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Faculty of Science

Department of Physics

Abstract of the Doctoral Thesis

MOLECULAR SIMULATION METHODS: RECENT PROBLEMS AND APPLICATIONS

by

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METODY MOLEKULÁRNÍCH SIMULACÍ: SOUČASNÉ PROBLÉMY A APLIKACE

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Goals of the thesis

The dissertation deals with advanced Monte Carlo (MC) simulation methods and their application. It addresses thus both their methodology and their use to solve certain theoretical problems of the fluid phase associated with long-term projects conducted in E. Hála Laboratory of Thermodynamics, Academy of Sciences. Specifically, as regards the methodology, the goals have been

1. to develop, implement, and optimize a Monte Carlo method suitable for molecular simulations of models, whose configurational energy is not given by the sum of individual intermolecular interactions between the pairs of particles, e.g., polarizable models;

2. to (re)examine various approximations simplifying simulations of systems with long-range interactions and provide recommendations for their use.

In the application part, the goals have been

1. to examine, using the developed new Monte Carlo method, the effect of polarizibility on the thermodynamic behavior of aqueous solutions of alcohols;

2. to investigate the effect of the cross interactions on the properties of binary mixtures;

3. to study the structure of the attractive hard-core Yukawa fluid as a part of a general project aiming at development of a novel perturbation theory of fluids.

Introduction

Computer simulations are able to substitute real world observations and allow us to study model systems necessary for understanding natural patterns of fluids. In addition, they provide a direct access to valuable microscopic properties beyond the reach of even the most expensive equipment available. Theoretically, the value of the simulation is limited only by the accuracy of microscopic models considered.

For simplicity, the models used both in theory and applications are usually based on the assumption that the configurational energy is given by the sum of individual intermolecular interactions between pairs of particles. If this assumption is dropped, even simple intermolecular potential models with triple interactions may cause nearly unsurmountable problems. First of all, the development of such non-additive interaction potentials is, with algorithms currently available, at the edge of feasibility, and simulations on such models are very time consuming. Hence, more efficient methods must be developed to be able to address such problems.

Regardless of the approach used, assuming pair-wise additivity or not, intermolecular interaction models of non-simple compounds include unavoidably long-range electrostatic interactions whose strength does not become negligibly small either at large distances. The question how to treat them correctly and efficiently does not seem to have been satisfactorily answered yet.

Even if all the methodological problems were solved, there are still questions regarding the interaction potentials of mixtures. Molecular modelling of mixtures relies on purely empirical principles. In the case of the interaction between two different molecules, empirical combining rules have to be applied which are incongruent with the physical nature of pure fluid effective potentials. The results obtained using this approach are therefore unpredictable.

As for developments in theory of liquids, there has been a renewed interest in simple fluids, particularly in the Yukawa model. This interest likely lies in the existence of analytic results within the MSA theory [4, 5], parametrized equation of state [6–8], and a possibility to model any simple fluid potential by an n-Yukawa model. An attempt to develop a novel perturbation theory based on a short-range Yukawa potential has been made recently [P6].

Results and discussion

Multi-particle Move Monte Carlo simulation method

To make the simulations of non-additive potential systems more efficient the biased multi-particle move (MPM) MC scheme has been proposed. It is based on the force bias method [9] extended to a simultaneous displacements/rotations of all particles at once.

To verify the validity and to assess the efficiency of the MPM MC method, it has been first implemented and applied to the polarizable Stockmayer potential fluid. To assess the efficiency of the MPM MC, several order parameters have been calculated, the convergence of thermodynamic properties has been examined, and the blocking method [10] has been applied to the total configurational energy. To exemplify the superior performance of the method in comparison with the standard one-particle move method and an unbiased multi-particle scheme, the convergence of translational order parameter [11] and rotational relaxation parameter [12] to their equilibrium values is presented in figure 1. In general, it has been shown that, in the case of this simple polarizable model, the proposed biased method is about a factor of 10 faster when compared with the other schemes. The detailed study is found in [P1].

