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Phase behaviour of a continuous shouldered well model fluid. A grand canonical Monte Carlo study *

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Abstract

The phase behavior of the continuous shouldered well model fluid proposed by Franzese [*J. Mol. Liq.* 136 (2007) 267] was examined using the Monte Carlo computer simulations in the grand canonical ensemble. The essential parts of the vapour-liquid and liquid-liquid coexistence envelopes were obtained. The Widom lines departing from coexistence envelopes were calculated using maxima of the fluctuations of the number of particles as a function of chemical potential along various isotherms. The region embracing anomalies in the properties of the model was located using the approximate criterion that involves the excess pair entropy. The temperature of maximum density line was built by performing canonical Monte Carlo simulations. Our results are consistent with previous results from molecular dynamics constant pressure-constant temperature simulations and provide wider insight into the phase behavior of the model by using the chemical potential as the external parameter.

Keywords

liquids; soft-core model fluid; grand canonical Monte Carlo simulations; phase diagram

1. Introduction

Isotropic core-softened models of fluids have gained much of the scientific interest in two past decades. They can be considered as effective potentials and are the result of reducing some of the degrees of freedom of interaction between the molecules of the system. Since the form of the potential function is rather simple, i.e. containing no orientational inter-particle dependencies, these models are relatively easy to handle both computationally and theoretically. Despite the simplicity, it was shown that some of the core-softened models can

*Dedicated to Prof. Vojko Vlady on the occasion of his 70th birthday.

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still mimic complicated behaviour of anomalous real liquids, such as water [1], phosphorus [2], silica [3], triphenile phosphite [4], and others. In addition to usual vapour-liquid coexistence, these models can exhibit a liquid-liquid phase transition [5–10]. Such phase transition is argued to exist in water [11–13], silica [14–16], BeF₂ [17], and in some liquid metals.

Core-softened potentials are characterized by two repulsive parts: a “hard” part at small inter-particle distances, and an additional “soft” part where the slope of the potential dramatically changes with respect to the core. This region can have the shape of a shoulder or a ramp. To get the anomalous properties, the ratio between these “hard” and “soft” repulsive length scales has to be within a relatively narrow range [18]. At larger inter-particle distances, the potential remains repulsive or it can have an attractive region. For some potential forms, it becomes somewhat difficult to analyze the system's properties due to occurring vapour-liquid phase transition and possible liquid-liquid phase transition where a significant jump in density between phases is observed [6].

Commonly studied models are (among others) those of Jagla [19–23], Barbosa et al. [24–27], Fomin et al. [28, 29], and Franzese et al. [6–8, 30–33]. The model of Jagla belongs to a class of ramp potentials, where the repulsive part consists of a “hard” ramp and a linear “soft” ramp. The phase diagram describing the Jagla-type potential shows anomalous properties similar to those observed for water (maximum in density and minimum in isothermal compressibility as a function of temperature). On the other hand, the potential of Barbosa et al. is a combination of a Lennard-Jones potential and a Gaussian-type well. The model exhibits rich variety of the structural, thermodynamic and dynamic anomalies, see e.g. Refs. [24, 25, 34]. However, since the attractive part of the potential is assumed weak, no liquid-vapour or liquid-liquid phase transition was observed for the original potential model [24, 25], whereas a more complex form of the potential (Lennard-Jones type part plus four Gaussians) yields liquid-liquid phase transition for selected parameters [9, 27]. Compared to real fluids, where the interaction between particles is attractive for the most of the inter-particle separation distances, the too weak attraction part is a disadvantage of this model. Same is observed in the smoothed repulsive-shoulder potential function used by Fomin et al. The increase in the repulsion depresses anomalies, while an addition of the attraction part to the potential function stabilizes them, and a shift to higher temperature is observed when an attractive well is present [35].

Franzese et al. proposed and studied a square-shoulder-square-well potential which yields a liquid-vapour and liquid-liquid transition, but no density anomaly [6]. On the other hand, a continuous version of this potential exhibits the density anomaly besides both phase transitions [7]. The potential consists of a steep repulsive part, a repulsive shoulder and an attractive Gaussian-type part. Commonly used name for this model is the continuous shouldered well (CSW). Further details necessary for the present work will be described below.

