

J. E. Purkinje University in Ústí nad Labem

Faculty of Science

Department of Physics

Abstract of the Doctoral Thesis

**TOWARDS A MOLECULAR THEORY OF
LIQUID MIXTURES**

by

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**K MOLEKULÁRNÍ TEORII
KAPALNÝCH SMĚSÍ**

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Aims of the thesis

The dissertation considers problems associated with a long-term multistage project conducted at the E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, with the ultimate goal to develop a molecular theory of complex liquid mixtures, i.e., mixtures containing polar and/or associating components.

Particular goals have been as follows:

1. To find an analytic description of model pseudo-hard body fluids, both pure and mixtures, that form the basis of primitive models;
2. To examine the effect of the cross interactions on the mixing properties, particularly, to what extent they can affect *qualitatively* the observed behavior.

Introduction

The aim of molecular theory of liquid mixtures is to explain and to predict their behavior on the basis of the input information on the molecular properties of the individual molecules constituting the solution. There has been considerable success in achieving that goal for mixtures of simple fluids, but not much progress has been made for mixtures containing polar and/or associating components.

The main difficulty in developing a molecular theory for complex liquid mixtures has been the absence of theory for pure strongly polar and associating fluids. Only at the beginning of the 1990's extensive molecular simulations revealed that the basic mechanisms governing the behavior of polar, both associating and non-associating, fluids are primarily short-range forces which, however, may be both repulsive and attractive [1]. This finding has made it legitimate to write various properties of associating fluids in a perturbed form with the leading reference term given by a suitably chosen short-range reference.

To implement the perturbation expansion, the properties of the chosen reference fluid must be well known and available, preferably, in an analytic form. Likely, the only feasible way to estimate the properties of the reference fluid is by mapping them onto the properties of an appropriate simple model. For associating fluids the so-called primitive models may play this role.

A method to construct primitive models for a number of these fluids has been recently developed [2]. These models do reproduce the structure of the parent realistic models, which is the necessary condition for the perturbation expansion to converge. Another necessary ingredient for the theory to be accomplished is its ability to estimate the properties of the primitive models in an analytic form. This problem includes the necessity to accurately describe their underlying bodies, the so-called pseudo-hard bodies [3].

Another difficulty in developing a molecular theory of liquid mixtures is the relatively poor knowledge of the intermolecular interactions between molecules of different species. While the intermolecular forces between particles of the same kind are relatively well-understood, the intermolecular forces between the molecules of different kinds are described only by so-called combining rules, the most well-known being the Lorentz-Berthelot

rule. Although there is only a very vague theoretical justification of this rule, due to the adjustment of the results to experimental data its inadequacy does not cause principal problems in developing pure fluid interaction models.

However, the situation is quite different when dealing with mixtures. In this case the developed pure fluid interaction models are used to *predict* the properties of mixtures and it is evident that the entire concept of combining rules is, in general, ill-footed: even the used pure fluid potentials cannot adequately describe the interaction between the like species in the mixture, because they do not account for the presence of the other species. It has been well known for decades that the mixture properties are very sensitive to the cross interactions, but this is only a consequence of the entire concept.

Achieved results

Fluids of pseudo-hard bodies

Since no theory of PHB fluids has been developed so far, it was necessary to start with molecular simulations and obtain data that could be at least parametrized. We have considered models descending from the realistic models of water, methanol, ethanol, ammonia, and hydrogen sulphide. For the purpose of the evaluation of some equations of state (EOS) we also computed their first four virial coefficients.

Having the simulation data, we first evaluated the EOS from a straightforward application of equations for hard bodies; namely, the PVE, RVE and ISPT [4]. Typical results are shown in Fig. 1. As it is seen, none of the considered EOS, as is, is able to describe the PHB fluid behavior with reasonable accuracy over the entire density range.

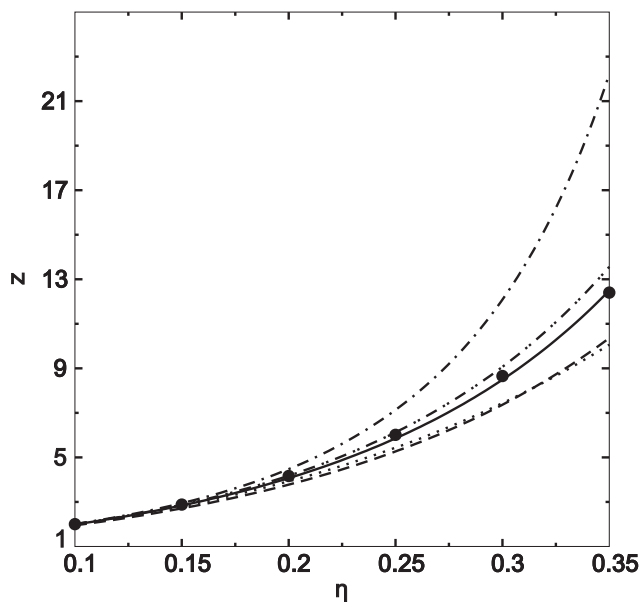


Figure 1: Comparison of various analytic equations of state (for details see [P1]) with simulation data (circles) for water.

