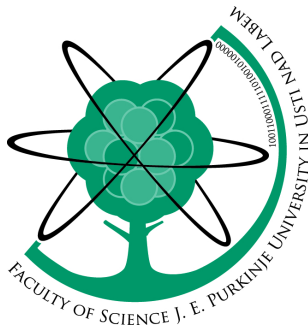


MOLECULAR SIMULATIONS AND NUMERICAL METHODS IN THEORIES OF FLUIDS



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ABSTRACT OF THE DOCTORAL THESIS

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MOLEKULÁRNÍ SIMULACE A NUMERICKÉ METODY V TEORII TEKUTIN



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Abstract

The topic of the thesis is to use numerical methods of the statistical mechanics for studying the thermodynamic and structural properties of the EXP6 fluid and possibilities of their theoretical description. This is related to studying the Yukawa fluids which can be used as a general reference system for the description of real non-polar substances, and also for the region of elevated temperatures and pressures, i.e., the region where it is necessary to use the EXP6 model and where the commonly used Lennard-Jones model and the related principle of the excluded volume fail.

The aim of this study has been to obtain data on the behavior of the EXP6 and Yukawa fluids, i.e., their thermodynamic and structural properties and higher virial coefficients, using the Monte Carlo simulation methods, simulation in the Gibbs ensemble and Mayer sampling method for the calculation of multiple integrals. From the point of theory then to study a possibility to make use of (i) the knowledge of the solutions of the Ornstein-Zernike equation for the Yukawa fluid to describe the EXP6 fluids and (ii) the knowledge virial coefficients to describe the thermodynamic functions.

Abstrakt

Předmětem předložené dizertační práce je aplikace numerických metod statistické mechaniky na studium termodynamických a strukturních vlastností modelové EXP6 tekutiny a možnosti jejich teoretického popisu. S tím souvisí i studium Yukawovy tekutiny, kterou je možno použít jako obecný referenční systém pro popis reálných čistých nepolárních látek a to i pro oblast vysokých teplot a tlaků, tj. oblast, kde je nutno použít právě EXP6 model a kde obecně používaný Lennard-Jonesův model a s ním související princip vyloučeného objemu selhávají.

Cílem této práce proto bylo získat simulační metodou Monte Carlo, simulací v Gibbsově souboru a metodou Mayerova vzorkování pro výpočet mnohonásobných integrálů data o chování jak EXP6, tak i Yukawovy tekutiny, tj. jejich termodynamické a strukturní vlastnosti a vyšší viriální koeficienty. Z hlediska teorie pak studovat možnost znalosti řešení Ornstein–Zernikeovy rovnice pro Yukawovu tekutinu pro popis EXP6 tekutiny a obecného použití viriálních koeficientů k popisu termodynamických funkcí.

Introduction

From the molecular point of view, fluids represent a classical system of many interacting particles. Then, statistical physics is the appropriate science describing the behaviour of such systems. Unfortunately, only few problems can be solved in an exact manner using only the apparatus of statistic physics and it is necessary to use many approximations. The problem stems from the fact that it is not possible to verify directly the statistical physics results and hence indirectly also the quality of the used approximations by real experiments. It was not until computers came to existence when the problem could be eliminated. These are mainly molecular simulations (computer experiments) providing experimental data for such model systems that do not exist in reality, which made it possible for theory of fluids to develop. These theories provide many different equations and relations, the analytic solution or numerical evaluation thereof is impossible (with the exception of a few simple models), so we have to use approximate numeric methods again. Most numerical problems within the theory of fluids are reduced to calculating multiple integrals. A typical example is the determination of higher virial coefficients or the average Boltzmann factor. However, common methods of numerical mathematics can not be used for such calculations.

Basically, two concepts are used to explain the behaviour of fluids:

- Excluded Volume Concept
- Hydrogen Bonding Concept

So there are two concepts to qualitatively explain the properties of fluids, each applicable only for certain types of substances and thermodynamic conditions.

Intensive simulations using all sorts of models of fluids in the last two decades suggested that the original interpretation of simulation results is too narrow

and that the structure of (pure) fluids is indeed determined by short-range interactions which, however, do not have to be only repulsive.

All the aforementioned facts have led to re-formulating the perturbation expansions and formulating the so-called "united view of fluids" concept [1]. This concept says that all pure fluids, regardless of the particular intermolecular interactions, can be described using fast-convergent expansion about a suitably chosen short-range reference system, but not necessarily only a repulsive one.

Apart from the perturbation expansion, the other theoretical tool that exists for describing fluids is the virial expansion. Its disadvantage is its poor convergence with increasing density and also the difficulty to obtain higher virial coefficients both experimentally and computationally. However, as has been shown recently, the virial expansion can be re-formulated into the form of the so-called perturbed virial expansion, which extends its range of applicability. Recently, also a numerical method enabling calculation of higher virial coefficients also for complicated models has been developed which has opened the possibilities of using the virial expansion also outside the range of low densities.