Studies of phase transitions and of anomalous behaviour of various substances may be related to several interesting applications. Recently, a core-softened model of fluid was used to study certain aspects of the hydrophobic solvation of amphiphilic molecules in aqueous

solutions, and of mixtures with apolar solutes [36–39]. The hydrophobic effect plays an important role in a wide variety of phenomena such as the collapse of polymers (and proteins) in water, and in the formation of micelles [40, 41]. Mixtures of ions with core-softened fluids and the effects of structural and thermodynamic anomalies in these mixtures were investigated by us [42, 43]. Partly-quenched systems involving the soft-core annealed fluid were as well studied by one of us [34, 44, 45]. Effects of confinement on the properties of core-softened model of water were investigated for nanotubes [46–48], plates [49–54], and nanopores [55–57].

The principal objective of the present study is to investigate the phase behaviour of a system in which particles interact via the CSW potential [7]. The equation of state of the system and in particular the liquid-vapour and liquid-liquid coexistence will be examined as functions of the chemical potential by using the grand canonical Monte Carlo (GCMC) computer simulations. Also, two Widom lines departing from the critical point of the respective coexistence envelope were built in the chemical potential - temperature plane. To do that we used the values of the fluctuations of the number of particles at different chemical potentials along various isotherms. The region of anomalies of the structural and thermodynamic properties has been located by using approximate criterion coming from the trends of behaviour of the excess pair entropy. However, precise evaluation of the points of the temperature of maximum density (TMD) line has been made by performing a set of canonical Monte Carlo (MC) simulations.

The paper has the following structure. After introduction we give the details of the model and brief description of the grand canonical Monte Carlo simulation. Results are presented and discussed next in detail. Conclusions are given in the final part of the manuscript.

2. The model

The CSW potential, describing the interaction between the pairs of particles separated by a distance r , is defined as [7],

$$\frac{U(r)}{U_A} = \frac{U_R/U_A}{1 + \exp[\Delta(r - R_R)/a]} - \exp\left[-\frac{(r - R_A)^2}{2\delta_A^2}\right] + \left(\frac{a}{r}\right)^{24}. \quad (1)$$

Here, U_R and U_A stand for the energy of the repulsive shoulder and of the attractive well, respectively, a is the particle's core distance (diameter), R_R is the repulsive average radius, and R_A is the width of the attractive minimum. Parameter Δ is related to the slope of $U(r)$ at distance R_R , and δ_A^2 denotes the variance of the Gaussian centered at R_A . Numerical values of the parameters used in this work are chosen to be the same as in the original model of Franzese [7]: $U_R/U_A = 2$, $R_R/a = 1.6$, $R_A/a = 2$, $\Delta = 15$, and $(\delta_A/a)^2 = 0.1$. In contrast to the molecular dynamics study of Franzese, cut-off and shift of the potential were not used in the present work. The potential is plotted in the inset of Figure 1a.

We report all the calculated quantities in reduced units: reduced density as $\rho^* = \rho a^3$, reduced temperature $T^* = k_B T / U_A$, reduced excess internal energy $E^{ex*} = E^{ex} / U_A$, reduced pressure $p^* = p a^3 / U_A$, and reduced chemical potential $\mu^* = \mu / U_A$.

3. Simulation details

To study the properties of the CSW model fluid (equation 1), a grand canonical Monte Carlo (GCMC) simulations were used (constant chemical potential, volume, and temperature). The method is well described in Refs. [58, 59] and will not be given here in details. We used a cubic simulation box (edge length L), and periodic boundary conditions with minimum image convention. Boxes with L/a between 30 and 50 were used for the vapour phase and 16–23 for the liquid phase. The average number of particles in the simulation box was between ~ 50 and ~ 200 for the vapour phase, and from ~ 600 to ~ 4000 for the dense “liquid” phases. The distribution of particles in the initial configuration was random. The number of particles corresponded to an initial guess for the density of the system. The systems were first equilibrated with $2 \cdot 10^6$ GCMC steps (one attempted move of a particle followed by one attempted insertion/annihilation). Next, the production cycles were performed over $(10 - 20) \cdot 10^6$ GCMC steps. A set of 5 – 15 production runs were performed for a selected state of the system and thermodynamic quantities were calculated as averages over these block values.