From the theoretical point of view, the reference HS fluid should be at the same packing fraction as the fluid under consideration, but this quantity is not known for the PHB models. Following [5], we tried to determine

a certain volume of the pseudo-hard body by fitting the PVE equation to simulation data. We have found, that the perturbed virial expansion with an adjusted size of the reference HSs seems to provide quite accurate results, see Fig. 1 (full line). Further details can be found in paper [P1].

The ultimate goal of studies of pure fluids is to address the problem of mixtures of PHB's without resorting to their simulations. As a first attempt, which should be viewed as a feasibility study, we have considered binary mixtures with one PHB component only and examined to what extent such an approach may be fruitful/promising. The chosen PHB represented the repulsive interactions in the PM of TIP4P water; the other component was a HS and we considered various mixtures with HS of different size, σ_{HS} .

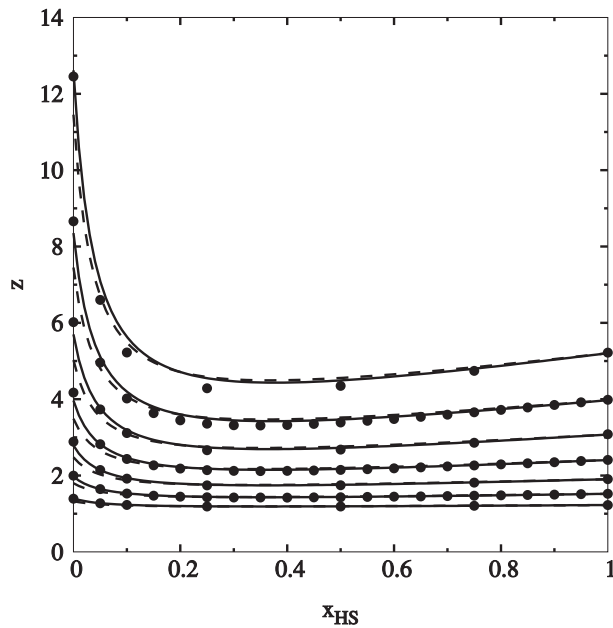


Figure 2: Comparison of the concentration dependence of the compressibility factors of the considered PHB mixture at constant packing fraction obtained from the perturbed virial equation of state (full line) and of the reference mixture of hard spheres (dashed line) with simulation data (open circles) for $\sigma_{\text{HS}} = 2.5$. The results are, from bottom to top, at packing fractions 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35.

Following the success achieved for pure PHB fluids, we considered the compressibility factor of the mixture also in the form of a perturbed virial

expansion with a HS mixture reference given by the BMCSL EOS [4]. Three main conclusions that can be drawn from the results are (see Fig. 2):

1. The perturbed virial expansion performs very well for all concentrations for large diameters of the dissolved HS.
2. This accuracy however decreases as the size of the HS decreases and becomes comparable with the hard core of the PHB. Yet, at least qualitative agreement, i.e., the curvature of the z vs. η curve, is maintained.
3. Likely surprisingly at first sight, the reference HS mixture performs quite accurately for large HS diameters. On the other hand, for small HS diameters the reference HS mixture exhibits the well known nearly linear dependence.

Non-Lorentz-Berthelot Lennard-Jones mixtures

To study effects of cross interactions we considered two identical LJ fluids with non-LB rules given by

$$\begin{aligned}\sigma_{12} &= (1 + \delta_\sigma)(\sigma_{11} + \sigma_{22})/2 \\ \varepsilon_{12} &= (1 + \delta_\varepsilon)(\varepsilon_{11}\varepsilon_{22})^{1/2} .\end{aligned}$$

As a first feasibility study [P3] we considered the mixture at only one state point but for a large number of non-LB cross parameters. Furthermore, we focused on and reported results for excess properties only. We found, that by varying the cross parameters a spectrum of the properties of excess functions can be obtained, including those observed for mixtures of complex compounds. Whereas consequences of the deviations for excess volume are rather straightforward, a variety of behavior types is found for excess enthalpy, including an excess function with three extrema. Details of this study can be found in paper [P3].

