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# ON A MOLECULAR THEORY OF WATER

by

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*Ph.D. Thesis*

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Herewith I declare that I have not used this work or any part thereof to obtain any other academic degree. I also declare that I have worked out this thesis myself and I have used only those literature sources that are cited in the list of references.

Prague, April 29, 2008

Jan Jirsák



*It has been a great honour for me to work under the supervision of Professor Ivo Nezbeda. His enthusiasm for science has always helped me to find a route through the overwhelming complexity of the subject. I appreciate the friendly and motivating atmosphere of the E. Hála Laboratory of Thermodynamics. I am also very grateful to my alma mater, Faculty of Science, for trust and support. The sources of financial funding are individually acknowledged in the attached papers.*



# Contents

<b>1</b>	<b>Introduction</b>	<b>3</b>
<b>2</b>	<b>State of the Art</b>	<b>7</b>
<b>3</b>	<b>Goals of the Thesis</b>	<b>11</b>
<b>4</b>	<b>Theoretical Background</b>	<b>13</b>
4.1	Potential Models . . . . .	13
4.2	Equation of State . . . . .	15
<b>5</b>	<b>Results and Discussion</b>	<b>17</b>
5.1	Primitive Models . . . . .	17
5.2	Equation of State Based on a Simple Primitive Reference . .	21
5.3	An Effective Primitive Reference System . . . . .	22
5.4	Notes on Correction Terms . . . . .	23
<b>6</b>	<b>Conclusions</b>	<b>25</b>
	<b>References</b>	<b>27</b>
	<b>Appendix</b>	<b>29</b>



# 1 Introduction

For humans, water is the most important liquid on Earth, nevertheless, it is not yet fully understood. Although it is considered by many to be “a typical liquid”, its physical behavior is not typical at all and it exhibits a lot of anomalous features (the famous density maximum at 4°C, for instance). Water’s peculiar properties are commonly explained by the uniqueness of its molecular structure induced by the strong associative intermolecular force, i.e., hydrogen bonding. Thermodynamic landscape of water has been explored in detail by a huge number of measurements, but no one has put forward so far a rigorous molecular theory that would build an interconnection between a complex realistic intermolecular potential on one side and an accurate equation of state on the other side. Molecular-based equations are evidently superior to the empirical and semi-empirical ones. They involve smaller number of parameters with clearly defined meaning and possess a great potential for extrapolation. Accurate molecular theory would not only lead to better understanding of the behavior of water but would also have a great impact on engineering and other applications.

The main obstacle to the development of the molecular theory of water is the complexity of the intermolecular potential. Having an analytic form of results as a goal, this complexity disqualifies integral equation methods leaving thus a perturbation expansion as the only tool [1]. However, early unsuccessful attempts based on an intuitive separation of the potential into reference and perturbation parts cast doubts on the applicability of the perturbation expansion [2, 3]. Only a systematic research in the 1990’s on the effect of the range of the potential on the structure of complex fluids showed that the perturbation expansion with a properly defined reference is a fully justified method (for a review see [4]).

To accomplish the perturbation expansion, a number of problems must be solved. Particularly, the problem of an estimation of the properties of the reference system in an analytic form. In this respect the application of simplified, the so-called primitive, models developed in E. Hála Laboratory has turned out to be promising [5]. The primitive models are simple enough to be amenable to an analytic statistical-mechanical treatment, yet they capture the essence of association that, in fact, determines the structure of fluid.

This thesis is devoted to exploring the possibilities of a perturbed equation of state based on primitive models and to the development of a rigorous basis for the molecular theory of water. It is based on the following four original papers published (or accepted for publication) in peer-review international journals:

- [A] Jirsák J., Nezbeda I.: *Molecular Mechanisms Underlying the Thermodynamic Properties of Water*, J. Mol. Liq. 134 (2007) 99.
- [B] Jirsák J., Nezbeda I.: *Molecular-based Equation of State for TIP4P water*, J. Mol. Liq. 136 (2007) 310.
- [C] Jirsák J., Nezbeda I.: *Toward a Statistical Mechanical Theory of Water: Analytical Theory for a Short-ranged Reference System*, J. Chem. Phys. 127 (2007) 124508.
- [D] Jirsák J., Nezbeda I.: *Fluid of Hard Spheres with a Modified Dipole: Simulation and Theory*, Collect. Czech. Chem. Commun. 73 (2008), in press.

Paper [A] explores the behavior of the equation of state based on primitive models. The proposed equation is then fitted to VLE data of TIP4P water and the results are given in paper [B]. Paper [C] presents an improved reference model which, without adjustable parameters, gives quite a consistent picture of the considered liquid-state anomalies. The last paper turns then the attention to the dipole-dipole correction term.

The thesis presents a concise description of the used methods and results with references for details to the above original papers. It consists of six

sections and the Appendix. Section 1, Introduction, ends by this paragraph, followed by Section 2, State of the Art, that overviews the state of the topic prior to this work. Section 3, Goals of the Thesis, clearly states the objectives of the research compiled into this dissertation. Section 4, Theoretical Background, defines the employed potential models and describes the terms of the proposed equation of state. Section 5, Results and Discussion, reviews outputs of computations, and Section 6, Conclusions, summarizes and comments the achieved results and sketches an outlook for the further development. The full texts of the above author's original papers [A–D], constituting the integral part of the thesis, are in the Appendix.