Results and discussion

The attached set of three original papers [P1] - [P3] constitutes the results of the study of the properties of model the EXP6 liquid

$$\begin{aligned}
 u_{\text{EXP6}}(r) &= \infty && \text{for } r \leq r_{\text{max}} \\
 &= \varepsilon \left\{ \frac{6}{\alpha-6} \exp \left[\alpha \left(1 - \frac{r}{r_{\text{min}}} \right) \right] - \frac{\alpha}{\alpha-6} \left(\frac{r_{\text{min}}}{r} \right)^6 \right\} && \text{for } r > r_{\text{max}}
 \end{aligned} \tag{1}$$

and the possibilities of their theoretical description using the Yukawa model of liquids. The reason for choosing the EXP6 model is the fact that it has a theoretical background and that it describes well the intermolecular interactions in realistic simple fluids also at high temperatures and pressures which are the typical conditions for geochemical applications and accuring also at detonations for which the Lennard-Jones (LJ) potential is highly unsuitable.

An alternative to the commonly used HS system is the Yukawa potential (hcY)

$$\begin{aligned}
 u_{\text{hcY}}(r) &= \infty && \text{for } r \leq \sigma \\
 &= \frac{\varepsilon}{r} \exp(-zr) && \text{for } r > \sigma,
 \end{aligned}$$

or, more precisely, a superposition of several hcY potentials (referred to as Y-model, in general). For this model, both an approximate analytical solution of the Ornstein-Zernike equation, and several accurate semi-empirical results are known. Another advantage of choosing this potential is its flexibility and the capacity to imitate different interactions between molecules. Therefore, the leading idea for developing the theory of the EXP6 liquid is using these properties of the Y-model and finding either a direct mapping of the EXP6 potential onto the Y-model or a suitable choice of a Y-model as the reference model in the perturbation expansion.

By molecular simulations using the Monte Carlo (MC) method [2] data on the thermodynamic behaviour (internal energy, pressure and chemical potential) and the structure of the EXP6 liquid for a large range of temperatures and pressures up to extreme conditions were obtained. Liquid–vapour phase equilibrium was also determined by using simulations in the Gibbs ensemble [3, 4] and virial coefficients B_2 to B_4 were calculated using the Mayer sampling method (MSMC) [5]. Simultaneously with the EXP6 fluid the model Y-model was also studied which should correspond to the studied EXP6 model. These results are contained in [P1] and [P2] papers. Paper [P3] deals with the possibility of using analytic results for the hcY potential for describing fluids with continuous interaction potential.

The fourth paper, [P4], is related to calculating the virial coefficients. It follows up the previous works and reacts to recent studies of the possibilities using virial coefficients when studying thermodynamical properties of both realistic and model systems.

Properties of EXP6 fluid and corresponding 2Y fluid

To ensure the compatibility with existing older data of Vörtler et al. [6] two extremely different values of α parameter (see Tab. (1)) were used to study the EXP6 fluid.

Simulations of thermodynamical and structural properties were performed in the range of temperatures for both the geochemical interest and the extremely high temperatures reached during detonations [P1]. Liquid-vapour equilibrium was also studied, virial coefficients B_2 to B_4 were calculated and the critical point was determined. As opposed to the results of paper [6], the chemical potential was also determined in all the studied thermodynamic points in order to complete the picture. The data in [6] were used to check the accuracy of the results.

Along with the EXP6 model, the two-Yukawa fluid (2Y) was studied

$$u_{2Y}(r) = \varepsilon_1 r_{\min}/r \exp[-\kappa_1 r] - \varepsilon_2 r_{\min}/r \exp[-\kappa_2 r] , \quad (2)$$

Table 1: Parameters of the 2Y potential function corresponding to the EXP6 fluid. Critical temperature T_c^* of the 2Y fluid is derived from liquid-vapor coexistence. Number in parentheses are the perturbed virial expansion and classical virial expansion results using the second virial coefficient.

	α	ϵ_1/ϵ	$\kappa_1 r_m$	ϵ_2/ϵ	$\kappa_2 r_m$	σ/r_m	T_c^*
SET I	11.5	15026.860731	9.454846	227.606845	4.649829	0.872	1.171 (1.18) (1.43)
SET II	14.5	389565.312772	13.344075	148.239824	4.513801	0.892	1.00 (1.05) (1.24)

which could be used for developing the theory of the EXP6 model. In addition to the model parameters, the 2nd virial coefficients were used to relate the EXP6 and 2Y models: it was imposed that the virial coefficients B_2 of the repulsive parts of the respective potentials were the same (if possible) throughout the whole range of considered temperatures. The repulsive parts of the potentials were defined in the usual manner:

$$\begin{aligned}
 u^{\text{rep}}(r) &= u(r) + \varepsilon && \text{for } r \leq r_m \\
 &= 0 && \text{for } r > r_m.
 \end{aligned}
 \tag{3}$$

The resulting parameters of both 2Y models studied are shown in Tab. (1). If we compare the 2Y model obtained in this manner with the original EXP6 model, see Fig. (1), we can see that both models are more or less the same in the repulsive region, certain differences exist in the region of attractive forces at the intermediate distances.

