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Modelling water with simple Mercedes-Benz models

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Abstract

The structures and properties of biomolecules like proteins, nucleic acids, and membranes depend on water. Water is also very important in industry. Overall, water is unusual substance with more than 70 anomalous properties. The understanding of water is advancing significantly due to theoretical and computational modeling. There are different kind of models, models with fine-scale properties and increasing structural detail with increasing computational expense and simple models which focus on global properties of water like thermodynamics, phase diagram and are less computational expensive. Simplified models give a better understanding of water in ways that complement more complex models. Here, we review a simple model, the two dimensional Mercedes-Benz (MB) model of water. We present results by Monte Carlo simulations for anomalies and phase diagram and application of various theoretical methods.

I. INTRODUCTION

The most important fluid in nature for life and industry is water^{1–4}. Liquid water covers 3/4 of the earth's surface; controls the planet's geochemical cycles; is a dominant driver of biomolecules, drug interactions, and biological actions; and central to green chemistry and many industrial processes. The structure and thermodynamics of water and aqueous solutions is of great importance for chemistry and biology. Water exhibits many anomalous properties that affect life at a larger scale. Mammals benefit from the large latent heat of water to cool them down through sweating. Water's large heat capacity prevents local temperature fluctuations, facilitating thermal regulation of organisms. The density anomaly and lower ice Ih density have a huge effect on surviving of organisms in frozen seas and lakes. Without the density maximum, ponds would freeze from the bottom. Water has almost universal solvent action⁵. Nearly all known chemical substances will dissolve in water at least to a small extent. Water is one of the most corrosive substances known and yet is physiologically harmless. In comparison to other liquids, it has the most puzzling behavior^{5,6}. It is said that water is anomalous liquid. Anomalous liquids are liquids that exhibit unexpected behavior upon variations of the thermodynamic conditions in comparison to normal (argon-like) liquids. Water is the classic example of those anomalous liquids. The most known examples of anomalous properties are its density maximum at 4 °C, lower density of the solid phase compared to the liquid phase, high and nearly constant heat capacity in the liquid phase, negative expansion coefficient below the temperature of the

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density maximum, as well as high surface tension and viscosity. The compressibility and specific heat increase anomalously by cooling. Water also has unusually high boiling, freezing and critical points. Water's complexity is due to its strong orientation-dependent hydrogen bonding and strong intermolecular associations. There are two very distinct mechanisms that give rise to the anomalous properties. Angular-dependent interactions, such as oriented hydrogen bonding in water, tetrahedral bonding in silica,^{7–9} and oriented bonds in BeF₂, can result in density maximum because of the competition between tetrahedral order (low density) and translational order (high density). On the other hand, density anomaly was also observed for Ga¹⁰, Bi¹¹, Te¹², S¹³, Be, Mg, Ca, Sr, Ba, P, Se, Ce, Cs, Rb, Co, Ge where system lacks oriented bonding. Speaking of water, it expands upon cooling at fixed pressure, diffuses faster upon compression at fixed temperature^{14,15}, and becomes less ordered upon increasing density at constant temperature¹⁶. These are the density, diffusion, and structural anomalies.

An understanding of the hydrogen bonding is therefore crucial to understand the behavior and properties of water and aqueous solutions. Yet, despite extensive theory and simulations, how water's properties come from its molecular structure remains poorly understood. A large number of models of varying complexity have been developed and analyzed to model water's extraordinary properties, for reviews, see, e.g.^{5,6,17–27}. Besides developing models, a key goal of liquid-state statistical thermodynamics is to develop a quantitative theory for water and aqueous solutions. Theory and simulations have not yet explained how water's molecular structure leads to its density, compressibility, expansion coefficient and heat capacity as functions of temperature and pressure, including its well-known anomalies. In principle, the properties of water can be determined with quantum-mechanical calculations^{28,29}. While they offer the highest degree of exactness, a high computational cost of these approaches limits their use to small water systems, but these insights should allow for the development and fine-tuning of simplified water models.^{30–32} There have been two main approaches to modeling liquids. One approach is to perform computer simulations of atomically detailed models. These models aim for realistic detail and include variables describing van der Waals and Coulomb interactions, hydrogen bonding, etc. (reviewed in¹⁹). Such approaches can depend critically on the force-field used in the calculation^{33,34}. However, many properties of water and aqueous solutions can also be captured by simpler models^{35,36}. One class of such simpler models has been developed by Nezbeda and coworkers^{18,37,38}. One of the simplest models for water is the so-called Mercedes-Benz (MB) model^{39,40} and is the main part of this review paper.