For a given input values of chemical potential, μ^* , system's volume, $V = L^3$, and temperature, T^* , in each production run, we determined the corresponding average number of particles in the system, $\langle N \rangle$, and the corresponding average reduced density, $\rho^* = (\langle N \rangle / V) \cdot a^3$. Reduced excess internal energy of the system, E^{ex*} , was calculated by averaging the system's total internal energy in each production step, and the equation of state was determined by [58, 59],

$$\frac{\beta_p V}{\langle N \rangle} = 1 - \frac{\beta}{3 \langle N \rangle} \left\langle r \sum_{i < j} \frac{\partial U_{ij}(r)}{\partial r} \right\rangle, \quad (2)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann's constant, and triangular parentheses denote the ensemble average of the quantity that they embrace. Isothermal compressibility, κ_T , was related to particle number fluctuations [58],

$$\rho k_B T \kappa_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (3)$$

The pair contribution to the excess entropy was calculated by using the expression [60–63],

$$\frac{S_2}{k_B} = -2\pi\rho\int_0^{L/2}[g(r)\ln g(r) - g(r)+1]r^2dr, \quad (4)$$

where $g(r)$ is the pair distribution function. The TMD line has been obtained by performing separately a large set of canonical MC simulations at constant density while changing temperature step by step. The procedure is similar to what was reported by us recently [42, 43].

4. Results and discussion

Here, we present the results of a GCMC study of a CSW model fluid defined by the pair potential (1). Our study is restricted to the temperature interval from an upper limit of $T^* = 1.7$ down to $T^* = 0.45$. According to molecular dynamics study performed by Franzese [7], this temperature range covers supercritical regime as well as the essential parts of the vapour-liquid and liquid-liquid coexistence envelopes.

Our initial objective is to describe one projection of the equation of state (EOS) of the model fluid, namely the dependence of the reduced density on the reduced chemical potential at different values of system's reduced temperature. Along with that, we show how the reduced excess internal energy and excess pair entropy depend on the chemical potential and on temperature. At the end, we present the $T^* - \rho^*$ projection of the phase diagram following from our GCMC simulations.

We first present the results for the temperature range *above* the vapour-liquid critical point. Panel a of Fig. 1 describes the $\rho^* - \mu^*$ projection, panel b the $E^{ex*}/N - \mu^*$ projection (reduced excess internal energy per particle), panel c the $S_2^* - \mu^*$ projection, and, finally, in panel d the dependence of particle number fluctuations on μ^* are given. This quantity is related to the isothermal compressibility via equation (3). Data for $T^* = 1.7, 1.35$, and 1.2 are shown.

We see that the dependence of the fluid density on the chemical potential along all isotherms is monotonous, the density grows with increasing μ^* (panel a). Moreover, it is a single-valued function: for each value of chemical potential the density takes certain unique value. Same applies also for the dependence of the reduced excess internal energy per particle (panel b), and for excess pair entropy (panel c) on μ^* . E^{ex*}/N decreases with increasing μ^* , and converges to a constant value at high values of μ^* , while S_2^* monotonously decreases with increasing μ^* . With decreasing temperature, the system starts showing more rapid changes in ρ^* , E^{ex*}/N , and S_2^* in the interval of μ^* between -6 and -4 .

To confirm that we are approaching a phase transition, we plotted the fluctuations in the number of particles in the system as a function of μ^* (panel d). For $T^* = 1.7$ particle number fluctuations show a weakly pronounced maximum at $\mu^* \approx -5.75$, while for $T^* = 1.35$ and 1.2 this function starts to develop sharper peak at $\mu^* \approx -5.1$, and -4.85 , respectively. Large fluctuations imply that by further reducing the temperature, the system will potentially undergo a vapour-liquid phase transition.

Anticipating our discussion slightly further, precise location of the maximum of the curves given in panel d for each isotherm is important for the construction of the Widom line. The Widom line is defined as a locus of points where the response functions (fluctuations of the particle number in the present case) exhibit maximum [64, 65]. It is expected that the Widom line is a continuation of the coexistence line conveniently given in the present study in $T^* - \mu^*$ variables.