## 2 State of the Art

Water, as the most abundant liquid on our planet, has been subject to a huge number of measurements. For practical reasons, enormous amount of data on water in a wide range of thermodynamic conditions was parametrized in several empirical equations of state (EOS's), for example, that of Saul and Wagner [6] or the equation of Wagner and Pruss [7] approved by the International Association for the Properties of Water and Steam (IAPWS) in 1995 and therefore called the IAPWS-95 formulation. In the course of the water research history, growing body of experimental data, gradually revealing the peculiar thermodynamic landscape of this unique fluid, has put the demand on theoreticians to explain this behavior [8].

In general, existing models<sup>1</sup> of water can be roughly divided into chemical (mixture) and physical ones. By the former class we understand the models which display water as a mixture of distinct chemical species, each formed by the hydrogen-bonded clusters of the same constitution or molecules in the same bonding state. This idea is more than one hundred years old and dates back to Röntgen [9], who is considered to be the first to suggest a mixture model of water, although there were some earlier remarks on this approach. For an overview of some another mixture models, see Ref. [10], for instance. In the case of the chemical models, hydrogen bonding is taken into account first at the level of partition function, whereas the physical models incorporate it directly into a suitable interaction potential. In early 1980's, simple models of this type succeeded in linking the presence of tetrahedral coordination in the first coordination shell to anomalous properties of water, by means of both computer simulations and theory [11, 12]. These

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<sup>1</sup>The word model means here an explanative concept rather than the mere definition of an interaction potential.

ideas were then explored by Nezbeda and Kolafa who introduced the concept of primitive models [13, 14, 5]. Quite recently, Jagla has shown [15] that even a very simple spherically symmetric potential characterized by two interparticle distances can exhibit a water-like behavior.

Modern realistic interaction-site potentials do not define the hydrogen bonding explicitly – it results as a net effect of the superposition of several realistic site-site interactions (Lennard-Jones and Coulombic in most cases) giving rise to a continuous spectrum of bonding states and structures. Potentials of this class, e.g., TIP4P [16], TIP5P [17], and SPC or SPC/E [18], have a quantum mechanical origin but are optimized to yield the desired properties of the condensed phase. Used then in simulations, they provide rather a faithful description of the properties of water over a limited range of thermodynamic conditions obtained by molecular simulations.

Theoretical description of fluids within the framework of the perturbation theory succeeded in describing simple fluids [19, 20] and its application was later extended to the entire class of non-associating molecular fluids [1], but only recently the class of associating fluids has been targeted [4]. It consists of three steps: (i) the separation of the interaction potential into short-range and long-range parts, with the former constituting the reference system, (ii) an estimation of the properties of the reference, preferably in an analytic form, and (iii) evaluation of corrections due to the long-range interactions. The partitioning of the intermolecular potential induces similar partitioning of any thermodynamic property, which can then be written as a sum of the reference and perturbation contributions. Step (i) is justified by the finding that even in the case of associating fluids or strongly polar fluids the effect of the long-range forces on the structure of fluids is negligible [21, 22]. The perturbation expansion about an appropriately chosen short-range reference therefore rapidly converges.

To accomplish step (ii), the primitive models (PM's) are conveniently used. Earlier primitive models (see, e.g., References [13, 23, 24]) were constructed more or less intuitively. A methodology to construct primitive models analytically from their realistic counterparts was developed and published by Vlček and Nezbeda in Ref. [25] followed by the paper [26] on the accurate determination of PM's thermodynamic properties. It is therefore

possible to tailor the reference term in the equation of state of whatever site-site model practically on demand. The equation of state is then completed by adding correction terms accounting, typically, for dispersion and dipole-dipole contributions.

It should be mentioned that a similar methodology is also behind modern engineering molecular-based equations of state called SAFT [27]. SAFT equations are also based on the use of the primitive models but further development is purely empirical: the primitive models are defined only intuitively without any reference to the actual interaction potential, and the correction terms are also purely empirical, usually without any relation to the used reference system.

In E. Hála Laboratory the above-mentioned perturbation scheme has been pursued to design a molecular-based equation of state for water. Ref. [28] was the first attempt followed by Ref. [29] proposing a successful equation of state which performed better than any corresponding empirical one, which indicated the superiority of the molecular approach. The present work represents a continuation along this line.



## 3 Goals of the Thesis

This thesis is a part of a long-term multistage project conducted in E. Hála Laboratory of Thermodynamics with the aim to develop a molecular theory of associating fluids and their mixtures both to improve the understanding of the related phenomena at the molecular level and to design accurate expressions for applications. It focuses on water as a typical and important representative of associating fluids. Particular goals have been as follows:

- (i) To Suggest a suitable functional form of the equation of state based on the primitive-model reference term;
- (ii) To explore its potential to capture the qualitative picture of liquid water, and possibly identify the individual interactions responsible for the observed behavior (anomalies);
- (iii) To apply the proposed equation of state to real water or to one of the realistic interaction-site models and assess its quantitative performance.



# 4 Theoretical Background

## 4.1 Potential Models

For the purpose of this work, common pair-wise additive site-site interaction potentials used in simulations of liquids are considered to be a good representation of pure water.<sup>2</sup> These models treat the molecule as a rigid body with embedded interaction sites that interact with corresponding sites on other molecules. Typically, there are two types of site-site interactions: (i) Lennard-Jones interactions and (ii) electrostatic interactions. In the case of water, the models of this family, e.g., TIP4P [16], TIP5P [17], and SPC or SPC/E [18], differ by the number and location of negatively charged sites, while positive charges are always located at the nuclei of hydrogens; however, bond lengths may also be different. The Lennard-Jones interaction acts only between the oxygen sites and these potentials can therefore be written as

$$\begin{aligned} u(1,2) &= 4\epsilon_{\text{OO}} \left[ \left( \frac{\sigma_{\text{OO}}}{r_{\text{OO}}} \right)^{12} - \left( \frac{\sigma_{\text{OO}}}{r_{\text{OO}}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \sum_{i \in \{1\}} \sum_{j \in \{2\}} \frac{q_i q_j}{r_{ij}} \\ &= u_{\text{LJ}}(1,2) + u_{\text{Coul}}(1,2), \end{aligned} \tag{1}$$

where  $r_{\text{OO}}$  is the distance between the oxygen atoms of molecules 1 and 2,  $\{k\}$  stands for the set of charged sites on molecule  $k$ , and  $r_{ij}$  denotes the distance between site  $i$  on molecule 1 and site  $j$  on molecule 2.

