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Posters 2: Molecular Modeling, Including Simulation

## Vapor-Liquid Phase Coexistence Properties for the Triangular Well Fluid of Variable Width

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### ABSTRACT

Equations of state (EoS) based on a two parameters model fall in a description of a corresponding state theory (CS) [1,2], which is not suitable to describe the properties of real fluids. To obtain a nonconformal behavior [1] that breaks down the CS for real fluids, it is necessary to use a three parameter potential. In this work, a fluid with molecules that interact with a triangular well potential of variable width was studied.

The non-conformal behavior of this fluid can be observed by the vapor-liquid equilibrium curve obtained for different values of the well width. No information for the phase equilibrium data of the fluid has been previously reported in the literature.

In this work, the vapor-liquid equilibrium for triangular well fluid was studied by a proposed equation of state based on the perturbation theory. The obtained curves were compared with new molecular simulation data obtained here for this fluid at different well widths. New data for this fluid in the one phase region is also presented.

The proposed EoS describes an equilibrium curve and critical compressibility factor function of the well width. These results are in agreement with the results obtained from molecular simulation. The proposed model over predicts the critical temperature of the triangular well fluid.

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### 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 [2]. The use of a third parameter allows a non-conformal behavior. The triangular-well potential of variable width can be used 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.

Typical fluids used in chemical engineering do not follow the CS principle mainly due the electrostatic interactions present in their structure, then the triangular well potential can be used to represent a effective potential for the interaction between molecules and reproduce a non conformal behavior.

The most clearly effect of a non conformal behavior can be observed in the vapor – liquid equilibrium curve for pure fluids when the critical point of the fluid change displace in the temperature – density plane for different well amplitudes of the interaction potential.

### EQUATIONS OF STATE FOR THE TRIANGULAR WELL

The model employed has been developed based on a second order expansion of the Helmholtz free energy according to the perturbation theory of Barker and Henderson [3]. The first order term is obtained by the mean field theory [3], while the second order term is a modification to the macroscopic approximation of Barker and Henderson. The EoS for the triangular well of variable width can be write in terms of the residual Helmholtz free energy as:

$$\frac{A^{res}}{NkT} = \frac{A_0}{NkT} + \frac{\varepsilon}{kT} \frac{A_1}{NkT} + \left(\frac{\varepsilon}{kT}\right)^2 \frac{A_2}{NkT} \quad (1)$$

$$\frac{A_1}{NkT} = 12\eta \sum_{m=1}^3 C_m(\lambda) \left(\frac{\eta}{1-\eta}\right)^m \quad (2)$$

$$\frac{A_2}{NkT} = -6(1+\beta\eta) \frac{(1-\eta)^4}{1+4\eta+4\eta^2-4\eta^3+\eta^4} \sum_{m=1}^3 D_m(\lambda) \left(\frac{\eta}{1-\eta}\right)^m \quad (3)$$

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. Comparison of the equation of state in the single phase region can be observed in fig. 1

As can be observed in eq. 1-3, the properties of the fluid are function of the reduced temperature, the reduced density and the well amplitude, this last variable is the one that allows recovering a non conformal behavior for the triangular well fluid. The representation of the vapor-liquid equilibrium (VLE) obtained from the equation of state for different well amplitudes of the triangular well can be observed in figs. 2-5.

This equation of state is based on the mean field theories, in order to include the fluctuations related to the region close to the critical point, the perturbation terms of order higher than 2 have been considered by using a Padé approximant proposed by Barker and Henderson [3]:

$$\frac{A^{res}}{NkT} = \frac{A_0}{NkT} + \frac{\varepsilon}{kT} \frac{A_1}{NkT} \frac{1}{1 - \frac{\varepsilon}{kT} \frac{A_2}{A_1}} \quad (4)$$

Comparison of eq. 1 and eq. 4 to represent the VLE of different well widths are plotted in figs. 2-5.

### MOLECULAR SIMULATION

The simulations for the fluid of triangular well of variable width were in two steps, first molecular simulations in NVT Ensemble [4] were made to locate the VLE curve, this simulations were made with a system composed by 512 molecules using the Metropolis sampling scheme [4]. The molecules were originally placed on a cubic lattice. The simulation was carried out in cycles, each one consisting in approximately 100 particle displacement attempts. The maximum allowed displacement were modified during the simulation to settle an acceptance ratio for the particle displacement of about 50%.