The main MB model is a 2-dimensional model which was originally proposed by Ben-Naim in 1971^{41,42}. In some publications it is referred also as BNMB (Ben-Naim-Mercedes-Benz) model. Each MB water molecule is modeled as a disk that interacts with other such waters through: (1) a Lennard-Jones (LJ) interaction and (2) an orientation-dependent hydrogen bonding interaction through three radial arms arranged as in the Mercedes-Benz (MB) logo. Interest in simplified models is due to insights that are not obtainable from all-atom computer simulations. Simpler models are more flexible in providing insights and illuminating concepts, and they do not require big computer resources. Second, simple models can explore a much broader range of conditions and external variables. Whereas simulating a detailed model may predict the behavior at a single temperature and pressure, a

simpler model can be used to study a whole phase diagram of temperatures and pressures. Third, analytical models can provide functional relationships for engineering applications and lead to improved models of greater computational efficiency. Fourth, simple models can be used as a polygon to develop and study theoretical methods. Our interest in using the MB model is that it serves as one of the simplest models of an orientationally-dependent liquid, so it can serve as a testbed for developing analytical theories that might ultimately be useful for more realistic models. Another advantage of the MB model, compared to more realistic water models, is that the underlying physical principles can be more readily explored and visualized in two dimensions. For the MB model, NPT Monte Carlo simulations have shown that the MB model predicts qualitatively the density anomaly, the minimum in the isothermal compressibility as a function of temperature, the large heat capacity, as well as the experimental trends for the thermodynamic properties of solvation of nonpolar solutes^{39,43–45} and cold denaturation of proteins⁴⁶. The 2D MB model was also extended to 3D by Bizjak et al.^{47,48} and Dias et al.^{45,49} and studied using computer simulations^{45,47–49}. The 2D model was also extensively studied with analytical methods like integral equation and thermodynamic perturbation theory^{50–55} and statistical mechanic modeling^{56–58}. Recently also phase diagram of liquid part and percolation curve of the model was calculated and reported⁵⁹. The MB model has also been used to study systems with water molecules confined in partially quenched disordered matrix^{60–62} and within small geometric spaces^{63,64}. The results obtained with Monte Carlo simulations were compared to solutions of associative replica Ornstein-Zernike equations by using the hypernetted chain approximation⁶⁰. The comparison shows that obstacles in the system perturb the network structure of water. High obstacle densities lead to a diminished ability of water to form hydrogen bonds, to reduced compressibility and to a disrupted water structure. Low obstacle densities cause an increased order in the water structure, enhanced ability of molecules to form hydrogen bonds and increased compressibility. It was found that confinement and crowding effects influence water in a similar way as the temperature change in bulk water systems. Nonequilibrium Monte Carlo and molecular dynamics simulations were used to study the effect of translational and rotational degrees of freedom on the structural and thermodynamic properties of the simple Mercedes-Benz water model⁶⁵. By holding one of the temperatures constant and varying the other one, the effect of faster motion in the corresponding degrees of freedom on the properties of the simple water model was investigated. The situation where the rotational temperature exceeded the translational one is mimicking the effects of microwaves on the water model. A decrease of rotational temperature leads to the higher structural order while an increase causes the structure to be more Lennard-Jones fluid like.

Even though computer simulations play an important role in understanding the properties of liquids, they can be quite time consuming, even for simple two-dimensional 2D models. So it is equally important to develop simplified, more analytical approaches. In past decades, a theory has been developed for fluids comprised of molecules that associate into dimers and higher clusters due to the presence of highly directional attractive forces^{66,67}. This theory has been successfully applied to a number of different three-dimensional fluid systems, including water and aqueous solutions (see, for example^{18,68,69} and references therein). Wertheim^{66,67,70,71} proposed his statistical-mechanical approach for strongly associating

systems of molecules and a corresponding thermodynamic perturbation theory and for MB water, in previous works^{50–55,72,73}, we applied Wertheim's theory for associating fluids^{66,67} to the MB model and some other simple models through both a thermodynamic perturbation theory (TPT) and orientationally averaged and angle-dependent integral equation theories (IET). We found that both TPT and IET approaches gave good quantitative agreement with NPT Monte Carlo results for the molar volume, isothermal compressibility, and other thermodynamic properties as a function of temperature. It is also possible to use even more analytical theories for MB-like models which are allowing the inclusion of orientation-dependent hydrogen bonding within a framework that is simple and nearly analytical. One such model is a statistical mechanical model, developed by Urbic and Dill's⁵⁶. The model is directly descendant from a treatment of Truskett and Dill, who developed a nearly analytical version of the 2D MB model^{74,75}. In the model each water molecule interacts with its neighboring waters through a van der Waals interaction and an orientation-dependent interaction that models hydrogen bonds.

In this paper, we made review of calculations for pure MB model of water. The outline of the paper is as follows. We present the 2D and 3D MB model in Sec. II, and the details of the Monte Carlo simulations, overview of thermodynamics perturbation theory, theory of integral equation and statistical mechanical methods are done in Sec. III. In Sec. IV we show and discuss the results and summarize everything in Sec. V.