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<sup>2</sup>Although controversial, such an assumption is inevitable as an explicit input for the statistical-mechanical theory is needed. Precise quantum computations of many-particle systems undoubtedly provide more ‘realistic’ interaction energies, nevertheless, not in simple closed formulas.

In order to investigate the effect of long-range forces on the behavior of polar and associating fluids, a short-range reference potential,  $u_{\text{SRR}}$ , has been constructed [21]:

$$u_{\text{SRR}}(1, 2) = u(1, 2) - S(r_{\text{OO}}; R_1, R_2)u_{\text{DD}}(1, 2), \quad (2)$$

where  $S$  is a switch-function,

$$S(r; R_1, R_2) = \begin{cases} 0 & \text{for } r < R_1, \\ (r - R_1)^2(3R_2 - R_1 - 2r)/(R_2 - R_1)^3 & \text{for } R_1 < r < R_2, \\ 1 & \text{for } r > R_2, \end{cases} \quad (3)$$

and  $u_{\text{DD}}$  stands for the dipole-dipole term in the multipole expansion of  $u_{\text{Coul}}$ .

Extensive molecular simulations [21] have shown that the structure of the short-range model is (nearly) identical to that of the full-range one. In other words, the short-range forces (both repulsive and attractive) determine the structure of fluid, whereas the effect of the long-range forces is negligible.

In accord with the usual division of the intermolecular forces it is also reasonable to detach a dispersion force,  $u_{\text{disp}}$ , from the intermolecular potential. The particular functional form of  $u_{\text{disp}}$  is not specified, but it is assumed to be attractive and radially symmetric. After deducting the dispersion, the ‘core’ model,

$$u_0(1, 2) = u_{\text{SRR}}(1, 2) - u_{\text{disp}}(r_{\text{OO}}), \quad (4)$$

describes only the excluded-volume effect and association which are supposed to underlie the liquid state anomalies, whereas the dispersion contribution should present only a quantitative correction.

Analytic theories of molecular fluids can be explicitly applied only to simplest stepwise interaction potentials. In this regard neither of the above is suitable for a theoretical treatment. Nevertheless, one can construct simple potential models, that approximate the structure and the thermodynamics of the considered reference systems. A class of the so-called primitive models (PM’s) [25] seems to be very promising in this respect. Primitive

models assume the following form of the pair potential:

$$\begin{aligned} u_{\text{PM}}(1, 2) &= u_{\text{HS}}(r_{\text{OO}}; d_{\text{OO}}) + \sum_{\substack{i \in \{1\}, j \in \{2\} \\ q_i q_j > 0}} u_{\text{HS}}(r_{ij}; d_{ij}) + \sum_{\substack{i \in \{1\}, j \in \{2\} \\ q_i q_j < 0}} u_{\text{SW}}(r_{ij}) \\ &= u_{\text{PHB}}(1, 2) + \sum_{\substack{i \in \{1\}, j \in \{2\} \\ q_i q_j < 0}} u_{\text{SW}}(r_{ij}), \end{aligned} \quad (5)$$

where HS denotes hard spheres, SW coreless square well, and PHB pseudo-hard body [30]. Symbols  $q_i, q_j$  stand for the charges of Coulombic sites in the original realistic model which PM simplifies.

It remains to determine how to relate the parameters of primitive models to the parameters of the realistic ones. Vlček and Nezbeda [25] developed the methodology of construction of primitive models and showed that, despite their simplicity, they reproduce the site-site correlation functions in a semiquantitative manner. In order to determine site-site diameters,  $d_{ii}$ , they use the ideas of the RAM theory [31] that defines a site-site effective potential,  $u_{ii}^{\text{eff}}$ , by means of the angle-averaged Boltzmann factor. Thus,

$$\exp[-u_{ii}^{\text{eff}}(r_{ii})/k_{\text{B}}T] = \int_{r_{ii}=\text{const}} \exp[-u_{\text{SRR}}(1, 2)/k_{\text{B}}T] d(1)d(2) . \quad (6)$$

The repulsive branch of the effective potential,  $u_{ii}^{\text{rep}}$ , is then used to compute the desired diameter by the Barker-Henderson formula [20]

$$d_{ii} = \int_0^{r_{ii}^{\text{min}}} \{1 - \exp[-u_{ii}^{\text{rep}}(r)/k_{\text{B}}T]\} dr , \quad (7)$$

where  $r_{ii}^{\text{min}}$  is the distance at which  $u_{ii}^{\text{eff}}$  attains minimum value. For a more detailed description of the method see the attached paper [C] or the original work of Vlček and Nezbeda [25].

## 4.2 Equation of State

Following the partitioning of the intermolecular potential, the equation of state is assumed in the form

$$\begin{aligned} PV/Nk_{\text{B}}T \equiv z &= z_{\text{SRR}} + \Delta z \\ &= z_{\text{PM}} + z_{\text{disp}} + z_{\text{DD}} , \end{aligned} \quad (8)$$

where  $z_{\text{disp}}$  and  $z_{\text{DD}}$  are contributions due to dispersion forces and dipole-dipole interaction, respectively.