In Fig. 2 projections of EOS are shown for $T^* = 1.1, 0.9$, and 0.7 (and in panel d also for 0.6 , and 0.55). In contrast to the cases of higher temperatures discussed above, two distinct branches are observed in $\rho^* - \mu^*$ (panel a), $E^{\text{ex}*}/N - \mu^*$ (panel b), and $S_2^* - \mu^*$ planes (panel c): one corresponds to the vapour, and the other to the liquid phase of the system. We have systematically calculated the $\rho^* - \mu^*$ dependencies at $T^* = 1.05, 1.07, 1.1, 1.12, 1.14$.

The hysteresis loops are very well pronounced at low temperatures, well below the critical temperature. It is very difficult in practice to approach the critical temperature from below, because the hysteresis loops become very narrow. According to our analysis, the critical temperature should be close to $T^* = 1.1$ (see also Fig. 5)). Two isotherms, at $T^* = 1.12$ and $T^* = 1.14$, are already continuous and will be used in the exploration of the Widom line emanating from the liquid-vapour coexistence. It is well known that standard GCMC computer simulation procedure does not permit to capture the critical point precisely. To do that one needs to resort to more sophisticated techniques, see e.g. Ref. [66, 67]. Nevertheless, our data can serve as a good estimate of the shape of phase diagram of the system.

With increasing chemical potential the reduced excess internal energy decreases, except at low temperatures (after the vapour-liquid phase transition, $T^* < 0.9$) where in a narrow range of μ^* the energy of the liquid phase slightly increases with increasing μ^* , reaches a maximum and then decreases again. S_2^* starts to increase with μ^* after the vapour-liquid transition, reaches a maximum, and then again decreases. To further examine the properties of the system in this region of temperatures, the dependence of S_2^* on ρ^* along isotherms was constructed from the S_2^* on μ^* curves, and is shown in Fig. 2d. It has been discussed already in different occasions that $(\partial S_2^*/\partial \rho^*)_{T^*} > 0$ is one of the approximate criteria used to locate the region of states where the properties of a system are anomalous [29, 34, 63, 65, 68].

Actually it is known that the use of the pair contribution to entropy in contrast to the total entropy shifts upward the anomaly region in T^* . From our calculations, one can clearly see that the lower the temperature, the more pronounced the region with $(\partial S_2^*/\partial \rho^*)_{T^*} > 0$ is. We marked it with up-triangles to make a comparison with precise result of calculation of the TMD line below. In order to locate these phase transition points between different branches, we resort to the calculation of pressure as a function of chemical potential. Pressure is rather difficult to obtain accurately at low temperatures; one needs to monitor the quality of the pair distribution functions to be sure that the number of particles in the box is sufficient.

A representative example of our calculations is given in Fig. 3, where we show the dependence of the reduced pressure on chemical potential to find the values of both variables at the transition point between vapour and low-density liquid (LDL) and between two liquid phases (LDL and high-density liquid (HDL)) for a given temperature, $T^* = 0.5$. This procedure has been previously described in detail on several occasions, and it is formally similar to the one used in the studies of different-type surface phase transitions in confined fluids where the calculation of the grand thermodynamic potential as a function of the chemical potential is necessary to perform, see e.g. Refs. [69, 70].

The value of the chemical potential at the phase transition for a given temperature is obtained as the intercept of the straight lines (p^* vs. μ^*) corresponding to the given vapour or liquid phase (for clarity of representation only fits are shown in Fig. 3). Knowing the value of μ^* at phase transition for each temperature permits to establish coexisting densities, that are for vapour-liquid coexistence points indicated by vertical dashed lines in Figs. 2a, b, and c.

Finally, the results for the region of the low temperatures studied in this work ($0.6 > T^* > 0.5$) are shown in Fig. 4. Each branch in these cases was obtained by performing simulations for either increasing or decreasing values of the chemical potential. In contrast to the regions of higher temperatures described above, three different branches in $\rho^* - \mu^*$, $E^{ex*}/N - \mu^*$, and $S_2^* - \mu^*$ plane were obtained for this region of temperatures. The vapour branch is omitted in Fig. 4 for the sake of clarity, and only the value of μ^* where the vapour-liquid branch occurs is marked with up-triangles. The two branches given in this Figure correspond to two different liquid phases: low-density liquid (LDL), and high-density liquid (HDL), as designated in de Oliveira et al. [65]. The coexisting densities are, as in Figs. 2 and 4, indicated by vertical dashed lines.