The results of thermodynamical quantities are complemented with a selection of several of pair correlation functions in the Fig. (2), which clearly show the equality at the considered conditions. Although small discrepancies occur in thermodynamics quantities, the structures presented by the pair correlation function are almost identical. To verify the quality of mapping the 2Y potential on EXP6, Fig. (3) shows comparison of the pair correlation functions of purely repulsive parts of potentials, where the discrepancies occur only within the tole-

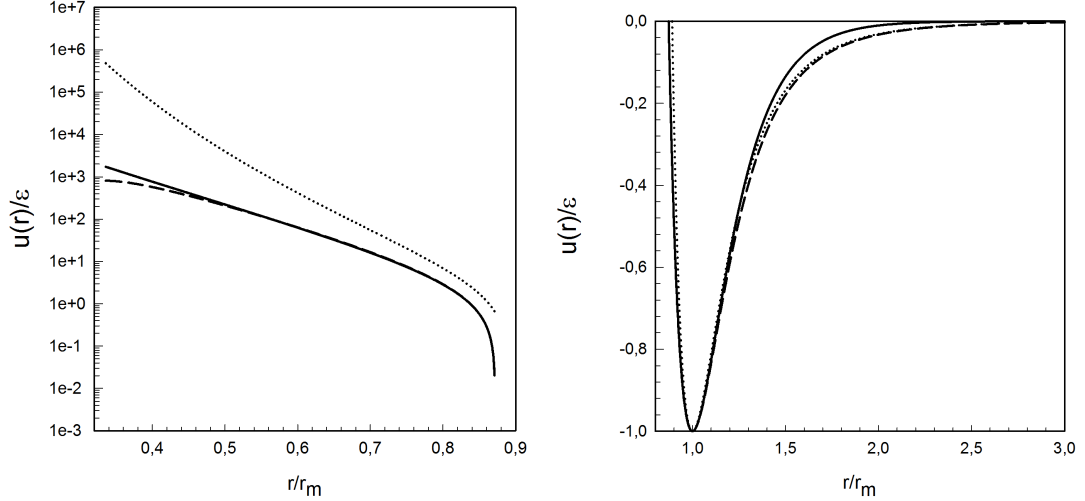


Figure 1: The repulsive (left) and attractive (right) parts of the considered EXP6 ($\alpha = 11.5$; dashed line) and 2Y (**SET I**; solid line) models and their comparison with the Lennard-Jones (dotted line) potential.

range of simulation data. Both ranges of temperatures were considered. As it was expected, it turned out that the discrepancies were caused by discrepancies in the course of potentials which could be compensated using van der Waals approach similarly as in papers [7, 8].

As regards the virial coefficients [P2], the data serve to complete the description of the thermodynamical behaviour of the studied systems.

The Y- and LJ- models correspondence: Theory

The realistic models do not contain hard core (infinite repulsion) while the known solutions of the Y-models exist only for the hcY model. It is necessary to perform the description of fluids with continuous potential in two steps: (1) the original model is approximated first with the 2Y model, and (2) then this one is described by the Y model with a hard core. In step (2) the MSA solution is used for superpositioning two hcY models (hc2Y):

$$\begin{aligned}
 u_{\text{hc2Y}}(r) &= \infty && \text{for } r \leq R \\
 &= \frac{R}{r} \exp[-\kappa_1(r - R)] - \frac{R}{r} \exp[-\kappa_2(r - R)] && \text{for } r < R .
 \end{aligned} \tag{4}$$

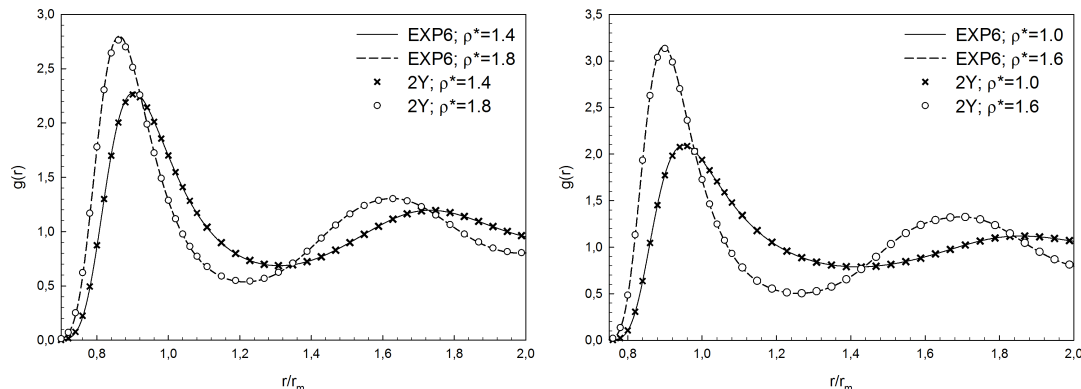


Figure 2: The pair correlation functions of the EXP6 fluids ($\alpha = 11.5$, left part) and ($\alpha = 14.5$, right part) and corresponding descending 2Y fluids at $T^* = 2$ and different densities.

The problem is the choice of the core diameter R and its influence on the final results. LJ potential was used to study this problem. Apart from the condition of coincidences of the positions of minima of the LJ and 2Y potentials and their depths, the position of the inflex point of LJ model R_{inf} was chosen in paper [P3] as another condition. This choice ensures the equality of both potentials in the important short-range distances, including the potential well.