In order to simplify the theoretical expressions let us introduce the notation  $\beta^* = \epsilon/k_{\text{B}}T$  and  $\rho^* = (N/V)d_{\text{O}^3}^3$  for the reduced inverse temperature and density, respectively. Symbol  $\epsilon$  stands for the depth of the square well in Eq. (5) (energy of hydrogen bonding).

For the reference term,  $z_{\text{PM}}$ , the second-order thermodynamic perturbation theory (TPT2) [32] is used because it has been shown to be quite accurate, particularly for the asymmetric models as, e.g., PM/TIP4P. In general [26, 32],

$$z_{\text{PM}} = z_{\text{PHB}} - m(1 - \nu) \left( 1 + \frac{I'_{+-} + m\nu\rho^*I'_{+--}}{I_{+-} + 2m\nu\rho^*I_{+--}} \right), \quad (9)$$

where  $\nu$  is the solution of the cubic equation

$$m^2\rho^{*2}I_{+--}\nu^3 + [(2mn - m^2)\rho^{*2}I_{+--} + m\rho^*I_{+-}]\nu^2 + [(n - m)\rho^*I_{+-} + 1]\nu - 1 = 0. \quad (10)$$

Integers  $m$  and  $n$  stand for the number of (+)-sites and (-)-sites, respectively. Quantities  $I_{+-}$  and  $I_{+--}$  are the fundamental integrals of the TPT2. For their definitions see Ref. [32]. Their primed versions are defined as  $I' = \rho^*(\partial I/\partial \rho^*)_{\beta^*}$ .

As regards the contribution of the dispersion forces,  $z_{\text{disp}}$ , the quadratic form [33],

$$z_{\text{disp}} = -\beta^*\rho^*(I_0 + 2I_1\beta^*\rho^*), \quad (11)$$

is employed. Here  $I_0$  and  $I_1$  are constants. Setting  $I_1 = 0$  one gets the simple mean-field formula.

The dipole-dipole contribution,  $z_{\text{DD}}$ , is more complicated to determine. Expressions based on Padé approximants due to Rushbrooke et al. [34] are usually employed. In general, for dipole-dipole contribution to Helmholtz energy it holds

$$A_{\text{DD}} = \frac{A_2}{1 - A_3/A_2}, \quad (12)$$

where  $A_2$  and  $A_3$  are the perturbation terms of the second and the third order, respectively. See Ref. [D] that addresses this issue in more detail.

