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Vapor liquid equilibrium and critical behavior of square well fluids of variable width using Pavlyukhin perturbation theory

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Abstract

Vapor liquid equilibrium and critical behavior of square well systems with hard-sphere diameter, σ well-depth, ε and with well-width $1 \leq \lambda \leq 2.5$ have been derived by using Pavlyukhin fourth order perturbation theory. The graphs for varying well-width have been compared with the available simulation data. Plotted curves for the square-well systems with $\lambda=1.25, 1.375, 1.5$ and 1.7 , are very nearly cubic in shape. The comparison shows that except the middle region the left and right part of the vapor-liquid coexistence curve matches with the available simulation data. The calculated critical points have a small shift for all widths of potential well. Though, this work confirms the validity of Pavlyukhin fourth order perturbation theory.

Keywords: vapor liquid equilibrium, critical behavior, pavlyukhin perturbation theory

1. Introduction

Simple liquids with the inter-particle interaction potential of the type hard sphere (HS) plus square well are one of the most frequently discussed topics in the literature deal in with the theory of simple liquids and comparing its results with molecular simulation data. The interest stems from the fact that the square well (SW) potential reflects the properties of more realistic potentials and allows the analysis of the properties of both simple liquids in a wide range of relationships between repulsion and attraction. Square-well fluids have been extensively studied by computer simulations and statistical mechanical methods. The SW potential is the simplest model that is appropriate as a testing ground for theories of fluids^[1-4]. The potential energy $u(r)$ for a pair of square-well particles separated by a distance r is given by

$$u(r) = \begin{cases} +\infty, & \text{if } r < \sigma \\ -\varepsilon, & \text{if } \sigma \leq r < \lambda\sigma \\ 0, & \text{if } r \geq \lambda\sigma \end{cases}$$

Where σ the hard sphere diameter of the particle is, λ is the reduced range of the potential well, and ε is its depth.

A fundamental problem in statistical mechanics is to compute thermodynamic properties by means of the interactions between molecules that make up the system. When the intermolecular interaction is established, calculation of macroscopic equilibrium properties requires either a theory of fluids or computer simulation^[5-7]. Several methods, including Monte Carlo (MC) simulation, molecular dynamics (MD) simulation and perturbation theory, have been used to study square well fluids.

Werheim^[8-10] first proposed a thermodynamic perturbation theory to approximate a density expansion of the free energy of fluids of associating hard sphere molecules. The first-order version of this formalism is commonly referred to as first order perturbation theory or TPT1.

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The basic result of TPT1 is that the Helmholtz free energy can be separated into two terms that represent the reference contribution of free monomers, and the bonding energy required to Form chain of monomers, respectively. The TPT series is an expansion of the Helmholtz free energy of the SW fluid in a series in powers of attraction parameter of the SW potential (the depth of the square well related to the temperature). In this case, the coefficients of the TPT series are determined by only two variables, i.e., the fill factor of the HS system and the width of the square well. Thus, TPT greatly simplifies the task because the original three-parameter problem is, in fact, reduced to a two-parameter problem.

Perturbation theory [11-15] has often been used to calculate the thermodynamics properties of square-well fluids. In this paper we compare the critical constants obtained from the Pavlyukhin perturbation theory for systems with a range of values of λ with estimates from computer simulation. The study is of two-purpose: first, to provide accurate vapor-liquid coexistence data for the square-well systems for comparison with mean-field and perturbation theories; second, to determine the dependence of critical constant on λ and to analyze the overall shape of coexistence curve.

2. Theory

In perturbation theory the Helmholtz free energy of the system is expanded in the inverse temperature around that of a reference system whose thermo-dynamical structural properties are known. The second order expansion of the Helmholtz free energy is of the form [4-6]

$$\frac{A^{ex}}{Nk_B T} = \frac{A_0}{Nk_B T} + \frac{1}{T^*} \frac{A_1}{Nk_B T} + \frac{1}{T^{*2}} \frac{A_2}{Nk_B T}, \quad (1)$$

Where A^{ex} the Helmholtz is free energy in excess of that of an ideal gas at the same temperature and number density and A_0^{ex} is the excess Helmholtz free energy of the reference system. A_1 and A_2 are the first- and the second-order perturbation terms for the Helmholtz free energy, respectively. N is the number of molecules, k_B is the Boltzmann constant, T is the reduced temperature, and T^* ($T^* = k_B T / \epsilon$). A_1 and A_2 are derived from knowledge of the equation of state and the RDF of the reference fluid.

Pavlyukhin has derived a fourth order perturbation theory on the parameterization for $A_1 - A_4$, which has been used here to derive the liquid-vapor equilibria for square-well fluids with $1 \leq \lambda \leq 2.5$. Similar to equation (1), the Pavlyukhin [13] fourth order perturbation theory is given by

$$\frac{A^{ex}}{Nk_B T} = \frac{A_0}{Nk_B T} + \log \rho + \frac{1}{T^*} \frac{A_1}{Nk_B T} + \frac{1}{T^{*2}} \frac{A_2}{Nk_B T} + \frac{1}{T^{*3}} \frac{A_3}{Nk_B T} + \frac{1}{T^{*4}} \frac{A_4}{Nk_B T}, \quad (2)$$

Where $\rho = \frac{6\eta}{\pi}$ and η is the packing fraction.