Simulations were used to study both the thermodynamical properties and structure of the homogenous phase of the hc2Y model with different choices of the hard core, and the liquid-vapour equilibrium of hc2Y model. Reduced temperatures $T^* = 1.25$, $T^* = 1.45$ a $T^* = 4.85$ were considered, which represent three most important areas of interest, subcritical, supercritical and extreme for the LJ potential and these choices of hard core were considered: $R/\sigma = 0.80, 0.85, 0.90, 0.95$ a 1.

The obtained MC results suggest that, in general, the final results of hard core influence depend on temperature. At lower temperatures, the hard core loses influence already for $R < 0.95\sigma$, while choosing $R = \sigma$ leads to discrepancies both in the thermodynamic and structural properties. At higher temperatures, the hard core does not lose influence until $R < 0.85\sigma$ values. As for the application of the MSA theory, it turns out that it basically copies the results of MC simu-

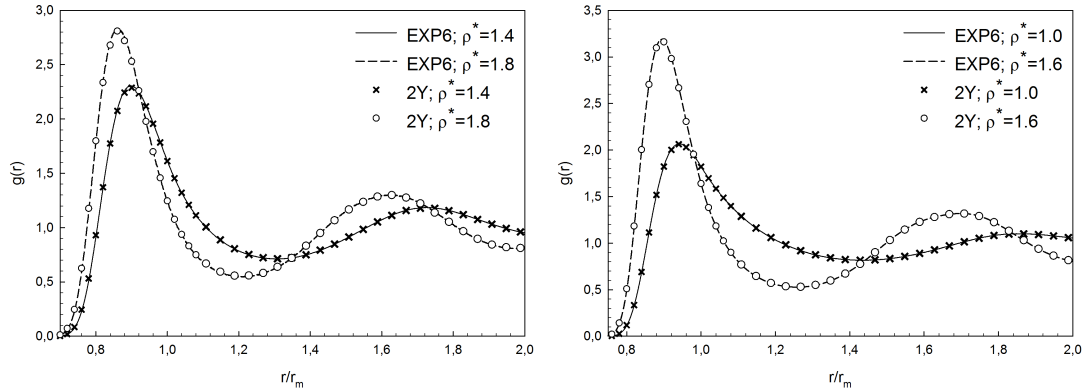


Figure 3: The same as Fig. (2) but for the purely repulsive fluids at the same thermodynamic conditions.

lations regarding the choice of the core. It can be generally summarized that for temperatures that are not much higher than the critical temperature, $R = 0.95\sigma$ is the optimal choice of the core. Even for the highest temperature considered ($T^* = 4.85$), this choice provides reasonable results. In contrast to results of MC, another reduction of the hard core leads to quick deterioration of results of MSA, which is natural because the hard core defines the density in the MSA theory.

The typical results for the internal energy are shown in Fig. (5) and for correlation functions in Fig. (6).

Application of the perturbed virial expansion

The perturbed virial expansion (PVE)

$$\beta P/\rho = (\beta P/\rho)_{\text{ref}} + \sum_{i>1} [B_i(T) - B_{i,\text{ref}}(T)] \rho^{i-1} , \quad (5)$$

was originally designated for extending the applicability of lower-order virial expansion (VE) also to higher densities. PVE also constitutes the basis of the so far most exact equation of state for LJ liquids [9]. It has been recently used also for developing the theory of polar systems [10].

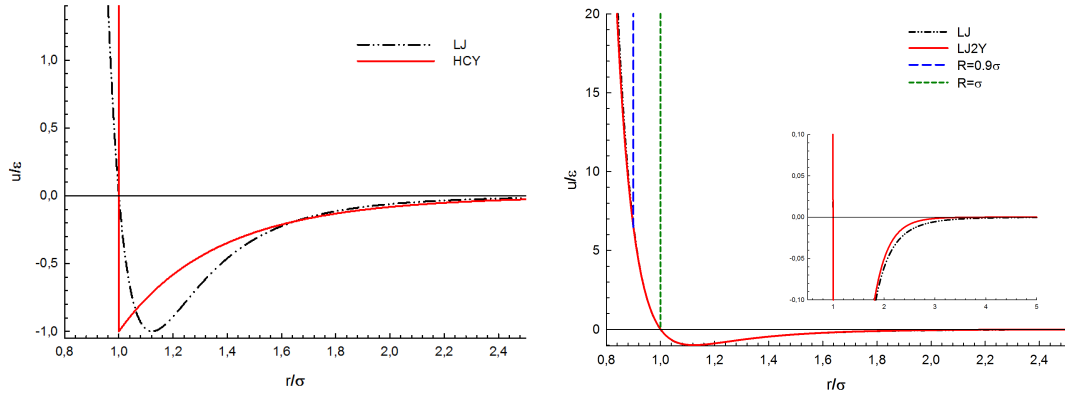


Figure 4: The Lennard-Jones potential in comparison with the hard-core attractive Yukawa (hcY) potential (left part) and with the Lennard-Jones-like two Yukawa (LJ2Y) potential with different positions of the hard-core (right part).