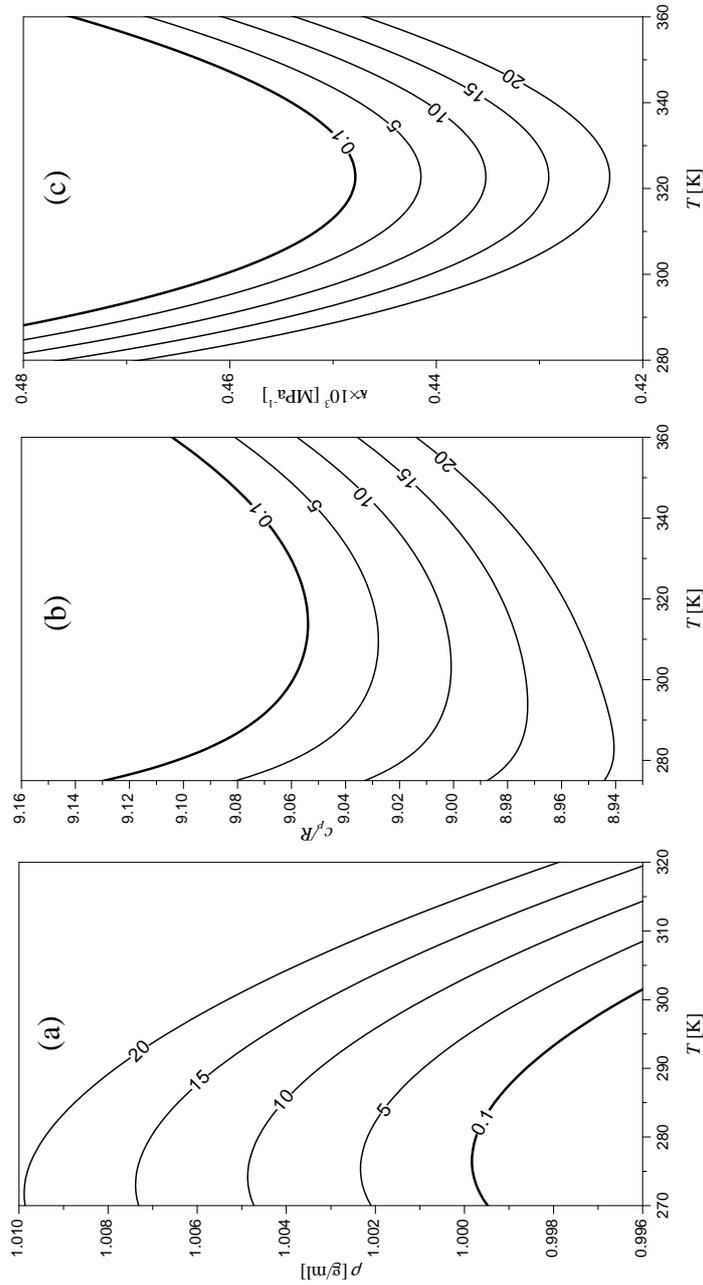
## 5 Results and Discussion

In order to test the performance of the proposed equations of state, three thermodynamic functions are considered, namely: number density,  $\rho$ , isothermal compressibility,  $\kappa_T$ , and heat capacity at constant pressure,  $C_P$ . Their isobars as functions of temperature are known to exhibit distinctive features (see Fig. 1) [8]. The most famous anomaly is probably the temperature of maximum density. It decreases upon compression until the anomaly finally disappears above ca 200 MPa. The isothermal compressibility possesses a minimum against temperature which also diminishes under pressure and vanishes at about 300 MPa. Heat capacity possesses a shallow minimum at normal pressure. As mostly qualitative trends have been of the main interest in this work so far, dimensionless quantities are used to avoid particular choice of the values of some parameters of the model. Moreover, zero pressure is used instead of 1 atm. This difference really doesn't matter if we realize that the critical pressure is about 22 MPa.

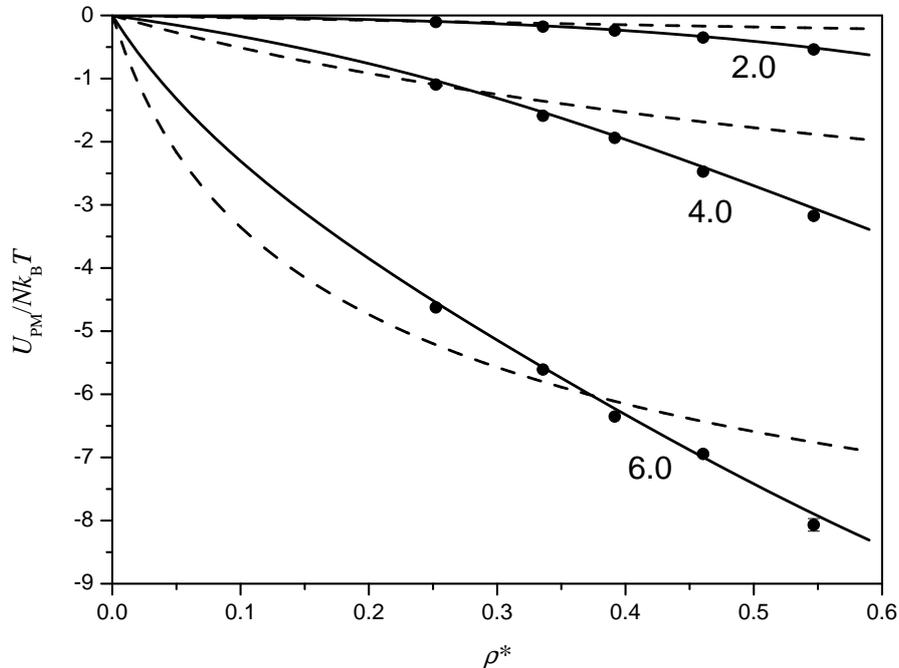
### 5.1 Primitive Models

The accuracy of TPT2 in the supercritical region is very good (as shown in Fig. 2 for the potential energy), whereas for lower temperatures (higher  $\beta^*$ ), where direct simulation is problematic, one can only expect prediction to some degree. Since mostly liquid-state anomalies are investigated, the use of TPT2, as regards a quantitative comparison, may be questioned but no better analytical theory is available for primitive models at present.

As regards the thermodynamics of individual PM's defined by Eq. (5), there appears to be no qualitative difference between three-, four-, or five-

