Triangular-Well of Variable Width: Theory and Simulation

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ABSTRACT

The use of a two-parameter potential results in a simple re-scaling of the properties of the fluid [1]. This leads to the corresponding states (CS) principle already established in the classical statistical mechanics [2]. Most of the fluids do not follow this principle so the use of a three-parameter potential is required in order to obtain deviation from the CS principle.

The square-well (SW) potential of variable width is the simplest three-parameter model. This potential gives a non-conformal behavior of the fluids [1]. It has been already used to develop different equations of state and discrete potentials to model real fluids [3,4]. An alternative to the SW potential is the use of another simple model like the triangular-well (TW) potential. This potential has the advantage that it changes softly as the distance increases, which is characteristic of real fluids instead of the drastic change presented in the SW potential [2].

The TW potential of variable width has not been widely studied in the literature except for some Monte Carlo simulation results for the case of a width of two times the sphere diameter [5,6]. No equation of state (EoS) has been reported for the TW potential of variable width.

In this work, an EoS for the TW of variable width based on the perturbation theory of Barker and Henderson is presented. This EoS is compared with Monte Carlo simulation results previously reported in the literature [5,6] and with new results obtained in this work by Monte Carlo simulation of the TW fluid for different potential widths.

INTRODUCTION

It has been shown that the use of a two-parameter model to represent the properties of real fluids falls in the use of the CS principle. This is the case for the cubic EoSs [7]. The use of a third parameter allows a non-conformal behavior. The use of non-conformal potential has been previously studied by means of the square-well potential, which expresses the basic behavior of the real fluids, however it cannot represent the slow decay at long distances from the center of the molecule, which is more like the behavior of the real molecules.

The triangular-well potential of variable width can be use to represent a non-conformal behavior with a relative simple algebraic potential, having the advantage that only the discontinuity raised from the hard core is presented in the radial distribution function (RDF) of this fluid.

THEORY

The perturbation theory introduced by Barker and Henderson [8] was used to represent the properties of the triangular-well of variable width. According to this theory a reference fluid is needed, being the hard-sphere fluid the natural choice because of the presence of the hard core in the triangular-well. The required expression of the RDF for the reference fluid is expressed as

$$g(x) = \frac{1}{\eta}\sum_{m=1}^{3} g_m(x)\left(\frac{\eta}{1-\eta}\right)^m \tag{1}$$

$$g_m(x) = \sum_{n=0}^{3} A_{mn}\left(x - \frac{1}{x^7}\right)^n \tag{2}$$

Where the A_{mn} coefficients have been obtained by fitting Monte Carlo results for the RDF of the hard-sphere fluid obtained previously in this work. The expression presented is valid for distances from 1σ up to 2σ. The AAD obtained is 1.17 %.

Using equation (1) and (2), the first and second order perturbation terms were evaluated. For the second order term the approach made by Zhang [9] was used. The EoS for the triangular well of variable width can be write in terms of the residual Helmholtz free energy as

$$\frac{A^{res}}{NkT} = \frac{A_0}{NkT} + \frac{\varepsilon}{kT}\frac{A_1}{NkT} + \left(\frac{\varepsilon}{kT}\right)^2 \frac{A_2}{NkT} \tag{3}$$

$$\frac{A_1}{NkT} = 12\eta\sum_{m=1}^{3} C_m(\lambda)\left(\frac{\eta}{1-\eta}\right)^m \tag{4}$$

$$\frac{A_1}{NkT} = -6\eta(1+8.26\eta)\frac{(1-\eta)^4}{1+4\eta+4\eta^2-4\eta^3+\eta^4}\sum_{m=1}^{3} D_m(\lambda)\left(\frac{\eta}{1-\eta}\right)^m \tag{5}$$

Where A_0 is the Helmholtz free energy of the reference fluid, $C_m(\lambda)$ and $D_m(\lambda)$ are functions of the well width obtained by the use of the perturbation theory. The behavior for the first term at various values for the well width is presented in Figure 1.

The thermodynamic properties can be obtained using the classical relationships. No temperature dependence has been tested for the sphere diameter.

