state obtained here has been applied to the HCLJ fluid which has demonstrated fairly similar behaviour. This potential function is shown in Fig. 1, which was firstly proposed by Stell and Weis [58] and is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma \leq r \leq 2^{1/6} \sigma \\ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r > 2^{1/6} \sigma \end{cases} \quad (24)$$

Sowers and Sandler [59] obtained internal energy and compressibility data of this potential by means of Monte Carlo simulation and then they have used their results to derive two new equation of states based on the perturbation theory. Shen and Lu, [1] and Farrokpour and Parsafar [42] developed an equation of state for their potential functions with four parameters based on the perturbation theory of BH, and then applied the expressions obtained to the HCLJ fluid. To adopt the expressions obtained in both studies to the HCLJ fluids, an analytical method was used to define the parameters of potential functions considered in terms of the HCLJ potential parameters. However, this method allows to determine only two parameters analytically (well depth ε and steepness of the potential tail α), and the remaining two parameters (reduced well width λ and hard core diameter σ) have been kept constant ($\lambda = 1.3$ ve $\sigma = \sigma_{HCLJ}$) in both studies. The ε parameter associated with the related potential functions used these studies seems to be very close to ε_{HCLJ} ($\varepsilon/\varepsilon_{HCLJ} = 0.914$). The results obtained by using these parameters have been compared with the simulation data.

In this study, we chose $\sigma = \sigma_{HCLJ}$ and $\varepsilon = \varepsilon_{HCLJ}$ because of the formal similarity of SWS potential to the HCLJ potential (see Fig. 1) and also considering the results of [1,42]. For the value of λ parameter, we have taken into account the preliminary results of another work in progress performed by our group. In that study, the SWS potential parameters have been determined by means of a fitting

procedure to the second virial coefficients and it is found that the values of λ are in the range of 1.2-1.3 for the noble gases such as Ar, Kr and Xe. Thus, an average value of $\lambda = 1.23$ is used in the calculations. So, the residual internal energy and the compressibility factor for the HCLJ fluid were calculated using the mentioned values. A comparison of the obtained results for the compressibility factor and residual internal energy with the computer simulation data [59] and with the results of different equations of state [1,42,59] are presented in Figs. 2 and 3, respectively. As can be seen from Fig. 2 which represents the compressibility factor results, all equations are in a good consistency with each other at the high temperature region, while deviations become apparent as the temperature is reduced. Minimum deviation seems to happen for the Eq. (20) in the whole temperature range. On the other hand, it is clearly seen that all equations give rise to dramatical deviations in the whole temperature range except for Eq. (23) in Fig. 3 for the residual internal energy results. The main reason of these deviations may be the form of the potential functions used. At lower temperatures, intermolecular attraction is dominant over the repulsion forces and therefore, this part of the potential function play an effective role in the equilibrium and/or transport properties. The potential functions associated with the results given in Figs. 2 and 3 here have a finite attraction, while SWS potential shows an infinite extension. A finite range means that probable small contributions in the long ranges can be neglected, and this situation can give rise to dramatical influence on the results. Another important factor at this point is the possible deficiencies arising from the determination procedure of the potential parameters in terms of HCLJ parameters, while, for SWS potential, one does not encounter such a situation. Considering all the results obtained in this study, it seems that the equations given here are reliable and correct.

CONCLUSIONS

We showed that it is possible to obtain analytical expressions for the thermodynamic properties of SWS fluid from a second order Barker-Henderson perturbation theory. The expressions derived here may be of interest for several reasons. First, due to their analytical character, they require less computational effort than other procedures and it is