After collecting all the data for the phase transitions in the temperature range of $1.05 > T^* > 0.45$, it was possible to construct the phase diagram. In panel a of Fig. 5 we show the vapour-LDL (circles) and LDL-HDL (squares) part of the phase diagram in the $T^* - \rho^*$ plane. Each of the branches terminates at the corresponding critical point. The branches converge, but seemingly the triple point, if it exists (and remains stable with respect to the solid phases) should occur even at lower temperature than we study.

In panel a of Fig. 5 the TMD line enclosing the density anomaly region is shown with diamonds. Numerical data presented in this panel of Fig. 5 are listed in the Table 1 for the sake of convenience of the reader. Franzese determined the following values of parameters for the critical points [65]: $T_{C_1}^* = 0.95 \pm 0.06$, $p_{C_1}^* = 0.019 \pm 0.008$, and $\rho_{C_1}^* = 0.08 \pm 0.03$ (vapour-LDL critical point) and $T_{C_2}^* = 0.49 \pm 0.01$, $p_{C_2}^* = 0.285 \pm 0.007$, and $\rho_{C_2}^* = 0.247 \pm 0.008$ (LDL-HDL critical point). Our estimate of the vapour-liquid reduced critical temperature is somewhat higher, around 1.1, and of the of LDL-HDL between 0.6 and 0.55. Slight deviations from the originally reported values for critical points can be a consequence of the cut-off and shift of the potential used in molecular dynamics study of Franzese [65], while no such adjustments were made in this work.

The region of the positive slope of the excess pair entropy discussed above is located between $\rho^* \approx 0.18$ and $\rho^* \approx 0.25$ at $T^* = 0.6$. It is closed above at $T^* \approx 1.1$. The density anomaly region determined by the area below the TMD line occupies a small portion of the area where $(\partial S_2^*/\partial \rho^*)_{T^*} > 0$. However, this latter region should also contain the structure anomaly area in terms of the order parameter and the dynamic anomalies region, see e.g. [68].

Two coexistence envelopes plotted in panel a of this figure are not closed due to limitations of the GCMC technique. However, another insight on the liquid-vapour and liquid-liquid coexistence is given in panel b of Fig. 5. It is important to mention that two Widom lines really represent continuation of the respective coexistences and the critical points can be inserted approximately into these curves.

5. Conclusions

The GCMC simulations were used to study the phase behavior of the continuous shouldered well model. Properties of the model behave differently in three distinct intervals of temperature, reflecting the number of co-existing phases in the particular temperature range. At high reduced temperatures (above $T^* \approx 1.1$) single phase is observed, whereas below $T^* \approx 0.6$ three coexisting phases (vapour, LDL and HDL) are found, the intermediate liquid phase (LDL) being observed at relatively low density. The region of thermodynamic states where the system exhibits anomalies was established from the approximate criterion based on the positive slope of S_2^* vs. ρ^* . It has the shape slightly similar to the vapour-liquid coexistence but shifted to higher densities. The maximum point is of the same order as the critical temperature for vapour-liquid coexistence, cf. panel d of Fig. 2. and Fig. 4. The right, higher density boundary of this region terminates while meeting the liquid-liquid coexistence envelope close to the corresponding critical point. All works for which the cut-off and shift of the potential was used [7, 32, 65] give estimates of critical parameters that are consistent among them. The TMD line embraces much less space in the $T^* - \rho^*$ plane than the pair excess entropy anomalous region. The TMD is located in-between the two coexistence envelopes. The maximum of the TMD line is at a higher temperature compared to the liquid-liquid critical temperature. Two Widom lines constructed in this work from the maxima of the particle number fluctuations represent continuation of the liquid-vapour and liquid-liquid coexistences. The approximate location of the critical points can be then established. As noted previously [64], the effect of critical points on the response functions is seen even at temperatures twice higher than the critical one.

Similar to the work of Franzese, we excluded possible solid phases of different symmetry from our consideration. This problem requires additional efforts. However, it would be interesting to re-validate data for presently observed liquid phases by using Gibbs ensemble Monte Carlo simulations. Computer simulation results of this study can serve as useful benchmark for the development of theoretical approaches. Our preliminary calculations show that the integral equations method (Ornstein-Zernike equation with either hypernetted chain or Zerah-Hansen closure) is successful only at high temperatures well above the critical temperature of vapour-liquid coexistence. To describe the region of lower temperature would require non-trivial decomposition of the interaction potential into

separate contributions. Nevertheless, our results for the phase diagram of the model, can be extended further to study solvation of various solutes and hydrophobic hydration, as well as to explore gas expanded liquids of interest in chemical technology by using computer simulations techniques.