The shape of the excess volume for certain combinations of the non-LB cross parameters indicated that the mixture may also exhibit *qualitative* changes in its behavior, e.g., the minimum in the partial molar volume instead of a monotonous dependence on the concentration. In paper [P4]

we have considered only selected combinations of the cross parameters focusing particularly on qualitative changes in the thermodynamic behavior. These changes, if there are any, must result from and reflect changes in the structure and therefore we also examined the impact of the cross interactions on the pair correlation functions. Furthermore, we have considered the mixtures at three state points in order to find the impact, if any, of the thermodynamic conditions on the mixing properties.

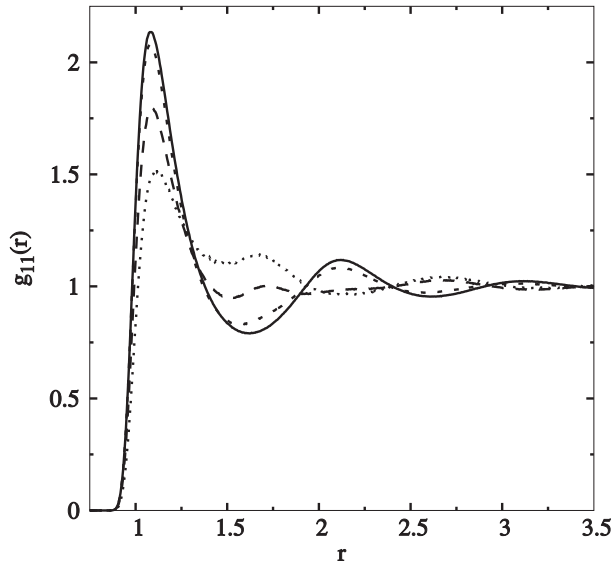


Figure 3: The pair correlation functions for $\delta_\sigma = -0.2$ and $\delta_\varepsilon = +0.2$ and different concentrations (full line, pure fluid; short dashed line, $x = 0.25$; long dashed line, $x = 0.5$; dotted line, $x = 0.75$).

As regards the excess functions, the trends found previously remain valid also at other thermodynamic conditions. Regardless of the changes in the energetic interaction, for $\delta_\sigma < 0$ we observe a minimum in the partial molar volume, whereas for $\delta_\sigma > 0$ it is a monotonously decreasing function. A typical result of the pair correlation function is shown in Fig. 3. As it is seen, a considerable change in the course of g_{11} is found in the second coordination shell: The curve gets deformed around the first minimum where a sort of secondary peaks start to evolve. Thus, what we observe is first a certain restructuring in the second coordination shell followed then by a shift of the second peak to closer separations.

Conclusions

The dissertation is a concise summary of the work carried out during author's doctoral study and that has been published in four original papers [P1–P4]. The main goal of the research projects, in which the author has been involved, has been to enhance understanding of molecular mechanisms governing the behavior of complex mixtures, enabling then ultimately to develop a molecular theory of complex fluids and their mixtures.

As a first step, a semi-empirical description of the properties of several pure pseudo-hard body fluids by means of a perturbed virial expansion has been presented. The results are valuable, since these fluids constitute the basic part of equations of state based on perturbation expansions about the primitive model reference. Although a simple rough empirical recipe for determining the size of the reference HSs has been given, its theoretically footed data-independent determination should be the nearest future task of theory.

To obtain fundamental information on the intermolecular interactions, the knowledge of the thermodynamic behavior of fluid mixtures is important. It has been well established that excluded volume effects are responsible for a number of observed properties of fluids. For many mixtures hard spheres can be and have been used to estimate these effects. But for mixtures of polar or associating fluids this may be hardly justified, and mixtures of PHBs should be used instead.

For this reason we presented an analytical study of mixtures of hard spheres and pseudo-hard bodies by means of a relatively simple alternative that works reasonably well, a perturbed virial expansion. This should be sufficient to justify its use in studies of, e.g., aqueous solutions of hydrocarbons whose full understanding is still missing, and to assess the entire concept of primitive models and its use in applications.

Mixing properties cannot be estimated purely on the basis of the pure fluid properties and LB rules; this has been known for decades. However, when seeking better numerical agreement with experimental data of excess functions, it has been the cross energy interaction parameter that has been primarily manipulated with the excluded volume parameter being kept, in most cases, intact. We have shown that the manipulation with the cross energy parameter is important for a fine tuning of results but that it is the excluded volume, i.e., deviations from the Lorentz rule, which affects the

results most and which may also cause qualitative changes.