The system was then equilibrated by  $1 \times 10^6$  cycles to ensure no influence of the initial configuration, and then the properties were calculated from the next  $1 \times 10^6$  cycles. The results for this simulation can be observed in fig. 1 for a reduced well width of 2. Similar behavior was observed for the different well widths used in this work (1.3, 1.5, 1.75 and 2). This results are in agreement with the proposed model.

Second, the determination of the properties of the VLE curve was done by simulation on the Gibbs ensemble [4]. In this case the system was composed by two systems, each one composed by 512 particles (Total of particles 1024). The simulation was done in cycles, each one consist in average 300 particle displacements attempts, 3 volume change attempts and 30 particle interchange attempts. The selection in the order was done randomly.

Both systems started with the particles situated in a cubic lattice with equal volumes. The system was equilibrated by  $3 \times 10^6$  cycles and the properties were sampled from the next  $3 \times 10^6$  cycles. The results are plotted in fig. 2-5 with the respective error bars. The critical point for VLE of the different well widths was estimated with the procedure presented in [5]. The internal energy profile for the two phases is shown in fig. 6

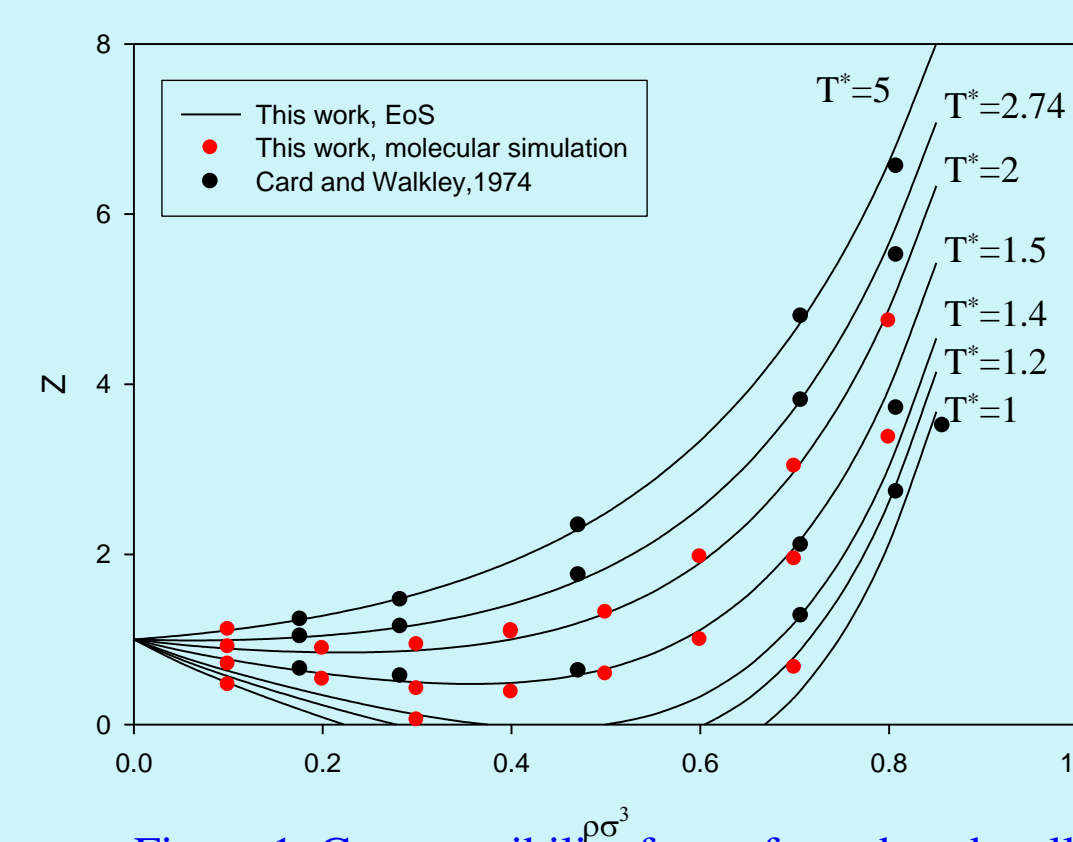


Figure 1. Compressibility factor for reduced well width of 2

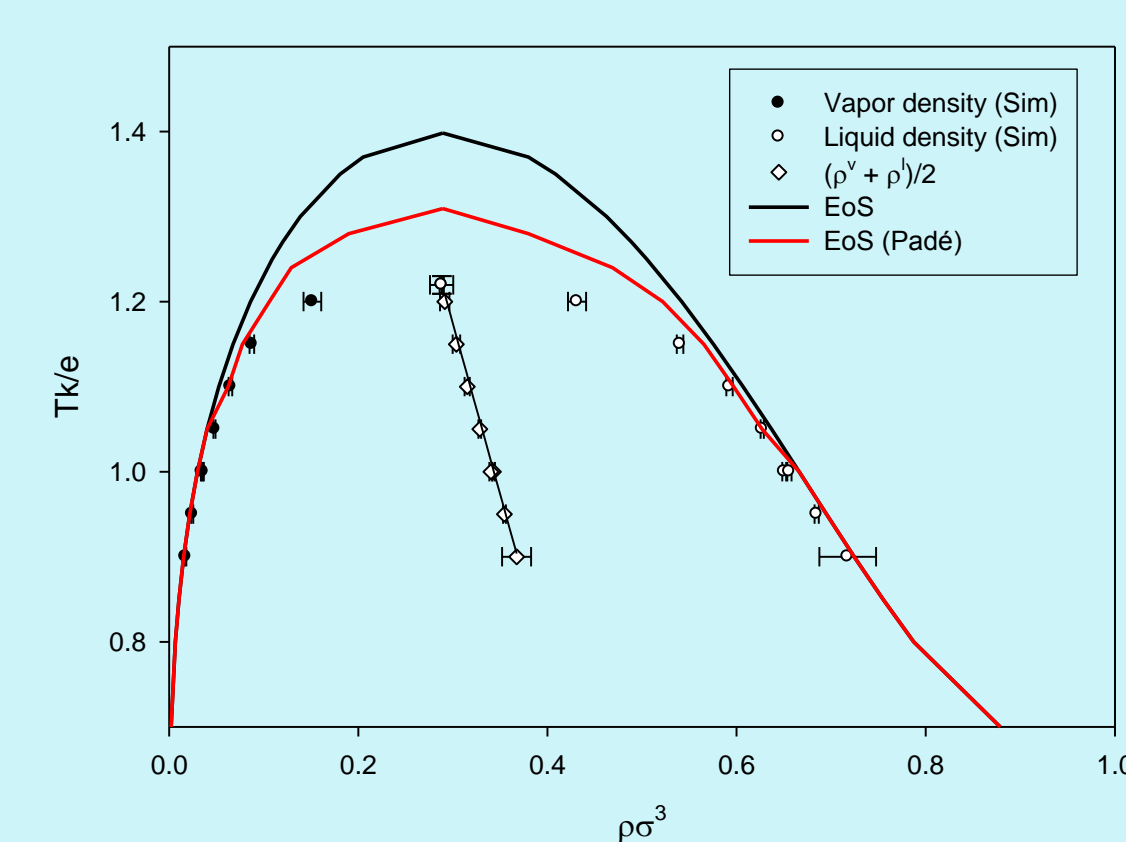


Figure 2. ELV curve for reduced well width of 2