The MPM MC has been designed for simulations of complex models. Hence, the necessary expressions for polarizable site-site interaction models had to be and have been derived. Preliminary test runs showed that the MPM method is, at some thermodynamic conditions, rather sensitive to discontinuities of the interaction potentials at the cutoffs. The discontinuities originate especially from the electrostatic potential truncation if the reaction field method is applied. Thus, as a by-product of the MPM MC, a novel smoothing of the potential at the cutoff distance has been proposed. The MPM MC, both with and without the potential smoothing, has been implemented for the Chialvo-Cummings (CC) [2] and the Brodholt-Sampoli-Vallauri (BSV) [3] polarizable models of water. The performance of the method and the dependence of the method on simulation parameters were studied. Moreover, the program was parallelized. The blocking analysis of the configurational energy data is presented in figure 2 where one can see that the machine time necessary to generate an independent block of configurations, is about ten times shorter for the MPM method in

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comparison with the conventional single-particle MC. All the other results and derivations are found in [P2]. It has been shown that the MPM MC is several times faster when compared with approximate methods, and its parallelized codes may, running on a standard 8-core computational node, perform about seventy times faster than the conventional non-parallelized MC.
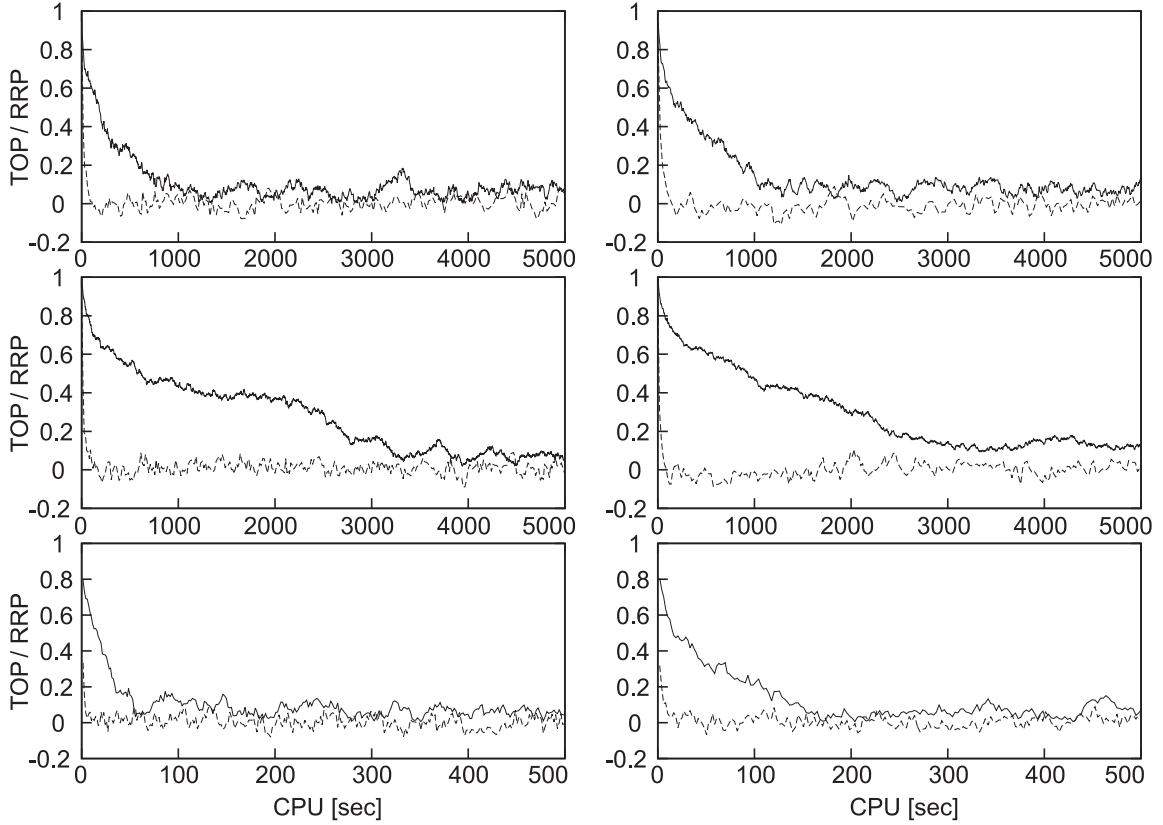