II. THE MODEL

A. 2D

In 2D the water molecules are modelled as a two-dimensional disk with three bonding arms separated by an angle of 120° ^{39,41} which is fixed. The arms mimic formation of hydrogen bonds (See Figure 1). The interaction potential between molecules i and j is a sum of a Lennard–Jones (LJ) and a hydrogen–bonding (HB) term

$$U(\vec{X}_i, \vec{X}_j) = U_{LJ}(r_{ij}) + U_{HB}(\vec{X}_i, \vec{X}_j). \quad 1$$

r_{ij} is the distance between centers of particles i and j . $\vec{X}_i$ and $\vec{X}_j$ are the vectors representing the coordinates and the orientation of the i^{th} and j^{th} particle. The Lennard–Jones part of the potential has a standard form

$$U_{LJ}(r_{ij}) = 4\epsilon_{LJ} \left(\left(\frac{\sigma_{LJ}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}} \right)^6 \right). \quad 2$$

ϵ_{LJ} and σ_{LJ} are the depth and the contact value of potential. The hydrogen bonding interaction is the sum of interactions U_{HB}^{kl} between all arms of different molecules

$$U_{HB}(\vec{X}_i, \vec{X}_j) = \sum_{k,l=1}^3 U_{HB}^{kl}(r_{ij}, \theta_1, \theta_2) \quad 3$$

and is described by Gaussian function in distance and both angles

$$U_{HB}^{kl}(r_{ij}, \theta_1, \theta_2) = \varepsilon_{HB} G(r_{ij} - r_{HB}) G(\vec{i}_k \vec{u}_{ij} - 1) G(\vec{j}_l \vec{u}_{ij} + 1) \quad 4$$

$$= \varepsilon_{HB} G(r_{ij} - r_{HB}) G\left(\cos\left(\theta_i + \frac{2\pi}{3}(k-1)\right) - 1\right) G\left(\cos\left(\theta_j + \frac{2\pi}{3}(l-1)\right) + 1\right) \quad 5$$

$\varepsilon_{HB} = -1$ is a HB energy parameter and $r_{HB} = 1$ is a characteristic length of hydrogen bond. $\vec{u}_{ij}$ is the unit vector along $\vec{r}_{ij}$ and $\vec{i}_k$ is the unit vector representing the k^{th} arm of the i^{th} particle. θ_i is the orientation of i^{th} particle with respect to x axes. $G(x)$ is an unnormalized Gaussian function

$$G(x) = \exp\left(-\frac{x^2}{2\sigma^2}\right) \quad 6$$

The strongest hydrogen bond occurs when an arm of one particle is co-linear with the arm of another particle and the two arms point in opposing directions. The LJ well-depth ε_{LJ} is 0.1 times the HB interaction energy ε_{HB} and the Lennard-Jones contact parameter σ_{LJ} is $0.7r_{HB}$. The width of Gaussian for distances and angles ($\sigma = 0.085r_{HB}$) is small enough that a direct hydrogen bond is more favorable than a bifurcated one.

B. 3D

In 3D, each water molecule is represented as a Lennard-Jones sphere (LJ) with four arms oriented tetrahedrally. The angle between neighboring arms in a molecule is 109.47° (see Figure 2). Like in 2D, in 3D the interaction potential between two water molecules is a sum of the Lennard-Jones potential and the hydrogen bond term

$$U(\vec{X}_i, \vec{X}_j) = U_{LJ}(r_{ij}) + U_{HB}(\vec{X}_i, \vec{X}_j), \quad 7$$

The Lennard-Jones part of the potential is same as in 2D. The hydrogen bonding part of the interaction potential is

$$U_{HB}(\vec{X}_i, \vec{X}_j) = \sum_{k,l=1}^4 U_{HB}^{kl}(r_{ij}, \vec{\Omega}_i, \vec{\Omega}_j), \quad 8$$

where $\vec{\Omega}_i$ is the orientational vector of i^{th} molecule and U_{HB}^{kl} describes the interaction between two HB arms of different molecules

$$U_{HB}^{kl}(r_{ij}, \vec{\Omega}_i, \vec{\Omega}_j) = \epsilon_{HB} G(r_{ij} - r_{HB}) G(\vec{i}_k \vec{u}_{ij} - 1) G(\vec{j}_l \vec{u}_{ij} + 1) \quad 9$$

$\vec{u}_{ij}$ is the unit vector along $\vec{r}_{ij}$ and $\vec{i}_k$ is the unit vector representing the k th arm of the i^{th} particle. Like in 2D, the strongest hydrogen bond occurs when an arm of one particle is co-linear with the arm of another particle pointed towards each other. The model does not make a distinction between hydrogen bond donors and acceptors. Apart from the dimensionality, we want to keep the 3D MB model as similar as possible to the original two-dimensional MB model. Hence, the parameters of our 3D model are the same as used in the two-dimensional MB model calculations, with an exception of the depth of the Lennard-Jones potential well ϵ_{LJ} . This change was made to maintain same ratio between strength of the Lennard-Jones and hydrogen bond potentials due to the different geometries; $\epsilon_{LJ} = \frac{1}{35} |\epsilon_{HB}|$. These model parameters were not chosen or optimized to compare with experiments, and can undoubtedly be improved for those purposes.