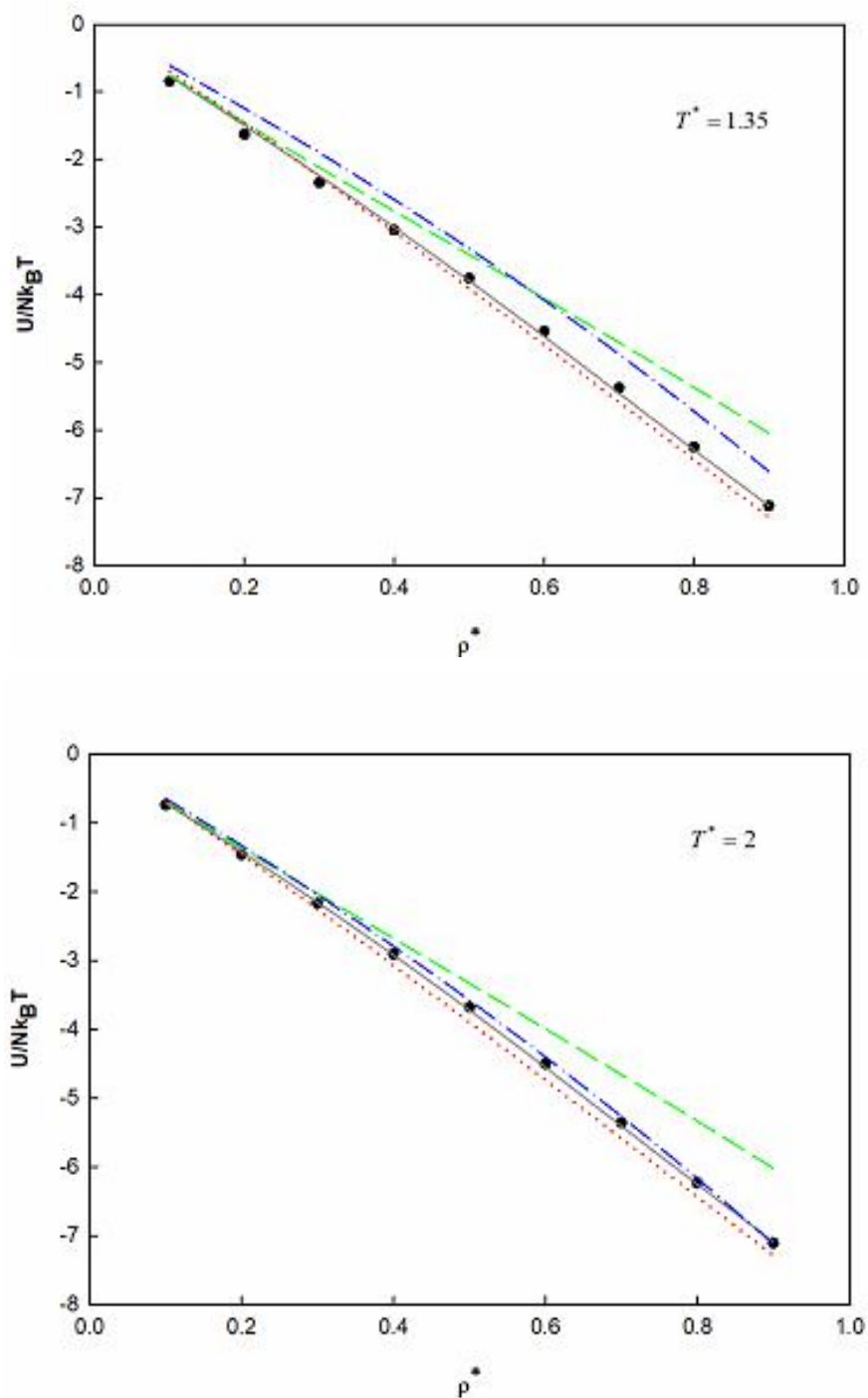


Fig. 3. Residual internal energy for HCLJ fluids as a function of the reduced density $\rho^* = \rho\sigma^3$ and reduced temperature $T^* = T\sigma^3/k_B\epsilon$. Points (black): simulation data from Ref. [59]; Continuous lines (grey): from Eq. (23); Dashed lines (green): from Ref. [42]; Dotted lines (red): from Ref. [1]; Dashed-dotted lines (blue): from Ref. [59].