Figure 1: Comparison of the development of the translational order parameters (solid line) and the rotational relaxation parameters (dotted line) in the polarizable Stockmayer fluids with polarizability $\alpha^* = 0.05$ (left column) and 0.10 (right column): Conventional one-particle MC (first row), unbiased MPM MC (second row), and biased MPM MC (third row).
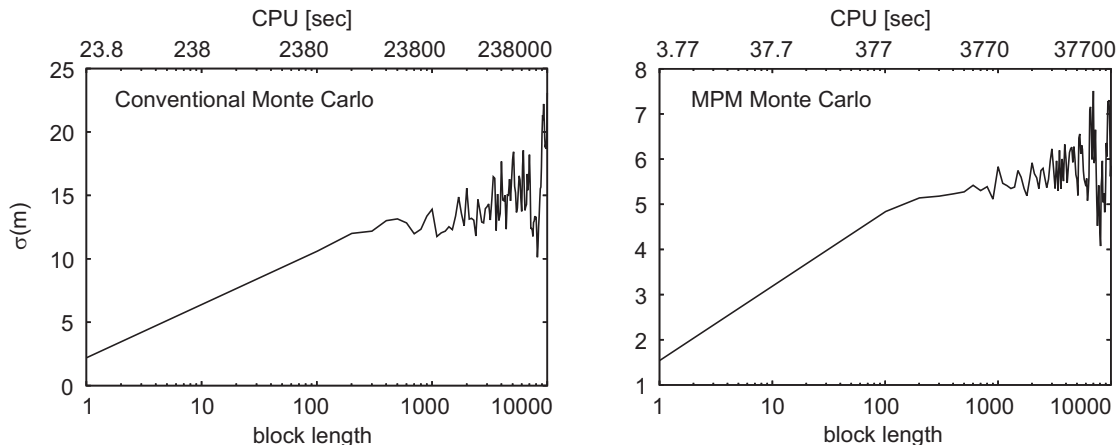
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Figure 2: Blocking analysis of the total internal energy at $T = 573K$ and $N/V = 0.0241\text{Å}^{-3}$ using CC model in the NVT: conventional MC method (left), MPM method (right). $\sigma(m)$ is the standard deviation.

Long-range interaction methods

To assess various methods treating the long-range interaction, two quantitatively different models of strongly polar fluids were studied, (1) non-associating fluid, modelled by dipolar Lennard-Jones diatomic molecules, and (2) water, modelled by the TIP4P/2005 potential [13], and four methods were considered: (1) Ewald summation, (2) reaction field, (3) short-range electrostatics adopted in the MACSIMUS package [14], and (4) pairwise approximation of Fennel and Gezelter [15]. Properties of both homogeneous and inhomogeneous systems were studied.

The analysis has shown that various short-range approximations of the Coulomb interaction can yield, if carefully implemented, satisfactory results for many systems but no unique recommendation can be proposed. Consequently, in addition to all the results presented in several tables [P3], there is also a number of questions that one should ask, and considerations that must be accounted for, before a specific method is chosen. Details of these considerations can be found also in paper [P3]. The contribution of the author of the thesis to this project has been all the MC and Gibbs ensemble simulations.

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The effect of polarizability on mixing properties of aqueous solutions of methanol