A. Vapor liquid equilibria

At phase equilibrium, for a pure component, the following three conditions must be satisfied:

$$\left. \begin{aligned} T_v &= T_L \\ P_v &= P_L \\ G_v &= G_L \end{aligned} \right\} \quad (3)$$

Where G is the Gibbs free energy.

B. Calculation of critical point

$$P = T \rho^2 \frac{\partial A}{\partial \rho}$$

And

$$dP = \frac{\partial^2 P}{\partial \rho^2} = 0 \quad (4)$$

In the discussion of above it is useful to reduce the temperature and pressure with respect to square well depth ϵ as $T^* = kT / \epsilon$ and $P^* = P\sigma^3 / \epsilon$, the density is reduced with respect to σ as $\rho^* = \rho\sigma^3$.

3. Result and discussion

The phase equilibria are determined using the Pavlyukhin fourth order perturbation theory [13] for square well fluids with potential ranges characterized by $\lambda = 1.25, 1.375, 1.5, 1.75$, and 2. The resulting vapor-liquid coexistence curves are shown in Figs. 1-5. In these figures the reduced temperature corresponding to the reduced density is plotted for each value of well-width λ . It is observed from these that at high densities the perturbation theory is more accurate. For all values of λ , the thermodynamic perturbation theory of Pavlyukhin makes good prediction for vapor-liquid density and critical point. The figures show the curve and the critical point from the Pavlyukhin perturbation theory and the simulation data.

4. Conclusion

The vapor-liquid coexistence curve for square-well fluids with variable well-width λ plotted in terms of the reduced temperature $t = t/t_r$ and reduced density $\rho^* = \rho / \rho_c$ and compare with the simulation data from ref [2, 3, 9, 10]. The critical points of square well fluids with variable well-width are taken from ref [2, 3, 9, 10]. Our results are in good agreement with del Rio [10] *et al.* and J K Singh [9].

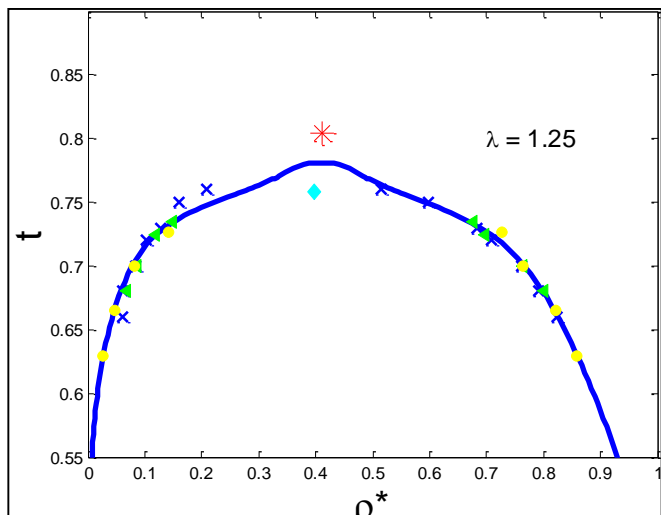


Fig 1: The temperature-density vapor-liquid coexistence curve for a square-well fluid with a potential range $\lambda = 1.25$. Solid line ^[13]. Critical points: 1. Asterisk ^[13] 2. Square ^[9] 3. Diamond ^[10]. Simulation data: Dot ^[3], Cross ^[2], Left Triangle ^[10] and Pentagon ^[9].

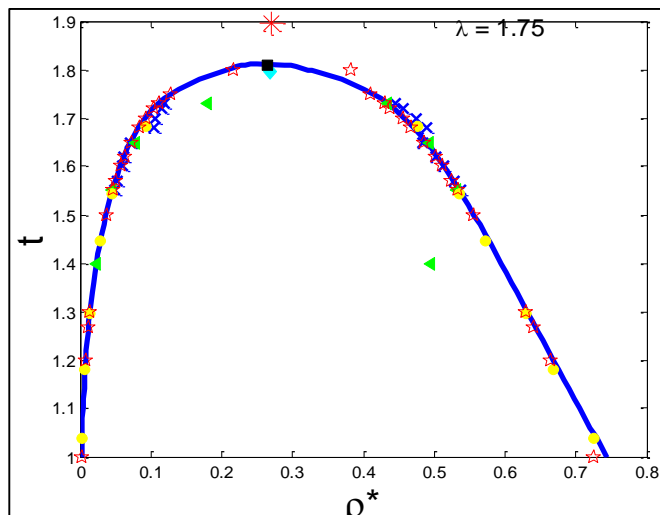


Fig 4: The temperature-density vapor-liquid coexistence curve for a square-well fluid with a potential range $\lambda = 1.75$. Solid line ^[13]. Critical points: 1. Asterisk ^[13] 2. Square ^[9] 3. Diamond ^[10]. Simulation data: Dot ^[3], Cross ^[2], Left Triangle ^[10] and Pentagon ^[9].