As for other use of knowledge of 2nd virial coefficient, it was found that the 2nd virial coefficient can be used to predict crystallization of proteins [11, 12] and solubility of proteins in water solutions [13, 14]. Since the critical temperature is one of the most significant properties of liquids and its accurate estimation is therefore very important, the PVE was used to estimate the location of the critical point of several model potentials with hard core: Square-Well (SW), Sutherland (S), and hcY. The results of this application are the content of paper [P4].

In the case of the models with hard core considered here, the system of hard spheres with the hard core diameter of R is used as the reference system. The results are listed in Tabs. (2) and (3) and compared with the common VE up to the 1st (VE1) and 2nd (VE2) order, with the Vliegenthatt and Lekkerkerker (VL) method and with "experiment".

The results for the SW liquid using the PVE method are reasonably equal up to the 1st order, the equality is very good when using the PVE up to the 2nd order (PVE2) and better than VE2 in all cases. It is appropriate to mention that the literal data for the SW liquids stated in [15] are out of other authors' trends. As for the Y liquid in Tab. (3), the results of numerical calculations PVE1 are fairly accurate, the results of PVE2 estimate the experimental data far better and

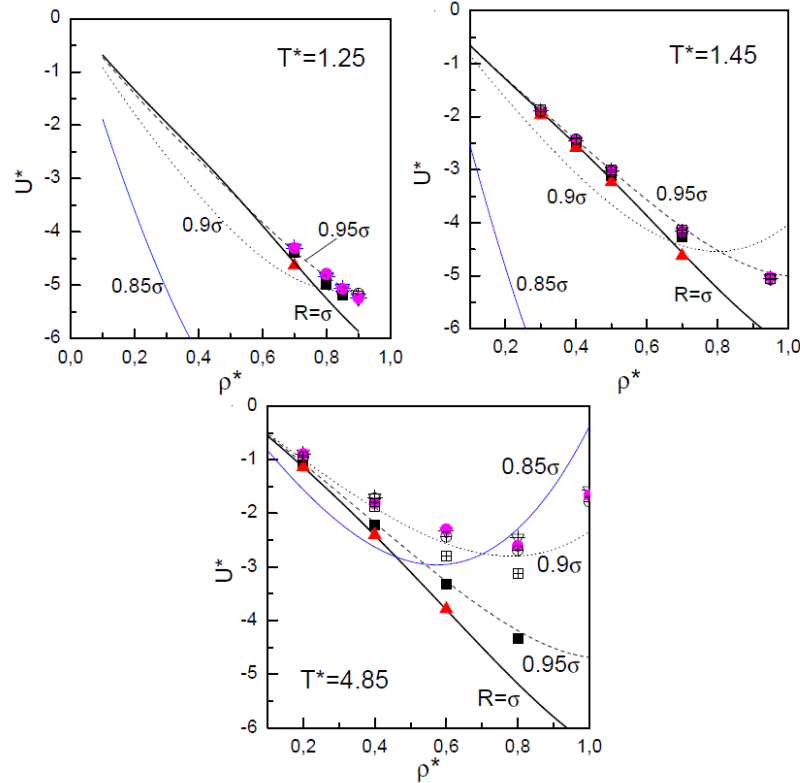


Figure 5: The internal energy of the LJ2Y fluid obtained from Monte Carlo computer simulations (symbols) and in compliance with the MSA theory (lines). The meaning of the symbols: filled triangles – $R = \sigma$, filled squares – $R = 0.95\sigma$, crossed squares – $R = 0.9\sigma$, crossed circles – $R = 0.85\sigma$, filled circles – $R = 0.8\sigma$, crossed triangles – without hard-core. The notes in the figures indicate the position of hard-core in MSA calculations.

the same applies to the results of the VL method. On the other hand, the results of VE2 methods are only a rough estimation and do not show such agreement with experimental data as the aforementioned methods. For the Sutherland potential, the agreement of PVE1 results is good again and the PVE2 results are far closer to the experimental results as well. Surprisingly, the results of VL and VE2 are completely different from the experimental data, thus also from the PVE1 and PVE2 estimations.

Of course, the PVE can be used also for continuous potentials. Such appli-

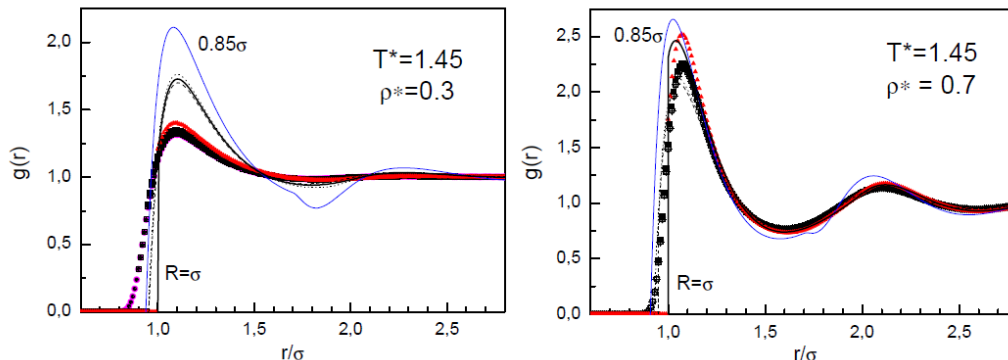


Figure 6: The radial distribution functions of the LJ2Y fluid obtained from Monte Carlo computer simulations (symbols) and in compliance with the MSA theory (lines) at a slightly sub-critical temperature $T^* = 1.45$ and two densities specified in the figure. The meaning of the symbols is the same as in Fig. (5).