As an important application of the developed MPM MC method, water-methanol mixture was studied over the entire concentration range using a polarizable model of water. The goal of this study was to find out whether the inclusion of polarizability is able to change *qualitatively* the thermodynamic behavior of the mixture, particularly, to produce the minimum in the partial molar volume of methanol. From available polarizable models of water the BSV model was chosen for its both accuracy and simplicity; for methanol the KBFF model [16] was used. As it is seen in figure 3, the excess volume exhibits a very pronounced concavity at low concentrations of methanol which gives rise to a minimum of its derivative. This behavior is in full *qualitative* agreement with experiment. The quantitative disagreement is rather typical and therefore not surprising because the used potential models were fitted to pure fluid data and no information on the properties of the mixture has been used for the cross interaction. Complete results of this investigation are presented in paper [P4].
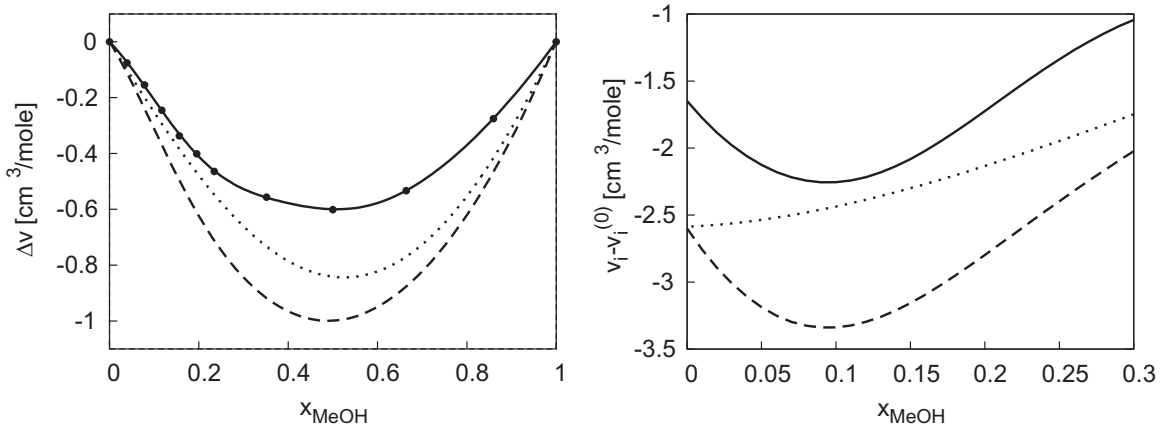

Figure 3: The excess volume of the water-methanol mixture (left graph) and the corresponding partial molar volume of methanol at low concentrations (right graph). The solid lines and filled circles are, respectively, the smoothed and raw simulation results, the dashed lines are smoothed experimental data [17], and the dotted lines are the results taken from [18].

The effect of cross interactions on mixing properties of simple liquids

In addition to polarizability, the behavior of mixtures can be changed by changing the combining rule. A feasibility study was conducted to examine the impact of the combining rules on the properties of mixtures by considering the mixture of two identical LJ fluids but with the cross interactions given by equations:

$$\sigma_{12} = (1 + \delta_\sigma)(\sigma_{11} + \sigma_{22})/2 \quad \text{and} \quad \varepsilon_{12} = (1 + \delta_\varepsilon)\sqrt{\varepsilon_{11}\varepsilon_{22}} \ .$$

A typical result, the dependence of the excess volume on the composition is shown in figure 4; results with additional details can be found in [P5]. It turns out that by varying the cross parameters, a spectrum of properties of excess functions can be obtained, including those observed for mixtures of complex compounds. The author of the thesis contributed to this project by cooperating on the development of the necessary simulation software.
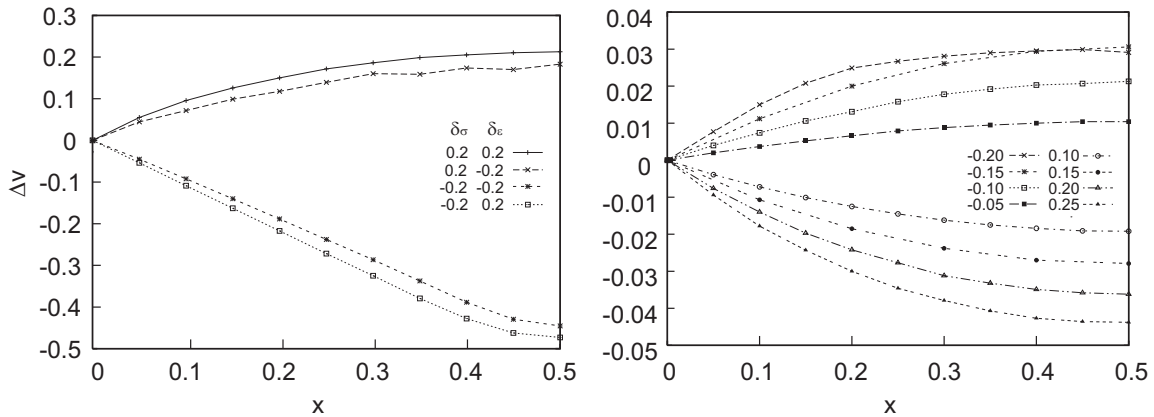