C. Nonpolar particles

The non-polar particles in 2D and 3D solutes are modeled as Lennard-Jones disks or spheres without hydrogen bond arms. The standard Lorentz-Berthelot rules⁷⁷ were assumed in calculating the solute-water and solute-solute interactions as the solute size parameter σ_{LJ} changed from $0.1 r_{HB}$ to $4.0 r_{HB}$. The LJ well-depth ϵ_{LJ} was the same for all interaction pairs and as above equal to one-tenth of HB interaction energy ϵ_{HB} .

III. THEORY

A. Monte Carlo computer simulation

In order to determine model properties in the 2D and 3D MB model of water we performed Monte Carlo computer simulations in different ensembles (canonical ensemble with constant N, V, and T; isothermal-isobaric ensemble with constant N, P, T; grand canonical ensemble with constant μ , V, and T)^{77,78}. In order to mimic an infinite size of system of particles we used the periodic boundary conditions and the minimum image convention. All starting configurations were selected at random. In each move, we randomly tried to translate or rotate random particle in canonical ensemble. In isothermal-isobaric ensemble we also tried to change volume and in grand canonical ensemble exchange particle. Probabilities for translation and rotation, change of volume and exchange of particles were the same. In one cycle (also one time step) we tried to translate and rotate each particle once on average,

make as many insertion and removals as the average number of particles in system in grand canonical ensemble and one change of volume per move of particle in isothermal-isobaric ensemble. The simulations were first equilibrated for as many cycles that equilibration was reached. Number of cycles depended on dimension, temperature and density. After equilibration production runs were taken for minimum 20 series consistent with as many cycles as required to obtain well converged results. In the system we had from 100 to 500 particles depending on density of the system in 2D. The system of 100 molecules in 2D is equivalent to 1000 particles in 3D. In 3D system consisted from 500 to 4000 particles. In 2D correlation are more complicated, correlation lengths are longer then in 3D⁷⁹. Most finite-size effects do depend on N, not on box size, but this was not a factor for our calculations. Thermodynamic quantities such as energy were calculated as statistical averages over the course of the simulations⁷⁸. Cut off of the potential was half-length of the simulation box. Increasing the number of particles had no significant effect on the calculated quantities. The cluster and bond analyses use an energy criteria wherein water molecules are considered bonded when their hydrogen bonded energy is less than -0.05 . Small variations of this energy cutoff did not account for significant differences in the bonding state of the system. The percolation line was determined as the density at which at least 50% of water particles were part of one big cluster connected by hydrogen bonds. The diffusion coefficient in canonical ensemble is determined using the mean square displacement averaged over different series. In these MC simulation runs, dynamic adjustment of maximum displacement was turned off and was kept fixed for all instances. The mean square displacement was calculated as average of displacements over all particles

$$\langle \Delta r(n)^2 \rangle = \langle (\vec{r}(n) - \vec{r}_0)^2 \rangle \quad 10$$

where $\vec{r}_0$ is initial coordinate of the particle and n is number of cycle. The pseudo diffusion coefficient which is proportional to real diffusion coefficient was obtained as

$$D^* = \lim_{n \rightarrow \infty} \frac{\langle \Delta r(n)^2 \rangle}{n} \quad 11$$

In the isothermal-isobaric ensemble the mechanical properties such as enthalpy and volume were calculated as the statistical averages of these quantities over the course of the simulations⁷⁸. The heat capacity, C_p , the isothermal compressibility, κ , and the thermal expansion coefficient, α are computed from the fluctuations³⁹.

$$\begin{aligned}
 C_p &= \frac{C_p}{k_B} = \frac{\langle H^2 \rangle - \langle H \rangle^2}{NT^2} \\
 k &= \frac{\langle V^2 \rangle - \langle V \rangle^2}{T \langle V \rangle} \\
 \alpha &= \frac{\langle VH \rangle - \langle V \rangle \langle H \rangle}{T^2 \langle V \rangle}
 \end{aligned} \quad 12$$

In the simulations we determined also the translational order parameter t and two orientational order parameters (with three fold symmetry, q_3 and with six-fold symmetry, q_6). The translational order parameter measures the degree of pair correlation in the system and is defined as

$$t = \int_0^{x_c} |g(x) - 1| dx \quad 13$$

where $x = \rho^{\frac{1}{2}} r$ is the distance r in the units of mean inter-particle separation and $g(x)$ the pair distribution function. x_c is the cut off distance and is set to half of the simulation box in the present paper. Orientational order parameters, q_l we calculated following this procedure. For each particle j we calculate

$$q_l^j = \frac{1}{n_j} \sum_k \exp(il\theta_{jk}) \quad 14$$

where n_j is the number of neighbors within the first atom shell of particle j and θ_{jk} is the angle between the vector connecting particles j and k and the horizontal axis. Parameter l specifies the type of symmetry (3 or 6). The local orientational parameter of the whole system is calculated as average of absolute value over all the particles in the system

$$q_l = \frac{1}{N} \sum_{i=1}^N |q_l^i|. \quad 15$$

B. Thermodynamic perturbation theory

Here we are briefly reviewing Wertheim's first order perturbation theory^{66,80}, used previously^{50,51,54}. The Helmholtz free energy for MB particles is a sum of an ideal term, A_{id} , a reference term, A_{LJ} , and a perturbation term, A_{HB} which takes into account the association of MB molecules into hydrogen bonded networks

$$\frac{A}{Nk_B T} = \frac{A_{id}}{Nk_B T} + \frac{A_{LJ}}{Nk_B T} + \frac{A_{HB}}{Nk_B T}. \quad 16$$