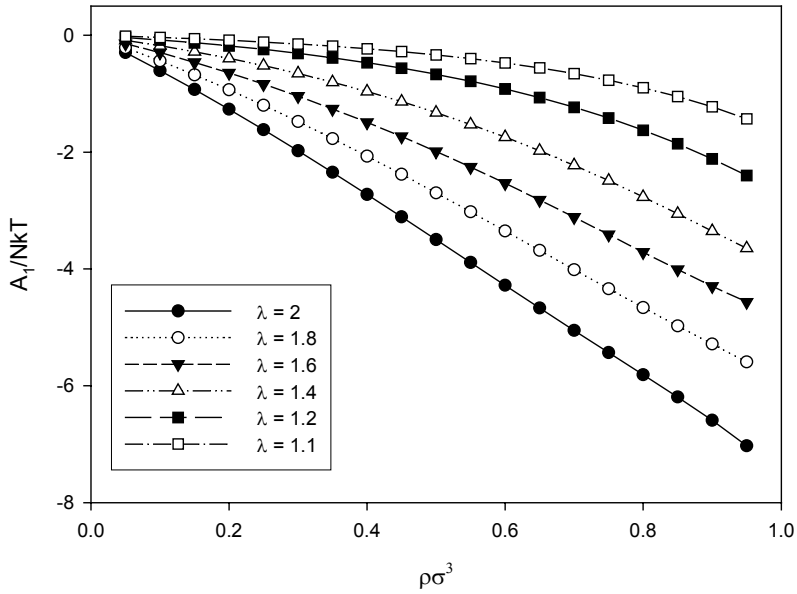

Figure 1. Behavior of the first perturbation term for various well widths.

MOLECULAR SIMULATION

The simulations for the fluid of triangular well of variable width were made on the NPT Ensemble [10] with a system composed by 512 molecules using the Metropolis sampling scheme [10]. The molecules were originally placed on a cubic lattice. The simulation was carried out in cycles each one consisting in approximately 200 particles displacement attempts and 2 volume change attempts. The order of the different attempts is chosen at random. The acceptance ratio for the particle displacement and volume change was settled to about 50%. The system was then equilibrated by $1x10^6$ cycles to ensure no influence of the initial configuration, and then the properties were calculated from the next $1x10^6$ cycles.

Potential wells in the range of 1.1 up to 2 times the hard sphere diameter were studied. Reduced temperatures from 1 to 5, and reduced densities from 0.1 to 0.8 were considerate. Neither the dependence in the size of the studied system nor correction to the thermodynamic limit of the properties has been done.

RESULTS

The properties of the triangular well of variable width were calculated with EoS introduced above and compared with Monte Carlo results reported by Card and Walkley [6] and new results presented in this work. Some of the results are presented in Figures 2-4.

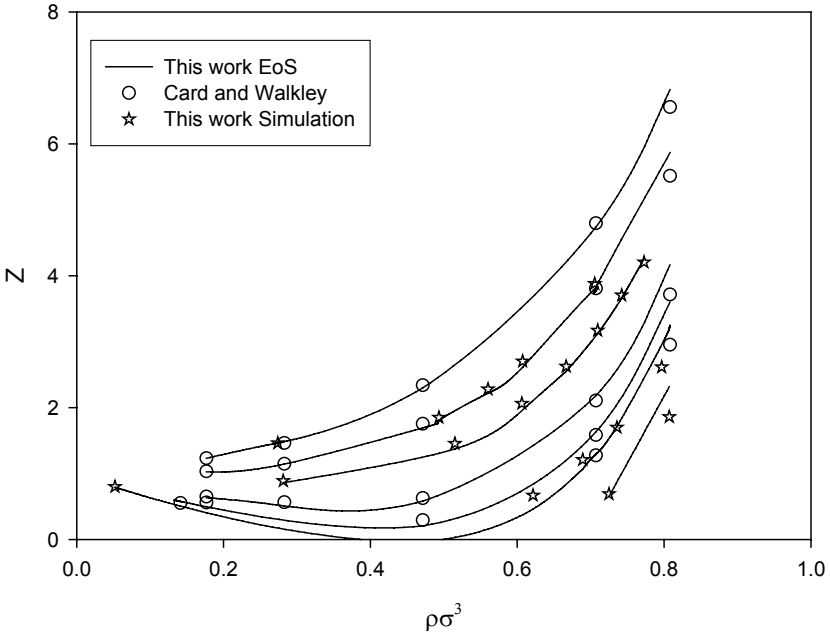

Figure 2. Compressibility factor for the triangular-well fluid of λ = 2.