Figure 4: Excess volume for a combination of non-zero values of δ_σ and δ_ε (left graph), and for $\delta_\sigma = 0$ and different values of δ_ε (right graph).

Structure factor of Yukawa fluid

As a part of a general project aiming at development of a novel perturbation theory based on the Yukawa reference system, it was necessary to study the structure of Yukawa fluids of different range. Standard MC simulations were performed and the structure factor was computed. It was shown that the proposed perturbation approach, based on the short-range Yukawa model, is in very good agreement with the simulation results, see figure 5. For details of both the theoretical and MC calculations we refer to [P6].
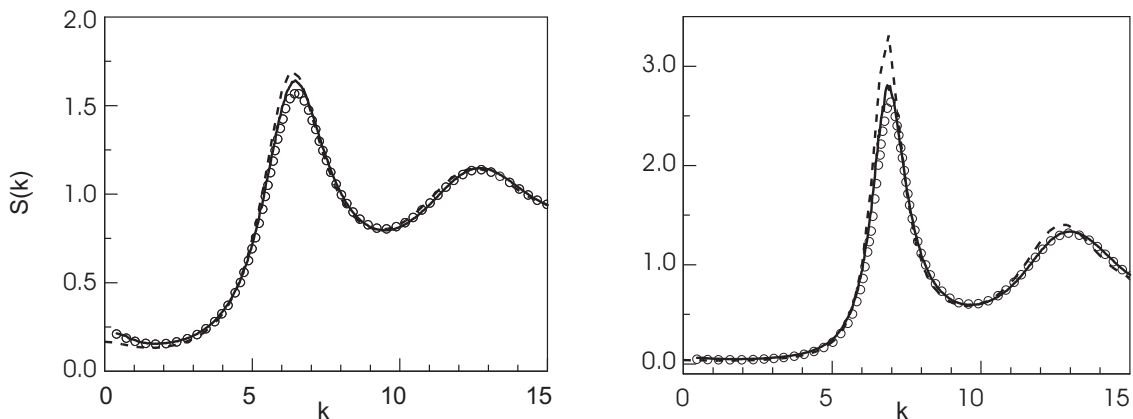
Figure 5: The structure factor $S(k)$ of the Yukawa Lennard-Jones-like fluid at $T^* = 1.5$, $\rho = 0.6$ (left graph) and $T^* = 0.75$, $\rho = 0.9$ (right graph) obtained from simulations (circles), and its comparison with the perturbed route using the simulation (full line) and MSA (dashed line) for the reference structure factor.

Conclusions

The dissertation summarizes results achieved in the past three years during author's Ph.D. study and which were published in six original papers [P1–P6]. A general goal of the conducted research has been to contribute to advancement of modern liquid state theory. Since molecular simulations form nowadays an indispensable part of theory, the research included both methodological problems and application of simulations.

The idea to go from one-particle to multi-particle MC scheme originated from the conviction that to achieve a better description of liquid mixtures one has to go beyond pair-wise additivity of interactions which, on the other side, must inevitably make MC simulations very much time consuming. We have developed the MPM MC method which has been shown to perform, in average, ten times faster in comparison with the conventional MC method. This efficiency has made it possible to embark on a study of the water-alcohol mixture modelled by a polarizable model of water because the pair-additive models have failed so far to yield results in qualitative agreement with experiments. The obtained results exhibit a minimum in the partial molar volume of methanol; to our best knowledge, this is the first result ever reported in literature to show this behavior. It is thus believed that the MPM MC method can contribute to the development of better (more realistic) interaction models of complex fluids.