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Highlights

Phase behaviour of CSW model fluid is studied by means of a GCMC simulations.

Model has supercritical phase, and vapour-liquid & liquid-liquid phase coexistences.

TMD is located in-between the liquid-vapour and liquid-liquid coexisting envelopes.

Widom lines were constructed in the chemical potential-temperature phase diagram.

Figure 1.

Equation of state of the CSW model fluid at high temperatures: dependence of reduced density ρ^* (panel a), reduced excess internal energy per particle (panel b), excess pair entropy S_2^* (panel c), and particle number fluctuations $[\langle N^2 \rangle - \langle N \rangle^2] / \langle N \rangle$ (panel d) on the reduced chemical potential μ^* . Data apply for $T^* = 1.7$ (circles), 1.35 (squares), and 1.2 (diamonds). All lines are only guides for the eye. Inset in panel a shows the pair interaction potential.

Figure 2.

Equation of state of the CSW model fluid in the temperature interval with solely vapour-liquid phase transition: $\rho^* - \mu^*$ plane (panel a), $E^{ex,*}/N - \mu^*$ plane (panel b), $S_2^* - \mu^*$ plane (panel c), and $S_2^* - \rho^*$ plane (panel d). Data apply for temperatures: $T^* = 1.1$ (circles), 0.9 (squares), 0.7 (diamonds), 0.6 (right triangles), and 0.55 (stars). Dashed lines denote the vapour-liquid coexistence points. On panel d, the excess pair entropy anomaly envelope (region with $\partial S_2^*/\partial \rho^* > 0$) is shown with up-triangles and dotted lines. All continuous lines are guides for the eye.

Figure 3.

Localization of the vapour-liquid and liquid-liquid phase transition points using the reduced pressure (p^*) vs. reduced chemical potential (μ^*) plot. For the sake of transparency the simulation points are omitted in the figure and only linear fits over the simulation “experimental” values at $T^* = 0.5$ are shown with lines. The vapour phase is marked with dashed line, LDL with continuous line, and HDL with dash-dotted line. Intersection of the selected two lines defines the μ^* at which the corresponding phase transition occurs.

Figure 4.

Equation of state of the CSW model fluid in the temperature interval with liquid-liquid phase transition: $\rho^* - \mu^*$ plane (panel a), $E^{ex*}/N - \mu^*$ plane (panel b), and $S_2^* - \mu^*$ plane (panel c). Data apply for temperatures: $T^* = 0.6$ (circles), 0.55 (squares), and 0.5 (triangles). Data for the vapour phase are not shown; only the values of μ^* where vapour-liquid (LDL) phase transition occurs are given by up-triangles. Dashed lines denote the liquid-liquid phase transition and continuous lines are guides for the eye.

Figure 5.

Panel a: A reduced density vs. reduced temperature ($\rho^* - T^*$) projection of the phase diagram and the TMD line (diamonds). All lines are guides for the eye. Panel b: $T^* - \mu^*$ projection of the phase diagram (solid symbols and continuous lines) and Widom lines (empty symbols and dashed lines). C_1 and C_2 mark approximate location of the vapour-LDL and LDL-HDL critical points, respectively.

Table 1

Tabulated values of the coexistence temperatures and densities for the vapour-LDL and LDL-HDL phase transitions and the TMD line (see also Figure 5a).

T^*	ρ^*	vapour-LDL	LDL-HDL	TMD
0.45	0.0001	0.1783	0.19	0.3263
0.48	/	/	0.1906	0.3175
0.50	0.0002	0.17888	0.1945	0.3128
0.55	0.0004	0.1778	0.2117	0.2971
0.60	0.00061	0.17674		0.62
0.70	0.002	0.1737		0.60
0.80	0.00518	0.16773		0.56
0.90	0.01145	0.16056		0.538
0.95	0.01532	0.1539		
1.00	0.021	0.14752		
1.05	0.0311	0.13523		
1.07	0.03525	0.13023		