cation requires a suitable choice of the reference system. It is theoretically possible to use methods of the theory of fluids, e. g. Barker-Henderson or Weeks-Chandler-Andersen reference systems. However, the legitimacy of such use for the vapour phase is debatable and a special study for these cases has not been conducted yet. The same applies also to use of the PVE for realistic substances.

The knowledge of higher virial coefficients should, in principle, extend the use of the VE to higher densities. Comparisons of VE and PVE results up to the 2nd order for pressure (compressibility factor) along the coexistence curve are shown in Fig. (7) and (8). These graphs indicate that while the VE results quickly deteriorate with increasing density, the PVE method is applicable to correct for the non-ideality of realistic vapour over a larger range of densities.

An important side result of the study of the virial expansions is the possibility to use them to assess accuracy of the equations of state obtained from molecular simulations. Fig. (9) shows the course of differences of the simulation data for the compressibility factor along the phase equilibrium obtained by simulations and virial expansions. As we can see, with the exception of the data from [16], the course of other cases is very chaotic, which indicates a significant inaccuracy of the simulation data at low pressures.

Table 2: Critical temperatures from virial expansions and simulations for the square-well fluid. Numbers at the models denote values of the appropriate potential parameters.

Model\method	simul	PVE1	PVE2	VE2
SW-1.25	0.780 ^a	0.75	0.75	0.80
	0.764 ^b			
	0.850 ^c			
SW-1.50	0.762 ^d			
	1.270 ^a	1.34	1.25	1.33
	1.219 ^b			
SW-1.75	1.330 ^c			
	1.218 ^d			
	1.217 ^e			
	1.218 ^f			
	1.790 ^a	2.11	1.88	1.98
	1.811 ^b			
SW-2.00	1.930 ^c			
	1.808 ^d			
	1.809 ^e			
	2.610 ^a	3.12	2.72	2.87
	2.764 ^b			
2.790 ^c				
2.691 ^d				
2.680 ^e				

^aRef. [17]; ^bRef. [18]; ^cRef. [15]; ^dRef. [16];

^eRef. [19]; ^fRef. [20]

Table 3: Critical temperatures from virial expansions and simulations for the Yukawa and Sutherland fluids. Numbers at the models denote values of the appropriate potential parameters.

Model\method	simul	PVE1	PVE2	VL	VE2
Y-1.8	1.177 ^a	1.15	1.18	1.20	1.33
	1.180 ^b				
Y-3.0	1.179 ^c				
	0.715 ^a	0.69	0.71	0.72	0.79
	0.722 ^b				
Y-4.0	0.725 ^c				
	0.576 ^a	0.56	0.57	0.57	0.62
	0.572 ^b				
0.593 ^c					
0.581 ^d					
Y-5.0	0.500 ^d	0.48	0.49	0.49	0.54
Y-6.0	0.448 ^d	0.43	0.45	0.44	0.48
Y-7.0	0.414 ^d	0.39	0.40	0.40	0.44
S-4.0	1.372 ^e	1.31	1.36	1.26	1.53
S-6.0	0.597 ^e	0.56	0.58	0.54	0.65
	0.583 ^f				
S-7.0	0.495 ^f	0.47	0.48	0.46	0.53
S-9.0	0.410 ^f	0.39	0.40	0.36	0.44

^aRef. [21]; ^bRef. [22]; ^cRef. [23]; ^dRef. [24]

^eRef. [25]; ^fRef. [7]

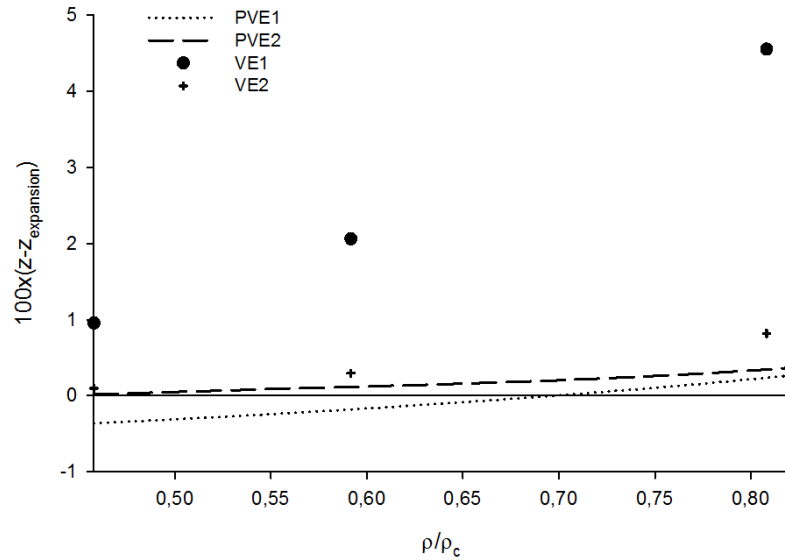


Figure 7: Deviations of the compressibility factor obtained from different virial expansions from simulation data computed along the vapor–liquid coexistence curve. Square-well fluid with $\lambda = 1.25$