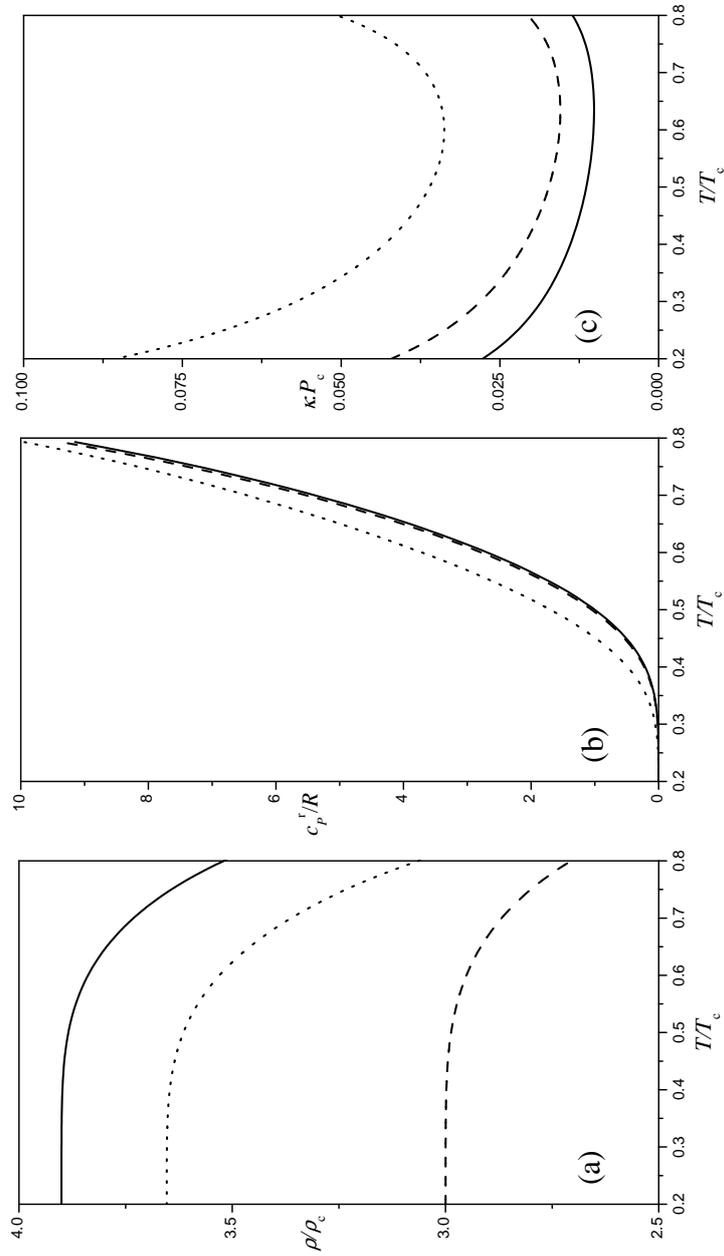


**Figure 1**—Anomalies in real liquid water at subcritical pressures. Isobars of (a) density, (b) heat capacity at constant pressure, and (c) isothermal compressibility. Density and compressibility were calculated from parametrization of Asada et al. [35], heat capacity from the IAPWS-95 formulation [7]. Numbers on curves are pressures in MPa.



**Figure 2**—Comparison of internal energy of PM/TIP4P from MC simulation (symbols), TPT1 (dashed line), and TPT2 (full line). Numbers at the curves are the values of the reduced inverse temperature,  $\beta^*$ . Note, that at the critical point it holds  $\beta^* = 7.89$  [A].

site models, as seen in Fig. 3. What deserves the attention is the occurrence of the compressibility anomaly, i.e., a minimum against temperature, which appears to be a very strong feature of all the considered primitive models. The minimum disappears at very high pressures [A] in agreement with experimental findings in real water [8]. This feature of primitive models of water was in fact described already years ago by Nezbeda and Iglesias-Silva [36], who used TPT1 [37] applied to the very first kind of PM's, and it has been invariably present in later studies ([28], [29], and so on). Extrema of the other two quantities, density and heat capacity, are not predicted at zero pressure. However, under positive pressures, the minimum of isobaric heat capacity develops and at negative values one obtains even the well-known



**Figure 3**—Comparison of (a) density, (b) residual heat capacity at constant pressure, and (c) isothermal compressibility of PM/SPC/E (full line), PM/TIP4P (dashed line), and PM/TIP5P (dotted line).

density maximum [A].

## 5.2 Equation of State Based on a Simple Primitive Reference

The previous subsection seems to imply that the mentioned anomalous features are somehow intrinsic to primitive models, which is not surprising as these features are commonly ascribed on account of associative forces forming hydrogen-bonded network, and that the adjustment to proper physical limits is just a matter of corrections. In Ref. [A] Eq. (8) is therefore employed, composed of the TPT2 primitive reference (with fixed parameters), the mean-field dispersion term, and two types of Padé approximants for a dipole-dipole contribution, to investigate the behavior of thermodynamic quantities of interest. It shows that the used correction terms increase the value of isothermal expansion coefficient and therefore suppress the occurrence of the desirable anomalous expansion on cooling. This can be readily explained if we realize that the corrections mostly decrease the pressure so that the density maximum, though inherently present, is pushed to even more negative pressures. The only exception is the second version of the dipole-dipole term (see Ref. [A] for details), where the density maximum is obtained under positive pressures. This case, however, is questionable due to the functional form of the mentioned term. On the other hand, correction terms neither extinguish the minimum of  $\kappa_T$  nor that of  $C_P$ , the latter becoming even more pronounced and being present at zero pressure.

The partial success of the proposed approach has encouraged the development of the equation of state [B] which would be directly applicable to water. Prior to real water, the equation has been fitted to the realistic model, namely TIP4P, instead, because the theory has been suited to the primitive model derived from TIP4P. As a data set, saturated-vapor pressures and equilibrium densities have been used. The fitting procedure consists of two steps. Firstly, the ‘core’ parameters of the model are fitted to the short-range reference to establish ‘SRR→PM’ mapping. Secondly, the ‘external’ (physical) parameters are fitted to full TIP4P. See Ref. [B]

for details. The deviations of equilibrium properties for both the short-range reference and the full model are quite small, however, comparison of the prediction of the new equation with several pseudoexperimental [38] isotherms of internal energy and pressure show only fair to bad agreement. On the other hand, the equation predicts the density maximum of TIP4P water in the temperature region suggested by Jorgensen et al. [39] in their simulation study. The occurrence of the anomaly at non-negative pressure is enabled by the use of quadratic dispersion term [33], Eq. (11), being positive<sup>3</sup> at higher densities. In this regard, the proposed equation is analogous to that of Nezbeda and Weingerl [29] who also predicted the density maximum, although they employed TPT1 instead of TPT2.

### 5.3 An Effective Primitive Reference System

In perturbation theories the PM's are used as a certain effective model for the short-range reference and should thus be considered in this context. It means, the PM must depend on the considered thermodynamic states (i.e., at least on temperature). This dependence has been neglected so far and the same representative primitive model at each temperature has been used. It is the natural next step towards a rigorous theory to take this dependence into account. This has been done in the latest study on this topic, Ref. [C], which explicitly includes the variation of  $d_{OO}$  with temperature.

We have used the Barker-Henderson formula (7), from which one obtains diameters that are temperature dependent. It has been then showed that the primitive model with a  $T$ -dependent OO diameter, without any additional corrections, suffices to yield the consistent and qualitatively appropriate picture of the anomalous behavior of interest. Not only is the density maximum obtained at positive pressures, but also the non-trivial pressure dependence of density isobars is reproduced. At the same time,

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<sup>3</sup>This is not necessary as nonphysical assumption as the reader may consider it. Eu and Rah [40] found that in a generic van-der-Waals-like EOS the dispersion contribution changed the sign from negative to positive at certain density.

both minima of isothermal compressibility and constant-pressure heat capacity are conserved.