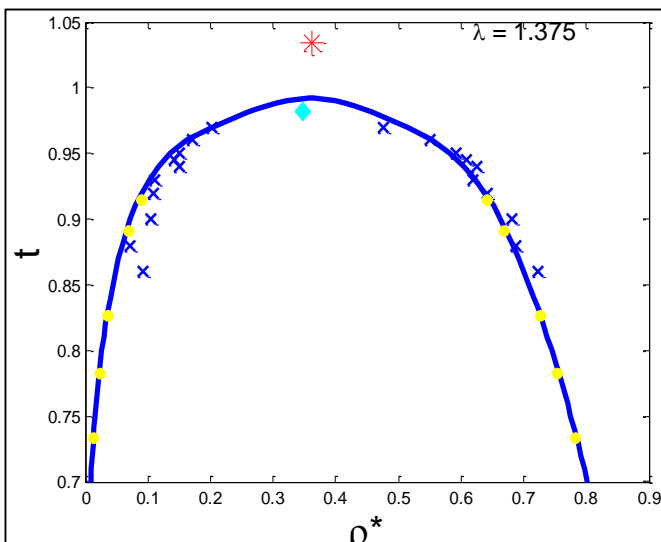


Fig 2: The temperature-density vapor-liquid coexistence curve for a square-well fluid with a potential range $\lambda = 1.375$. Solid line ^[13]. Critical points: 1. Asterisk ^[13] 2. Square ^[9] 3. Diamond ^[10]. Simulation data: Dot ^[3], Cross ^[2], Left Triangle ^[10] and Pentagon ^[9].

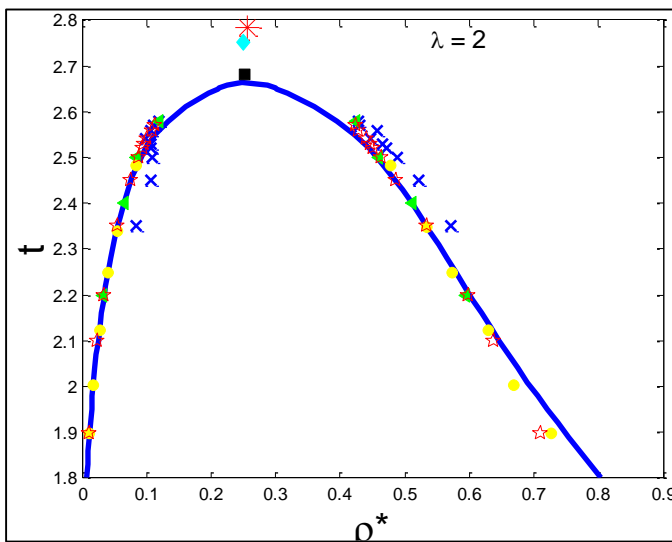


Fig 5: The temperature-density vapor-liquid coexistence curve for a square-well fluid with a potential range $\lambda = 2$. Solid line ^[13]. Critical points: 1. Asterisk ^[13] 2. Square ^[9] 3. Diamond ^[10]. Simulation data: Dot ^[3], Cross ^[2], Left Triangle ^[10] and Pentagon ^[9].

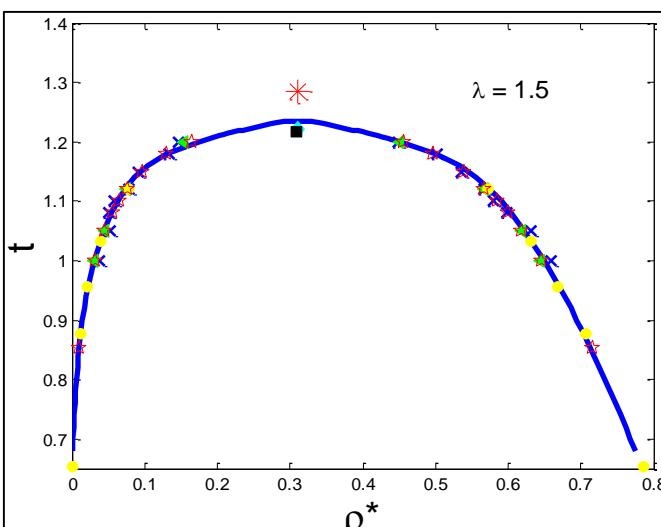


Fig 3: The temperature-density vapor-liquid coexistence curve for a square-well fluid with a potential range $\lambda = 1.5$. Solid line ^[13]. Critical points: 1. Asterisk ^[13] 2. Square ^[9] 3. Diamond ^[10]. Simulation data: Dot ^[3], Cross ^[2], Left Triangle ^[10] and Pentagon ^[9].

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