N is the number of particles, T is temperature, and k_B is Boltzmann's constant. The part A_{LJ} was calculated using the Barker–Henderson (BH) perturbation theory^{50,77}. In BH theory, the reference system was the hard disks

$$\frac{A_{LJ}}{Nk_B T} = \frac{A_{HD}}{Nk_B T} + \frac{\rho}{2k_B T} \int_{\sigma_{LJ}}^{\infty} g_{HD}(r, \eta) u_{LJ}(r) d\vec{r}. \quad 17$$

A_{HD} is the hard-disk part of the Helmholtz free energy, ρ is the number density of water particles, η is the packing fraction of the hard disk reference system, and $g_{HD}(r, \eta)$ is the pair distribution function of the hard disk reference fluid⁵⁰. Diameter of hard disc reference fluid was calculated by averaging of Boltzmann factor⁵⁰. We calculated the contribution of hydrogen bonding to the Helmholtz free energy using

$$\frac{A_{HB}}{Nk_B T} = 3 \left(\log x - \frac{x}{2} + \frac{1}{2} \right). \quad 18$$

x is the fraction of molecules not bonded at one particular arm and is obtained from the mass-action law⁶⁶ in the form

$$x = \frac{1}{1 + 3\rho x \Delta}. \quad 19$$

is defined by^{66,80}

$$\Delta = 2\pi \int g_{LJ}(r, \rho) \bar{f}_{HB}(r) r dr. \quad 20$$

$\bar{f}_{HB}(r)$ is an orientationally averaged Mayer function for the hydrogen-bonding potential of one site. The pair distribution function $g_{LJ}(r)$ is obtained by solving the Percus–Yevick equation for Lennard–Jones disks. Once the Helmholtz free energy is known, other thermodynamic quantities may be calculated using standard thermodynamic relations⁷⁷.

In the improved TPT,⁵⁴ the difference to standard TPT is that, instead of the density ρ , we use the effective density ρ^{ef} in Eq. (16)–(20) as an effective density. The logic for this is that the particles cannot access the whole space in the system when they form bonds. When two water molecules form a hydrogen bond, it sterically occludes space, which becomes inaccessible to any other molecule⁵⁴. The effective particle volume was calculated as

$$V^{ef} = \frac{1}{\rho} - \frac{\bar{n}V'}{2} \quad 21$$

where V' is the volume not accessible to other molecules when two molecules form a hydrogen bond and can be approximated by simple geometry. Two water molecules that form a hydrogen bond are separated by a distance 1. If the LJ core is approximated by diameter d of HD molecules from BH perturbation theory, V' can be approximated as

$$V' = \sqrt{d^2 - \frac{1}{2}} - \frac{\pi d^2}{4} \quad 22$$

In equation (21), $\bar{n}$ is the average number of hydrogen bonds per molecule. Each molecule has 3 arms. The probability that a hydrogen bond is formed at one arm is $(1 - x)$, where x is the ratio of non-bonded molecules at one arm. We now get:

$$\bar{n} = 3(1 - x). \quad 23$$

The effective particle density can now be calculated as

$$\rho^{ef} = \frac{1}{V^{ef}}. \quad 24$$

Now, the set of equations (19)–(24) must be solved iteratively to get the effective density, ρ^{ef} , and the fraction of molecules x that are not hydrogen bonded. The effective packing fraction is then calculated as $\eta^{ef} = \rho^{ef} \pi d^2 / 4$. Once the effective density and packing fraction are known, the Helmholtz free energy can be calculated with equations (16)–(18) and other thermodynamic properties with standard thermodynamic relations⁷⁷.

C. Integral equation theory

In this section we briefly overview the orientationally-averaged version of the multidensity Ornstein–Zernike (OZ) equation with the so-called polymer Percus–Yevick (PPY) closure^{50,66,82} which was most accurate for this kind of systems with short range interactions. An extensive description of the theory for pure water was given in our previous paper⁵⁰. The orientation averaging of the OZ equation is an additional approximation of the theory not present in the Monte Carlo studies of the MB model.^{39,40,43} An advantage of this approximation is that it allows a relatively simple numerical evaluation of the structural and thermodynamic properties for this system.