## 5.4 Notes on Correction Terms

The perturbation corrections are expected to constitute just a minor contribution, nevertheless, their importance should not be underestimated. It has been already mentioned above that primitive models, since mimicking hydrogen bonding, are supposed to give the qualitative picture of the most characteristic trends that water exhibits as they are supposed to be imprinted to it by a hydrogen-bonded network. Correction terms are then supposed just to bring the results to quantitative agreement. On the other hand, corrections can either emphasize or hinder such subtle features as extrema of density or heat capacity (cf. Subsection 5.2).

There are two qualitatively different perturbation interactions: (i) the spherically symmetric dispersion potential and (ii) the angle-dependent dipole-dipole interaction. While the former appears to be quite appropriately captured by simple, even mean-field-like formulas, the latter seems to be of more complex nature. Although the effect of long-range dipole-dipole forces on the site-site correlation functions was proven [21] to be negligible, their influence on the properties that are more sensitive to angular correlations (than internal energy, for instance) cannot be excluded.

The lack of an expression for the dipole-dipole contribution adequate to the proposed equation of state has led to the investigation of the modified dipolar hard-sphere system both by simulation and theory [D]. The model pair potential consists of the hard-sphere interaction plus the dipole-dipole interaction switched off below certain interparticle distance. The short-range dipole-dipole interactions are turned off because they do not contribute to the perturbation as they are already present in the reference model (cf. division (2)). Many MC simulations have been performed to compute internal energy along several isotherms and it has been attempted to reproduce the results by means of two analytical formulas based on Rushbrooke's theory for dipolar hard spheres [34]. Although the employed theory performs well for dipolar hard spheres, the performance for the modified

system has shown to be poor, partly because the sample with the modified potential was more prone to undergo the ferroelectric transition than ordinary dipolar hard spheres. Further details can be found in the original work [D].

## 6 Conclusions

This text gives a brief summary and evaluation of the results achieved past four years during author’s Ph.D. study and published in four original papers [A–D]. The goal of the research project has been to build a rigorous molecular theory of water based on primitive models and employ this theory to develop an equation of state of water in three successive steps: (i) proposal and (ii) test of a functional form of the equation of state, and (iii) determination of its parameters (see Section 3: Goals of the Thesis).

As regards steps (i) and (ii), the qualitative study of a PM-based EOS has been carried out thoroughly with promising results. Systematic research [A] of the perturbed EOS with a PM TPT2 reference has revealed its potential to reproduce the desired behavior of real water. The qualitative picture has been further improved by taking the temperature dependence of the reference potential model into account [C]. In addition, the achieved results are consistent with the general belief that the strong short-range forces are sufficient to give rise to liquid-state anomalies. It has been also attempted to improve the dipole-dipole term [D] employing the hard-sphere system with a modified dipole-dipole potential.

Major difficulties has been encountered while trying to accomplish step (iii), i.e., to fit the mathematical model to real data. It has shown that the original parameters of TPT2 description working well for primitive models [26] have to be readjusted to establish a “thermodynamics-based” mapping of the short-range reference model instead of the “structure-based” one having been used so far. This route was adopted in Ref. [B] to develop the equation of state of TIP4P water with only moderate success. The attempts to put forward a reasonable parametrization for physical water have not been successful yet.

There are several issues that should be addressed in further research on the topic. (i) It is necessary to define the clearer relationship between the parent realistic reference model and the representative primitive model. The present RAM-based approach for determining diameters of the underlying pseudo-hard body works well for the structure, nevertheless, the thermodynamics is also sensitive to the parameters of the square-well association interaction for what so far no unique recipe exists. Fitting of the resulting EOS to reality [B] is neither easy nor rigorous way to interconnect both models. (ii) The TPT2 description of PM's might be questioned and improved. The parameters of the expressions for thermodynamic functions ( $\alpha_i$ ,  $a_{ij}$ , for details see Ref. [A]) are not transparently linked to the parameters of the potential model ( $\lambda$ ,  $\epsilon$ ,  $d_{ii}$ ). As regards the accuracy, the TPT2 has been thoroughly tested only in supercritical region, so its predictions at subcritical temperatures might not correspond to how PM's really behave.<sup>4</sup> (iii) It is possible that for an accurate description of the SRR model, PM's are too simple. More complex models should be proposed and studied. (iv) An appropriate dipole-dipole correction term should be developed. (v) The lack of reliable and accurate simulation data on temperature and pressure dependence of properties of the realistic models the theory is tailored for (TIP4P, for instance) has forced us to compare the theoretical predictions to measurements on real water. Since the behavior of real and simulated water could be even qualitatively different for some properties, a systematic study should be carried out to explore the thermodynamic landscape in the  $PT$ -plane of commonly used models (TIP4P, TIP5P, SPC/E, etc.).

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<sup>4</sup>De Michele et al. [41] performed the simulation of an earlier primitive model and they found the density maximum at positive pressures in contrast to the theoretical findings of Ref. [A]. In addition, their internal-energy isotherms seem to behave differently at low temperatures from those of the theory.