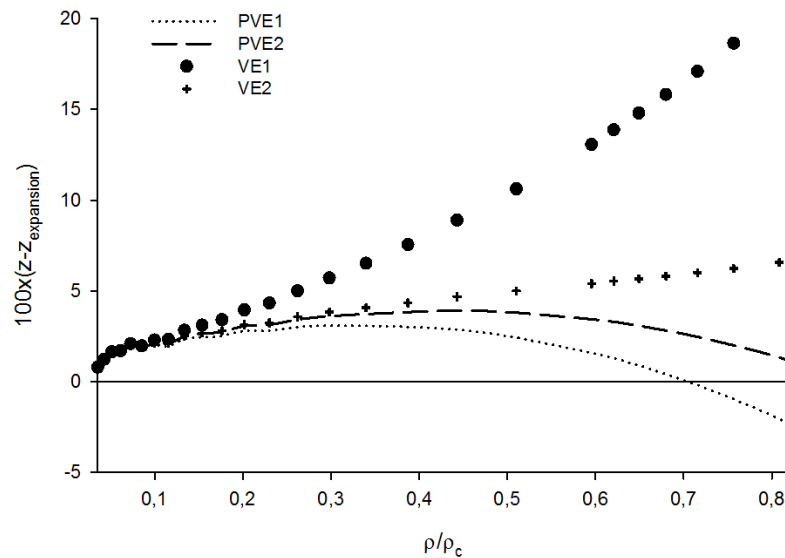


Figure 8: The same as Fig. (7) for the Yukawa fluid of $z = 4$.