Results of other papers of this collection may be viewed as computer aided support for theory. Results for the mixture of two identical LJ fluids show that there may be a simple alternative to the description of complex liquid mixtures behavior. Namely, instead of, or in addition to commonly used deviations from the Berthelot rule for the energetic parameter it is primarily the deviation from the Lorentz rule for the distance parameter that can significantly change thermodynamics of mixtures and bring thus results closer to experiment. Finally, as for the development of a novel perturbation theory, without the simulation results for the structure of the Yukawa fluid this would not have been possible. Importance of both these sets of results is underlined by the fact that there has already been a further development in both fields, mixtures of complex fluids and simple fluid theories, based on the results reported in the papers of this collection.

Shrnutí

Disertace shrnuje výsledky získané v uplynulých třech letech autorova Ph.D. studia publikované v šesti článcích [P1–P6]. Hlavním cílem tohoto výzkumu bylo přispět k vývoji moderní teorie kapalin. Molekulární simulace dnes představují neoddělitelnou část teorie. Výzkum proto zahrnoval metodologické problémy simulací i jejich aplikace.

Idea přejít od jednočásticového MC schématu k mnohačásticovému vznikla z přesvědčení, že k dosažení lepšího popisu kapalin je nutno opustit předpoklad párové aditivity interakcí. To však způsobuje velmi vysokou časovou náročnost MC simulací. Vyvinuli jsme proto metodu MPM MC, která se ukázala být ve srovnání s konvenční MC metodou desetkrát rychlejší. Toto zvýšení efektivity umožnilo začít studovat směsi polarizovatelných modelů vody s alkoholy. To je předmětem dnešního zájmu, neboť výsledky pro párově aditivní modely doposud vždy ve shodě s experimenty kvalitativně selhaly. Námi studovaný model směsi vykazuje minimum parciálního molárního objemu metanolu. Dle našich znalostí jde o první výsledek uvedený v literatuře popisující toto chování. Věříme proto, že metoda MPM MC může přispět k vývoji realističtějších modelů interakcí komplexních tekutin.

Na výsledky ostatních článků této kolekce je možno pohlížet jako na počítačovou podporu pro teorii. Výsledky směsí dvou identických LJ tekutin ukazují, že by mohla existovat alternativa k popisu chování směsí komplexních kapalin. Oproti obvykle užívaným odchylkám od Berthelotova pravidla pro energetický parametr totiž mohou odchylky od Lorentzova pravidla pro parametr vzdálenostní značně změnit termodynamiku směsí a přiblížit tak výsledky experimentu. Pokud jde o novou poruchovou teorii kapalin, její vývoj by bez znalosti strukturního faktoru Yukawovy tekutiny získané ze simulací nebyl možný. Důležitost obou těchto publikovaných výsledků potvrzuje fakt, že na ně již bylo navázáno dalším pokrokem v oblasti směsí komplexních tekutin i v teorii jednoduchých tekutin.

Papers included in the thesis

[P1] Moučka F., Rouha M., Nezbeda I.: *Efficient multiparticle sampling in Monte Carlo simulations on fluids*, J. Chem. Phys. 126 (2007) 224106.

[P2] Moučka F., Nezbeda I.: *Multi-particle sampling in Monte Carlo simulations on fluids: Efficiency and extended implementations*, submitted.

[P3] Kolafa J., Moučka F., Nezbeda I.: *Handling electrostatic interactions in molecular simulations: A systematic study*, Collect. Czech. Chem. Commun. 73 (2008) 481.

[P4] Moučka F., Nezbeda I.: *Partial molar volume of methanol in water: Effect of polarizability*, submitted.

[P5] Rouha M., Moučka F., Nezbeda I.: *The effect of cross interactions on mixing properties: Non-Lorentz-Berthelot Lennard-Jones mixtures*, Collect. Czech. Chem. Commun. 73 (2008) 533.

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