# References

- [A] Jirsák J., Nezbeda I.: *J. Mol. Liq.* 134 (2007) 99.
- [B] Jirsák J., Nezbeda I.: *J. Mol. Liq.* 136 (2007) 310.
- [C] Jirsák J., Nezbeda I.: *J. Chem. Phys.* 127 (2007) 124508.
- [D] Jirsák J., Nezbeda I.: *Collect. Czech. Chem. Commun.* 73 (2008), in press.
- [1] Gray C. G., Gubbins K. E.: *Theory of Molecular Fluids*, Oxford University Press, Oxford, 1984.
- [2] Hirata F.: *Bull. Chem. Soc. Jpn.* 50 (1977) 1032.
- [3] Müller E. A., Gubbins K. E.: *Ind. Eng. Chem. Res.* 34 (1995) 3662.
- [4] Nezbeda I.: *Mol. Phys.* 103 (2005) 59.
- [5] Nezbeda I.: *J. Mol. Liq.* 73 (1997) 317.
- [6] Saul A., Wagner W.: *J. Phys. Chem. Ref. Data* 18 (1989) 1537.
- [7] Wagner W., Pruss A.: *J. Phys. Chem. Ref. Data* 31 (2002) 387.
- [8] Eisenberg D., Kauzmann W.: *The Structure and Properties of Water*, Clarendon Press, Oxford, 1969.
- [9] Röntgen W. C.: *Ann. Phys. Chem.* 45 (1892) 91.
- [10] Franks F. (ed.): *Water, A Comprehensive Treatise*, Vol. 1–7, Plenum, New York, 1972–1982.

- [11] Bol W.: Mol. Phys. 45 (1982) 605.
- [12] Dahl L. W., Andersen H. C.: J. Chem. Phys. 78 (1983) 1980.
- [13] Kolafa J., Nezbeda I.: Mol. Phys. 61 (1987) 161.
- [14] Kolafa J., Nezbeda I.: Mol. Phys. 72 (1991) 777.
- [15] Jagla E. A.: J. Chem. Phys. 111 (1999) 8980.
- [16] Jorgensen W. L., Chandrasekhar J., Madura J. D., Impey R. W., Klein M. L.: J. chem. Phys. 79 (1983) 926.
- [17] Mahoney M. W., Jorgensen W. L.: J. chem. Phys. 112 (2000) 8910.
- [18] Berendsen H. J. C., Grigera J. R., Straatsma T. P.: J. Phys. Chem. 91 (1987) 6269.
- [19] Hansen J. P., McDonald I. R.: *Theory of Simple Liquids*, Academic Press, London, 1986.
- [20] Boublík T., Nezbeda I., Hlavatý K.: *Statistical Thermodynamics of Simple Liquids and Their Mixtures*, Academia, Prague, 1980.
- [21] Nezbeda I., Kolafa J.: Mol. Phys. 97 (1999) 1105.
- [22] Kolafa J., Nezbeda I., Lísal M.: Mol. Phys. 99 (2001) 1751.
- [23] Nezbeda I., Slovák J.: Mol. Phys. 90 (1997) 353.
- [24] Slovák J., Nezbeda I.: Mol. Phys. 91 (1997) 1125.
- [25] Vlček L., Nezbeda I.: Mol. Phys. 102 (2004) 485.
- [26] Vlček L., Nezbeda I.: Mol. Phys. 102 (2004) 771.
- [27] Müller E. A., Gubbins K. E.: Ind. Eng. Chem. Res. 40 (2001) 2193.
- [28] Nezbeda I., Pavlíček J.: Fluid Phase Equil. 116 (1996) 530.
- [29] Nezbeda I., Weingerl U.: Mol. Phys. 99 (2001) 1595.

- [30] Nezbeda I.: Mol. Phys. 90 (1997) 661.
- [31] Smith W. R., Nezbeda I., Melnyk T. W., Fitts D. D.: Faraday Discuss. Chem. Soc. 66 (1978) 130.
- [32] Vlček L., Nezbeda I.: Mol. Phys. 101 (2003) 2921.
- [33] Nezbeda I.: Fluid Phase Equil. 180 (2001) 175.
- [34] Rushbrooke G. S., Stell G., Høye J. S.: Mol. Phys. 26 (1973) 1199.
- [35] Asada S., Sotani T., Arabas J., Kubota H., Matsuo S., Tanaka Y.: J. Phys.: Condens. Matter 14 (2002) 11447.
- [36] Nezbeda I., Iglesias-Silva G. A.: Mol. Phys. 69 (1990) 767.
- [37] Slovák J., Nezbeda I.: Mol. Phys. 101 (2003) 789.
- [38] Nezbeda I., Lísal M.: Molec. Phys. 99 (2001) 291.
- [39] Jorgensen W. L., Jenson C.: J. Comp. Chem. 19 (1998) 1179.
- [40] Eu B. C., Rah K.: Phys. Rev. E 63 (2001) 031203.
- [41] De Michele C., Gabrielli S., Targalia P., Sciortino F.: J. Phys. Chem. B 110 (2006) 8064.



# Appendix

Full texts of the papers [A–D] are attached.

- [A] Jirsák J., Nezbeda I.: *Molecular Mechanisms Underlying the Thermodynamic Properties of Water*, J. Mol. Liq. 134 (2007) 99–106, 8 pages.
- [B] Jirsák J., Nezbeda I.: *Molecular-based Equation of State for TIP4P water*, J. Mol. Liq. 136 (2007) 310–316, 7 pages.
- [C] Jirsák J., Nezbeda I.: *Toward a Statistical Mechanical Theory of Water: Analytical Theory for a Short-ranged Reference System*, J. Chem. Phys. 127 (2007) art. no. 124508, 7 pages.
- [D] Jirsák J., Nezbeda I.: *Fluid of Hard Spheres with a Modified Dipole: Simulation and Theory*, Collect. Czech. Chem. Commun. 73 (2008), in press, 17 pages.