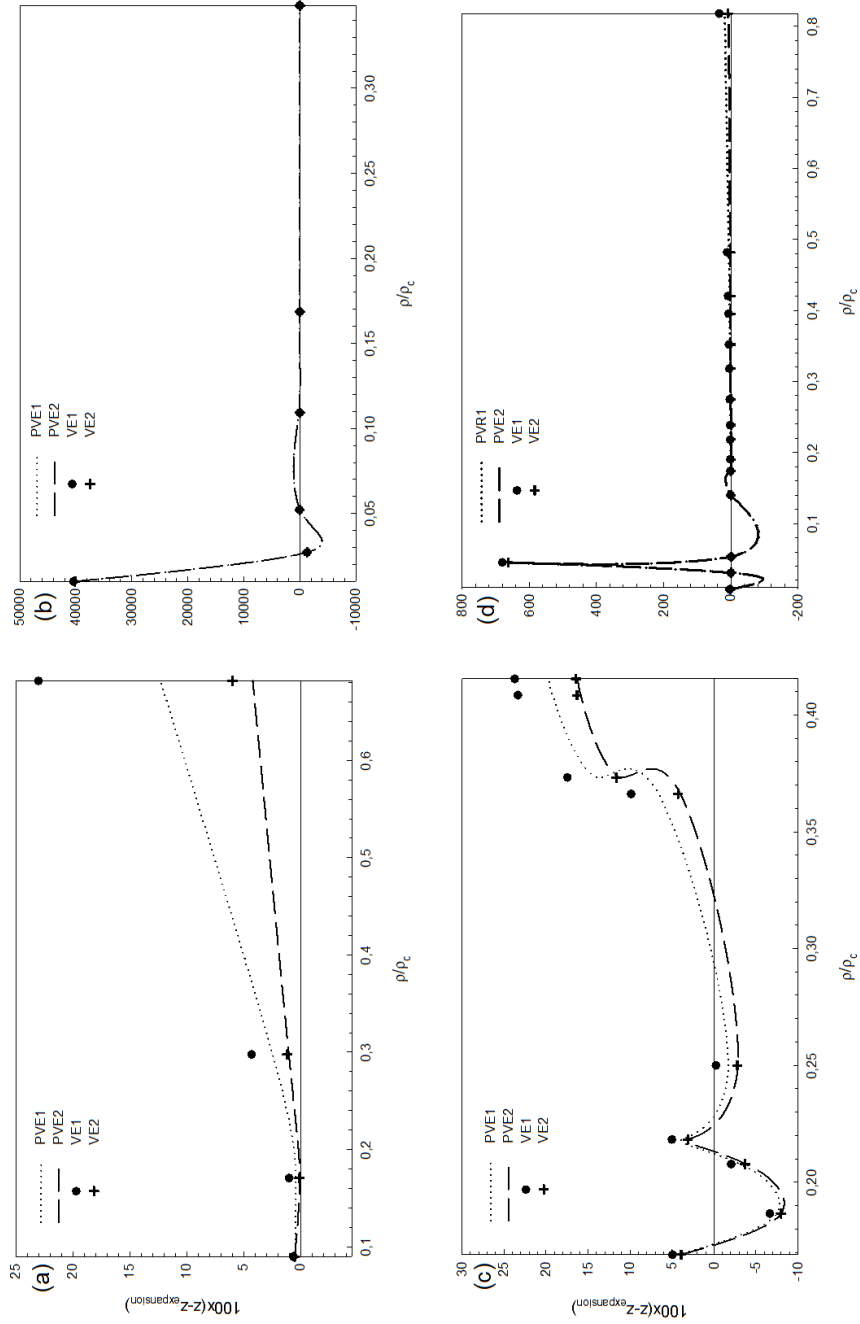


Figure 9: The same as Fig. (7) for the square-well fluid of $\lambda = 1.75$ using different sets of simulation data: (a) [16], (b) [17], (c) [18], (d) [5].

Conclusions

The presented work aims at obtaining knowledge on the thermodynamic behaviour and structure of fluids which are defined by the EXP6 and 2Y potential models and possibilities of their theoretical description. For these reasons, extensive molecular simulations were performed both in canonical and Gibbs ensembles and an extensive set of data obtained. For completeness and for their further use, the virial coefficients up to the fourth of these models over a wide range of temperatures were calculated using the Mayer sampling method.

The EXP6 fluid was used as a parent system with soft repulsions, which is used in applications at conditions usual in geochemistry and detonations, i. e., high temperatures and pressures. The 2Y system was then studied with respect to its possible use for developing a theory of the EXP6 fluid. This theoretical description is two-level and uses the knowledge of an approximate analytic description of the Yukawa fluid with hard core (or combination of these liquids). In the first step, the EXP6 model is projected onto 2Y model and this model is then described using Y-models with hard core (hc2Y). In the second step, it is necessary to choose the size of the hard core and that is the reason why the hc2Y liquids with different choices of hard cores were studied using separate simulations. The result of these simulations serves as recommendation how to choose the hc2Y system to obtain accurate results using an approximate analytic theory.

The separate part of the thesis is the study of possibilities of use of the perturbed virial expansions. It has been shown that the knowledge of only the second virial coefficient is sufficient to account for non-ideality up to much higher temperatures and densities and allows for the critical temperature to be reasonably estimated.

Shrnutí

Předložená práce je zaměřena na získání znalostí o termodynamickém chování a struktuře kapalin definovaných potenciálními modely EXP6 a 2Y (two Yukawa) a možnosti jejich teoretického popisu. Za tímto účelem byly prováděny rozsáhlé molekulární simulace, a to jak v kanonickém, tak i Gibbsově souboru a získán tak obsáhlý soubor dat. Pro úplnost a možnost jejich dalšího využití byly také metodou Mayerova vzorkování vypočítány viriální koeficienty těchto modelů až do čtvrtého pro širokou oblast teplot.

EXP6 kapalina hrála v těchto studiích roli rodičovského systému s měkkými repulzemi, který se používá v aplikacích pro podmínky obvyklé v geochemii a při detonacích, tj. vysoké teploty a tlaky. 2Y systém byl pak studován z hlediska možnosti vypracovat pomocí něho teorii EXP6 tekutiny. Tento teoretický popis je dvoustupňový a využívá znalosti přibližného analytického popisu Yukawovy tekutiny s tuhým jádrem (či kombinaci těchto tekutin). V prvním kroku se EXP6 model projektuje na 2Y model a tento model se pak popíše pomocí Y-modelů s tuhým jádrem (hc2Y). V tomto druhém kroku je nutno volit velikost tuhého jádra a proto byly dále separátními simulacemi studovány hc2Y tekutiny s různými volbami tuhého jádra. Výsledkem těchto simulací je doporučení, jak by měl být hc2Y systém volen, aby přibližná analytická teorie poskytovala dobré výsledky.

Samostatným příspěvkem je studium možností použití poruchového viriálního rozvoje. Bylo ukázáno, že znalost již pouze druhého viriálního koeficientu dovoluje určit korekce na neidealitu do mnohem vyšších teplot a hustot a umožňuje rozumně odhadnout i kritickou teplotu.

Papers included in the thesis

- [P1] J. KREJČÍ, I. NEZBEDA, R. MELNYK, AND A. TROKHYMCHUK, **EXP6 fluids at extreme conditions modeled by two-Yukawa potentials**, JOURNAL OF CHEMICAL PHYSICS, **133**(9), 094503: 1–8, 2010.
- [P2] J. KREJČÍ, I. NEZBEDA, R. MELNYK, AND A. TROKHYMCHUK, **Virial coefficients and vapor-liquid equilibria of the EXP6 and 2-Yukawa fluids**, CONDENSED MATTER PHYSICS, **14**(2), 23004: 1–8, 2011.
- [P3] J. KREJČÍ, I. NEZBEDA, R. MELNYK, AND A. TROKHYMCHUK, **Mean-spherical approximation for the Lennard-Jones-like two Yukawa model: Comparison against Monte Carlo data**, CONDENSED MATTER PHYSICS, **14**(3), 33005: 1–11, 2011.
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