The multidensity OZ equation for the model described is written as:

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{c}}(k) + \hat{\mathbf{c}}(k) \boldsymbol{\rho} \hat{\mathbf{h}}(k) \quad 25$$

where $\hat{\mathbf{h}}(k)$ and $\hat{\mathbf{c}}(k)$ are the matrices whose elements are the Fourier transforms of the partial correlation functions $h_{ij}(r)$ and $c_{ij}(r)$. We use partial correlation functions which remain finite upon decrease of the temperature⁵⁶. In Eq. (25) $\boldsymbol{\rho}$ represents the matrix which replaces the Wertheim's density parameters σ and contains the partial number densities. Here we restrict ourselves to the so-called 'ideal network' approximation^{81,82}. This means that we neglect the part of correlation responsible for formation of the ring-like structures⁸². Originally the OZ equation involves the matrices $\mathbf{c}$, $\mathbf{h}$, and $\boldsymbol{\rho}$ of dimensionality 4×4 . By taking into account the equivalence of the bonding arms we obtain

$$\hat{\mathbf{w}}(k) = \begin{pmatrix} \hat{w}_{00}(k) & \hat{w}_{01}(k) \\ \hat{w}_{10}(k) & \hat{w}_{11}(k) \end{pmatrix}, \quad 26$$

where w stands for either the h or c correlation function, and $\boldsymbol{\rho}$ is the matrix containing the partial densities.

$$\boldsymbol{\rho} = \begin{pmatrix} \rho & 3\rho \\ 3\rho & 6\rho \end{pmatrix}, \quad 27$$

The coefficients 3 and 6 in $\boldsymbol{\rho}$ result from the reduction of the dimensionality of the OZ equation⁵⁰. In order to solve the OZ equation an additional relation between the h and c correlation functions is needed. In the present study we choose the polymer PY closure⁶⁶ in the form

$$c_{ij}(r) = f_{LJ}(r)(t_{ij}(r) + \delta_{i0}\delta_{j0}) + \delta_{i1}\delta_{j1}x^2\bar{f}_{HB}(r)e_{LJ}(r)[t_{00}(r) + 1], \quad 28$$

where $t(r) = h(r) - c(r)$, x is the fraction of MB particles not bonded at one arm, $f_{LJ}(r) = e_{LJ}(r) - 1$, and $e_{LJ}(r) = \exp[-\beta U_{LJ}(r)]$. Furthermore, $\bar{f}_{HB}(r)$ is the orientationally-averaged Mayer function for the hydrogen-bond potential (Eq. 3) and x follows from mass-action law as given by Eq. 19. The total pair distribution function $g(r)$ is calculated via the relations:

$$g(r) = g_{00}(r) + 3g_{01}(r) + 3g_{10}(r) + 9g_{11}(r) \quad 29$$

The OZ equation together with the polymer PY closures condition is solved by a direct iteration. The forward and inverse Bessel-Fourier transforms, needed to couple the correlation functions in real and Fourier spaces, have been performed by the method of Talman⁸³. Once the pair correlation function is known other thermodynamic properties can be calculated with standard thermodynamic relations⁵⁰.

D. Lattice model

The system consists from N water molecules. We keep track of the state of interaction of each possible hydrogen bonding arm of each water molecule by using as a bookkeeping tool

an underlying ice lattice. For this water model, the underlying lattice is hexagonal; (See Figure 3). We focus on a single water molecule in the hexagon and the relationship of that water to its clockwise neighbor. Figure 4 shows the three possible relationships: the test water can either form a hydrogen bond, a van der Waals contact, or no interaction at all. We compute the isothermal-isobaric statistical weights, ω_{HB} of the hydrogen-bonded molecules, ω_{LJ} of the van der Waals contacts, and ω_o of the unbonded population as functions of temperature, pressure, and interaction energies.

The hydrogen-bonded state.—We assume that if the test water molecule points one of its three hydrogen bonding arms at an angle θ to within $\pi/3$ of the center of its clockwise neighbor water, it forms a hydrogen bond (see Figure 4). The energy of interaction of the test water with its clockwise neighbor is

$$u_{HB}(\theta) = -\epsilon_{HB} - \epsilon_{LJ} + k_s \theta^2, \quad -\pi/3 < \theta < \pi/3 \quad 30$$

where ϵ_{HB} is an energy constant representing the maximal strength of a hydrogen bond. ϵ_{LJ} is the contact energy between neighboring waters and k_s is the angular spring constant that describes the weakening of the hydrogen bond as it becomes increasingly off-angle. We regard this type of hydrogen bond as weak insofar as it is not cooperative with neighboring hydrogen bonds. We consider a more cooperative type of hydrogen bonding below. To compute the isothermal-isobaric partition function, ω_{HB} , of this hydrogen bonded state, we integrate this Boltzmann factor over all the allowable angles and over all the allowable separations x and y of the test molecule relative to its clockwise neighbor,

$$\Delta_{HB} = c(T) \iint dx dy \int_{-\pi/3}^{\pi/3} d\theta \exp(-(u_{HB} + 2pv_{HB}/3)/k_B T), \quad 31$$