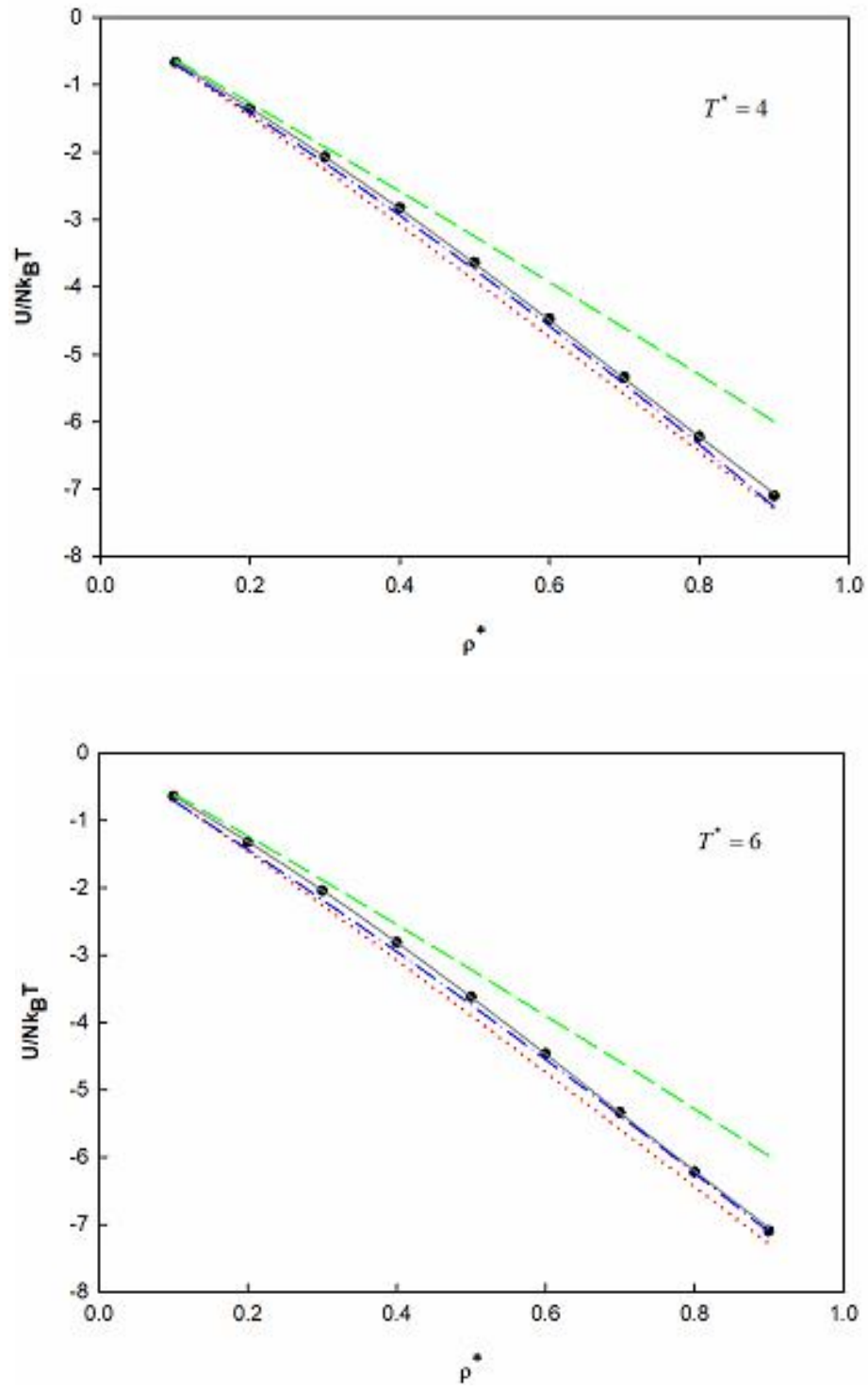


Fig. 3. Continued.

easier to perform some mathematical operations such as derivations or integrations over them. The second is that they might be useful to obtain the corresponding properties of fluids with more complicated intermolecular potentials such as the LJ or HCLJ potential provided that the parameter ε , σ and λ of the SWS potential are suitably chosen. Furthermore, Eq. (20) might be used to analytically represent the equation of state of simple real fluids, by treating the parameters of the SWS potential as adjustable parameters. A further work with this potential is now in progress for investigating the properties of elementary gases.

In summary, the SWS potential is more realistic than those of SW, TW and S potentials. Also it can be applied as easily as the other potentials such as LJ, and therefore we believe that this potential function will take the place of other potential functions and will be successful for the application in real systems.

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