We have focused on the partial molar volume whose behavior for aqueous solutions of alcohols has only recently been explained on the molecular level by diffraction experiments [6]. Using molecular simulations, this feature has been obtained only after incorporation of polarizability [7]; pairwise potential models have not been able to reproduce this phenomenon [8]. We have observed a similar behavior in a binary mixture of identical Lennard-Jones fluids for a certain combination of the cross parameters. There may be thus an alternative to polarizability to change mixture properties qualitatively. These findings may help to understand the behavior of mixtures on the molecular level and to develop combining rules for different classes of mixtures for practical applications.

Shrnutí

Tato disertace stručně shrnuje výsledky získané během autorova doktorského studia publikované ve čtyřech článcích [P1–P4]. Hlavním cílem výzkumu, kterého se autor účastnil, je pozvednout porozumění molekulárním mechanismům, které ovládají chování složitých směsí, což by nakonec umožnilo vyvinutí molekulární teorie komplexních tekutin a jejich směsí.

Jako první krok byl prezentován semi-empirický popis vlastností několika pseudo-tuhých tekutin pomocí poruchového viriálního rozvoje. Dosažené výsledky jsou hodnotné, protože tyto tekutiny tvoří základní část stavových rovnic založených na poruchovém rozvoji kolem reference popsané primitivním modelem. I když byl prezentován přibližný empirický postup pro získání velikosti referenční tuhé koule, nejbližším cílem teorie by mělo být jeho na datech nezávislé určení.

K získání základních informací o mezimolekulárních interakcích je nutno znát termodynamické chování směsí tekutin. Pro řadu vlastností tekutin jsou důležité efekty vyloučeného objemu. K odhadu těchto efektů se v případě jednoduchých tekutin používají tuhé koule. Pro směsi polárních a asociujících tekutin je jejich použití těžko ospravedlnitelné. Vhodnou alternativou jsou zde směsi pseudo-tuhých těles.

Z tohoto důvodu jsme prezentovali analytickou studii směsí tuhých koulí a PHB pomocí poruchového viriálního rozvoje. Relativně přesné takto získané výsledky ospravedlňují použití zvoleného postupu v dalších studiích, např. vodných roztoků uhlovodíků, jejichž úplný teoretický popis dosud nebyl nalezen, a následně k zhodnocení celého konceptu primitivních modelů a jejich použití v aplikacích.

Vlastnosti směsí nelze určit jen ze znalosti chování čistých látek a LB pravidla; to je již déle známo. Ve většině publikovaných studiích hledající lepší numerickou shodu excess funkcí modelového systému s experimentem bylo především manipulováno s energetickými křížovými pravidly. Ukázali jsme, že odchylky od Lorentzova pravidla pro parametr vzdálenostní, t.j. efekty vyloučeného objemu, ovlivňují výsledky podstatněji a mohou způsobit dokonce kvalitativní změny, zatímco energetické parametry jsou nezbytné pouze k jemnému doladění výsledků.

Soustředili jsme se na parciální molární objem, jehož nezvyklé chování v případě vodných roztoků alkoholů bylo pomocí difrakčních experimentů vysvětleno na molekulární úrovni teprve nedávno. Molekulárními simu-

lacemi se jeho chování podařilo zreprodukovat pouze po zahrnutí neaditiv-
ity/polarizovatelnosti molekul. Podobné chování parciálního molárního ob-
jemu jsme pozorovali v případě binární směsi identických Lennard-Joneso-
vých tekutin pro jistou kombinaci křížových parametrů. Mohla by tedy ex-
istovat alternativa k polarizovatelnosti pomocí níž lze kvalitativně změnit
vlastnosti směsí. Tato zjištění mohou napomoci při porozumění chování
směsí na molekulární úrovni a k vyvinutí v praxi použitelných kombinač-
ních pravidel pro různé třídy směsí.

Papers included in the thesis

- [P1] Rouha, M., Nezbeda, I., *Fluids of pseudo-hard bodies: From simulations to equations of state*, Fluid Phase Equilibria, submitted
- [P2] Rouha, M., Nezbeda, I., *Thermodynamics of pseudo-hard body mixtures*, Molecular Physics, in press.
- [P3] 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.
- [P4] Rouha, M., Nezbeda, I., *Non-Lorentz-Berthelot Lennard-Jones mixtures: A systematic study*, Fluid Phase Equilibria, in press.

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