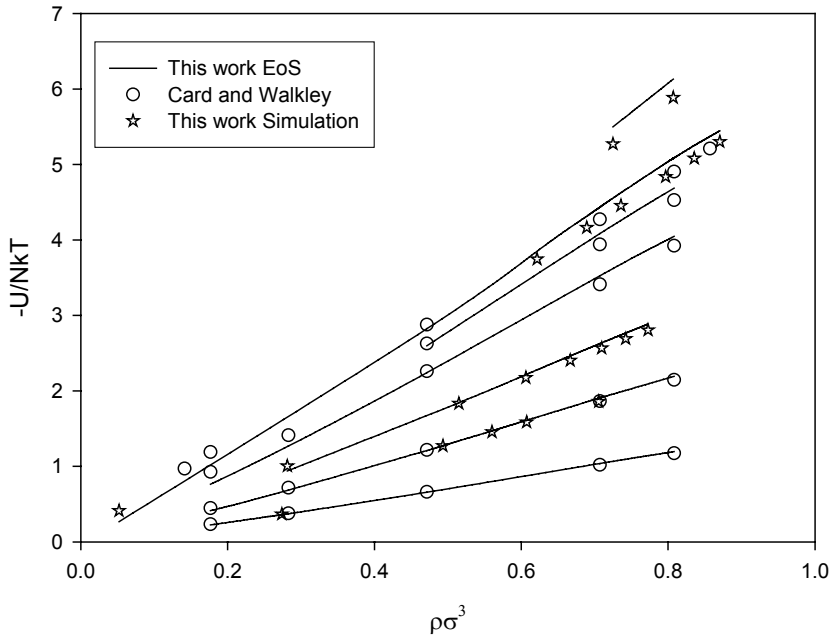

Figure 3. Internal energy for the triangular-well fluid of λ = 2.

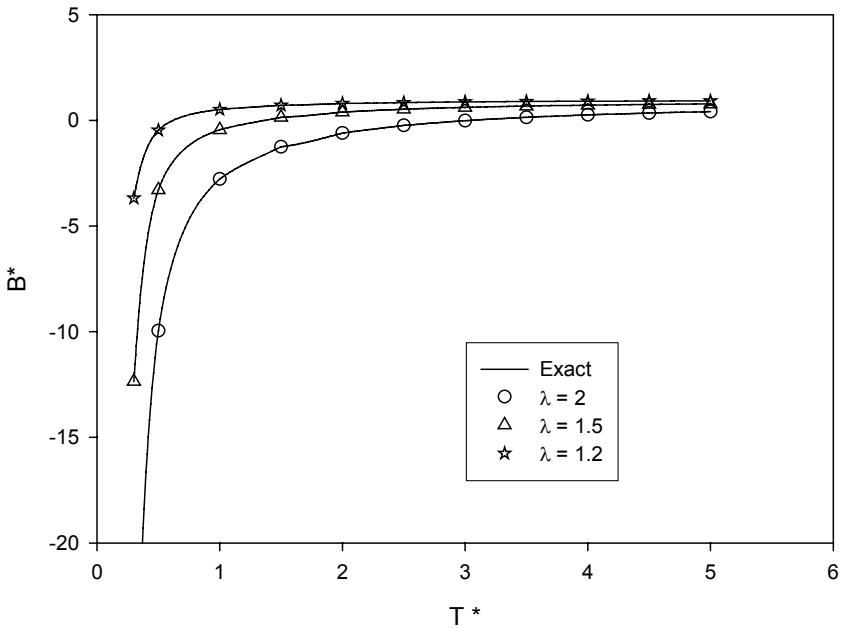

Figure 4. Second virial coefficient for the triangular-well fluid.

The proposed model has probed to give an accuracy description for the properties of the triangular-well fluid of variable width, i.e. an AAD of 5.8 % for compressibility and 4.1% for internal energy, however some error is introduced by the use of an expression fitted to the RDF of the reference fluid, it is necessary to use a more precise equation. The accuracy of the proposed EoS decreases at low temperatures. The correct representation of the reduced second virial coefficient at low temperatures requires the evaluation of higher perturbation terms.

No information about the phase diagram of the triangular-well fluid have been previously reported in the literature so it is important to explore this area to check the accuracy of the proposed expression to represent the region close to the phase transitions and close to the critical point of the fluid.

REFERENCES

[1] A. Gil-Villegas, F. del Río, A.L. Benavides, Fluid Phase Equilb. 119 (1996) 97-112.
[2] T.M. Reed, K.E. Gubbins, Applied Statistical Mechanics, McGraw-Hill, 1973.
[3] A.L. Benavides, A. Gil-Villegas, Mol. Phys. 97 (1999) 1225-1232.
[4] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, J. Chem. Phys. 106 (1997) 4168-4186.
[5] W.R. Smith, D. Henderson, J.A. Barker, Can. J. Phys. 53 (1975) 5-12.
[6] D.A. Card, J. Walkley, Can. J. Phys. 52 (1974) 80-88.
[7] M. Cismondi, J. Mollerup, Fluid Phase Equilibria 232 (2005) 74-89.
[8] J.A. Barker, D. Henderson, Rev. Mod. Phys. 48 (1976) 587-671.
[9] B.-J. Zhang, Fluid Phase Equilibria 154 (1999) 1-10.
[10] D. Frenkel, B. Smit, Understanding Molecular Simulation: From Algorithms to Applications, Academic Press, USA, 1996.