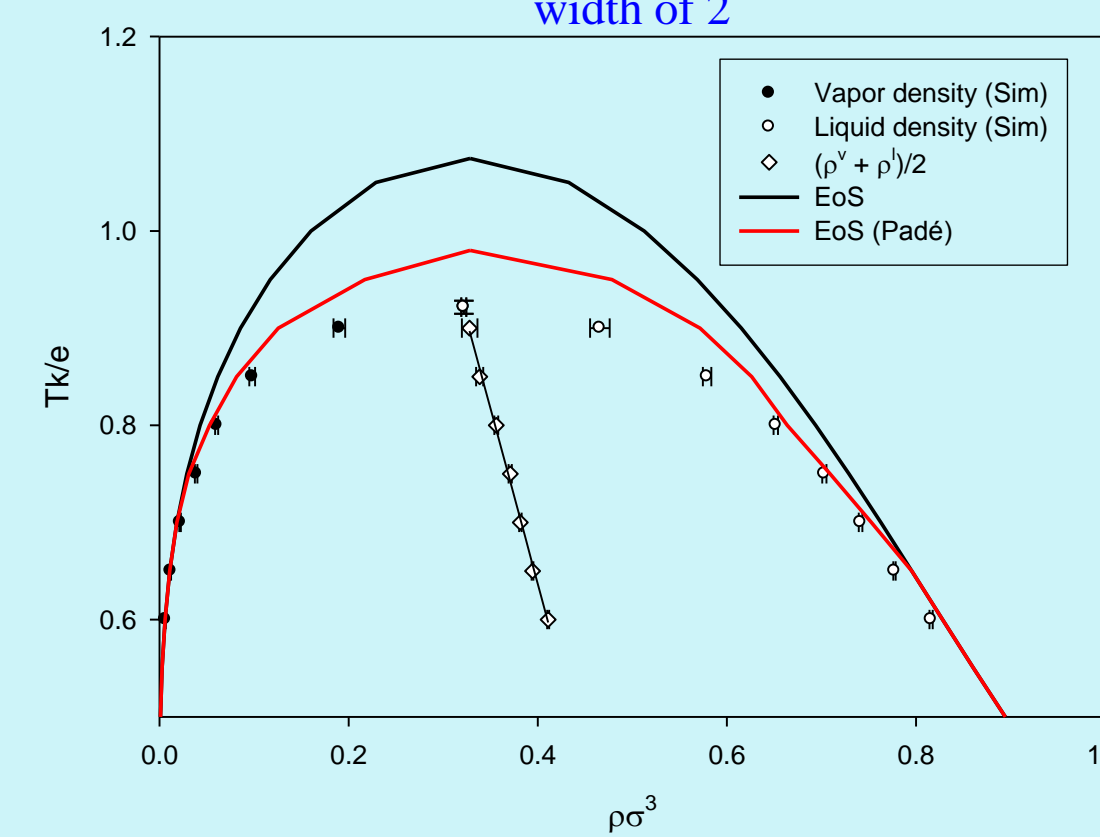


Figure 3. ELV curve for reduced well width of 1.75

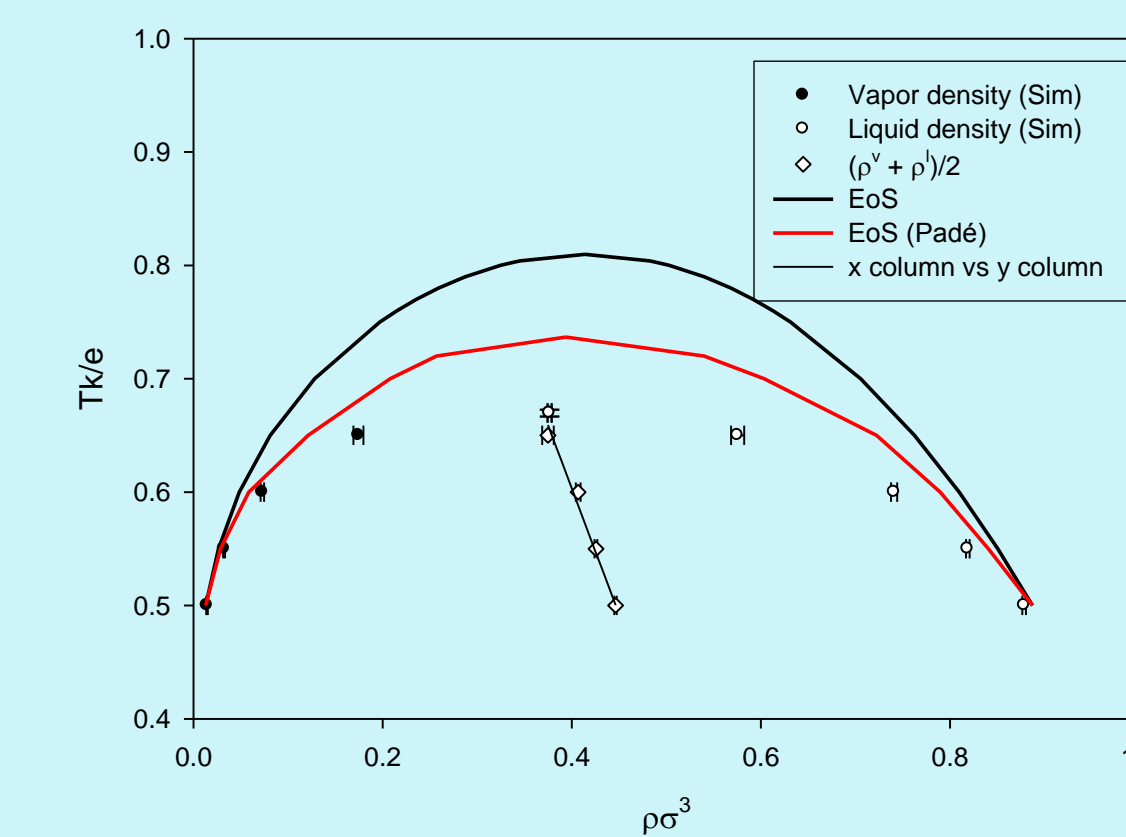


Figure 4. ELV curve for reduced well width of 1.5

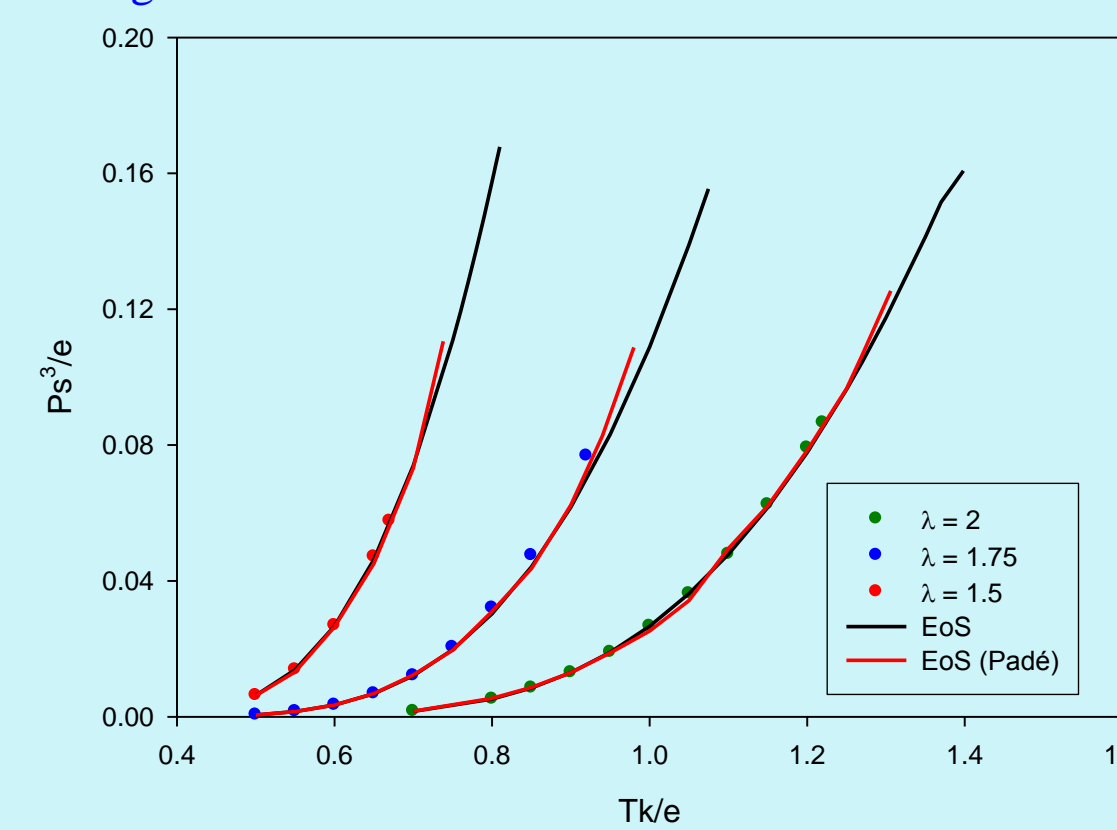


Figure 5. Vapor pressure curves from simulation and EoS

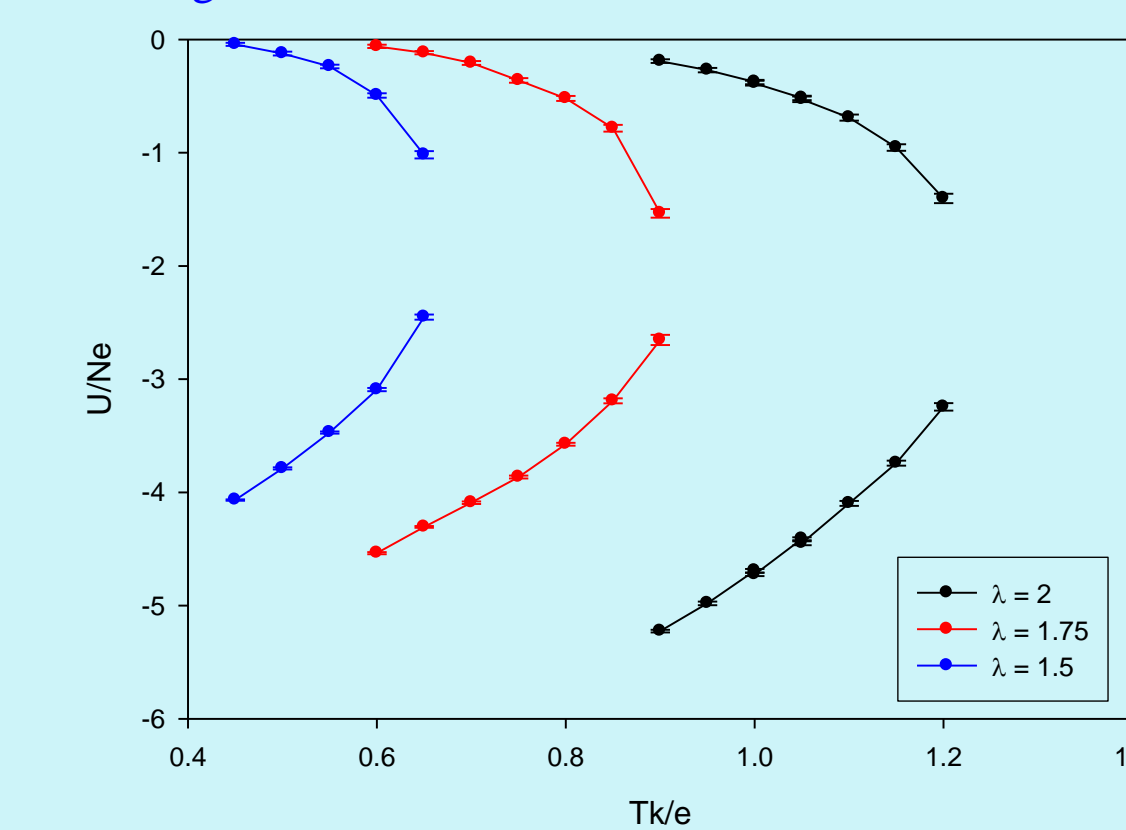


Figure 6. Internal energy profiles as function of well width from Gibbs simulations

### RESULTS

The VLE curve has been calculated by molecular simulation (Gibbs ensemble) on a first step the VLE has been traced by NVT simulations and compared with Monte Carlo results reported by Card and Walkley [6]. The proposed equation of state has been compared with the result from molecular simulation in figs. 2-4, The equations shows a good agreement with the simulation