where $c(T)$ is the 2D version of the kinetic energy contribution to the partition function, k_B is Boltzmann's constant, T is temperature, p is the pressure, and v_{HB} is volume per molecule. The double integral $\iint dx dy$ represents the volume over which the second molecule has translational freedom to form a hydrogen bond with the first water is equal to effective volume $v_{ef}^{HB} = 0.242$. The volume v_{HB} of the hydrogen-bonded state we determine this way. First, we estimate an upper bound on the volume, from a simple geometric calculation. For the perfect hexagon crystal, representing low-pressure ice, the volume of the solid is

$$v_s = \frac{3\sqrt{3}r_{HB}^2}{4}, \quad 32$$

provided the center of the hexagon is unoccupied, as in our current model. Second, since liquid water is denser than ice, we estimate a lower bound on the volume using high-pressure ice, where another MB water occupies the center of each hexagonal cage⁷⁴,

$$v_{HB} = \frac{\sqrt{3}r_{HB}^2}{2}. \quad 33$$

Finally, since the density of liquid water must lie between these limits, we estimate its volume as

$$v_{HB} = \frac{\sqrt{3}r_{HB}^2 x_v}{2}, \quad 34$$

where $x_v = 1.1$ is simply chosen empirically by fitting the density dependence *vs.* temperature. Using these definitions and performing the integration in Equation (31) gives

$$\Delta_{HB} = c(T)v_{ef}^{HB} \exp\left(\frac{\epsilon_{HB} + \epsilon_{LJ} - 2pv_{HB}/3}{k_B T}\right) \sqrt{\frac{k_B T \pi}{k_s}} \operatorname{erf}\left(\sqrt{\frac{k_s \pi^2}{9k_B T}}\right). \quad 35$$

The van der Waals state.—In this state, the test water molecule forms only a van der Waals contact with its clockwise neighboring water. This type of water molecule has energy

$$u_{LJ}(\theta) = -\epsilon_{LJ}, \quad -\pi/3 < \theta < \pi/3 \quad 36$$

where ϵ_{LJ} is the same as described above. The isothermal-isobaric partition function, Δ_{LJ} of this state is given by integrating over angles and positions of the test particle relative to its clockwise neighbor as before,

$$\Delta_{LJ} = c(T) \iint dx dy \int_{-\pi/3}^{\pi/3} d\theta \exp\left(-(u_{LJ} + 2pv_{LJ}/3)/k_B T\right), \quad 37$$

where we take the volume occupied by the test water in this state to be

$$v_{LJ} = \frac{\sigma_{LJ}^2 \sqrt{3} \sqrt{2}}{2}. \quad 38$$

The integral $\iint dx dy$ represents the translation volume when second molecule forms van der Waals contact with first and is equal to effective volume $v_{ef}^{LJ} = 0.364$. Integrating gives

$$\Delta_{LJ} = \frac{2\pi}{3} c(T) v_{ef}^{LJ} \exp\left(\frac{\epsilon_{LJ} - 2pv_{LJ}/3}{k_B T}\right) \quad 39$$

The non-interacting state.—In this third possible state, the test water has no interaction with its clockwise neighbor

$$u_o(\theta) = 0. \quad 40$$

The isothermal-isobaric partition function for the non-interacting state is obtained by integrating over translational degrees of freedom,

$$\Delta_o = c(T) \iint dx dy \int_{-\pi/3}^{\pi/3} d\theta \exp(-2pv_o/3k_B T), \quad 41$$

where v_o is volume available to the test molecule in this state. Following^{74,75}, we compute v_o using the van der Waals gas approximation,

$$v_o = \frac{k_B T}{p} + v_{LJ}. \quad 42$$

Integrating over all the ways this state can occur gives

$$\Delta_o = \frac{2\pi}{3} c(T) \frac{k_B T}{p} \exp\left(\frac{-2pv_o}{3k_B T}\right) \quad 43$$

These three expressions, Equations (35), (39) and (43), give the isobaric-isothermal ensemble Boltzmann weights of the three possible states of each water molecule – hydrogen-bonded, van-der-Waals-bonded, or non-bonded. Following TD^{74,75}, we assume a mean-field attractive energy,⁷⁶ $-N a/v$, among cages, where a is the van der Waals dispersion parameter (0.02, here) and v is the average molar volume, which we get from Equation (49) below. The partition function for a full hexagon of 6 waters would be given by:

$$Q_1 = (\Delta_{HB} + \Delta_{LJ} + \Delta_o)^6, \quad 44$$

where the subscript 1 indicates a single hexagon. However, we treat hexagons here a little differently instead. We believe that true ice cages in water's solid states involve a higher degree of hydrogen-bonding cooperativity than the hydrogen bonding that is just formed pairwise among nearest neighbor waters in the liquid state. So, for ice, throughout this paper, the total partition function for each hexagon will be given by