results except for the region close to the critical point of the fluid. A Padé approximant has been used to consider higher order perturbation terms, this new model has behavior closer to the results from molecular simulation.

### CONCLUSIONS

The proposed model gives a fair description of the VLE for the triangular-well fluid of variable width, i.e. an AAD of 5.5 % for saturation densities away from the critical point ( $Tr < 0.8$ ), however the errors increase as the critical point of the fluid approach. The proposed equation of state is based on a mean field theory, which fails to describe the region close to the critical point of a fluid.

To introduce a correction to the model a Padé approximant is used to represent the higher order terms of the perturbation expansion. The representation of the region close to the critical point is improved, however this correction is not enough and other considerations should be taken into account.

### ACKNOWLEDGMENTS

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### REFERENCES

- [1] A. Gil-Villegas, F. del Río, and A.L. Benavides, *Fluid Phase Equilib.* **119**, 97 (1996).
- [2] M. Cismondi, J. Mollerup, *Fluid Phase Equilib.* **232**, 74 (2005).
- [3] J.A. Barker, D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
- [4] D. Frenkel, and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, USA, 1996.
- [5] L. Vega, E. De Miguel, L.F. Rull, G. Jackson, and I.A. Lure, *J. Chem Phys.* **96**, 2296 (1992).
- [6] D.A. Card, and J. Walkley, *Can. J. Phys.* **52**, 80 (1974).