$$Q_1 = (\Delta_{HB} + \Delta_{LJ} + \Delta_o)^6 - \Delta_{HB}^6 + \delta\Delta_s^6 \quad 45$$

where $\delta = \exp(-\beta\epsilon_c)$ is the Boltzmann factor for the cooperativity energy ϵ_c that applies only when 6 water molecules all collect together into a full hexagonal cage. The terms on the right-side of this expression simply replace the statistical weight for each weakly hydrogen-bonded full hexagonal cage with the statistical weight for a cooperative strongly hydrogen-bonded hexagonal cage. δ_s is the Boltzmann factor for a cooperative hexagonal cage. It differs from δ_{HB} only in that the former uses the hexagonal cage volume per molecule, v_s , while the latter uses the liquid water hydrogen bonding volume per molecule, v_{HB} . We use Equation 45 for the full range of temperatures; it reduces to Equation 44 in the limit of high temperatures when all cage-like structuring of water has disappeared. Now we combine the Boltzmann factors for the individual water molecules to get the partition function Q for the whole system of N particles,

$$Q = Q_1^{\frac{N}{6}}, \quad 46$$

where the factor $N/6$ accounts for the 3 possible interaction sites per water molecule, and corrects for double-counting the hydrogen bonds.

We compute the populations of the states $i = 1$ (HB), 2 (LJ), 3(o), 4(solid) using

$$f_i = \frac{d\log Q_1}{d\log \Delta_i^6}. \quad 47$$

The chemical potential is given by

$$\mu = -\frac{k_B T}{N} \log Q, \quad 48$$

The molar volume is

$$v = \frac{V}{N} = \left(\frac{\partial \mu}{\partial p} \right)_T = \sum f_i v_i, \quad 49$$

and all the other thermodynamic properties below are obtained as described previously^{74,75}. For all the model calculations, we used the following parameters: $\epsilon_{HB} = 1$, $r_{HB} = 1$, vdW: $\epsilon_{LJ} = 0.1$, $\sigma_{HB} = 0.7$ (unchanged from TD^{74,75} and the MB model³⁹), $k_s = 10$, and $\epsilon_c = 0.06$.

IV. RESULTS AND DISCUSSION

We present our results below in dimensionless units, normalized to the strength of the optimal hydrogen bond ϵ_{HB} and hydrogen bond separation r_{HB} .

$$(T^* = k_B T / |\epsilon_{HB}|, u^{ex*} = u^{ex} / |\epsilon_{HB}|, V^* = V / r_{HB}^2, \text{ and } p^* = p r_{HB}^3 / |\epsilon_{HB}| \text{ for 2D MB model and } V^* = V / r_{HB}^3, \text{ and } p^* = p r_{HB}^3 / |\epsilon_{HB}| \text{ for 3D MB model}).$$

A. Thermodynamics

1. 2D MB model—Monte Carlo constant-pressure simulations of pure MB water at a reduced pressure of 0.19 reveal several similarities to pure water³⁹. Figure 5 shows that MB water has a density anomaly similar to that of real water. Like for real liquid water if the MB liquid water is heated above its melting temperature, the density at first increases, then ultimately decreases as in more normal liquids. Figure 5 compares predictions of different theories (original TPT⁵⁰, improved TPT⁵⁹, orientationally averaged IET⁵⁰, angle dependent IET⁵² and lattice model⁵⁶) for the density of 2D MB water to NPT Monte Carlo simulations³⁹. All the calculations were performed at same reduced reduced pressure of $p^* = 0.19$ as MC simulations. The theories reproduce computer results differently. Only lattice model and improved TPT are able to capture density anomaly, all other theories fail. We find that the improved TPT, which is based on the use of an effective density, yields quite good agreement with the simulations. The improved TPT correctly captures the density maximum, but it is slightly shifted $T^* = 0.165$ relative to the N-P-T Monte Carlo simulation $T^* = 0.18$. The lattice model is also in good general agreement with the simulations, but the density maximum is slightly shifted $T^* = 0.1825$ relative to the simulations. This may be either because of approximations in the theory, or because even though the theory is modeled roughly on the MB model, the theory does not have exactly the same underlying Hamiltonian, so it should not be expected to give exactly the same results. Although the other theories fail to predict correct behavior at lower temperatures they are doing well for temperatures higher than $T^* = 0.20$.

The next figures show the temperature dependencies of the other thermodynamic quantities of interest: the heat capacity, C_p^* (Figure 6), the isothermal compressibility, k_T^* (Figure 7), and the thermal expansion coefficient, α^* (Figure 8), respectively. For these quantities too, all the theories generally predict well the Monte Carlo results. However, while the Monte Carlo simulations of MB water show a minimum in the isothermal compressibility versus temperature, it is not as pronounced as in experiments³⁹. Only the lattice model also predicts a minimum in k_T^* . For pure water, MC simulations of the MB model qualitatively predicts the negative thermal expansion coefficient at low temperature, out of theories only the same theories that predict density anomaly can predict it. Water has an unusually high heat capacity. MB water also has a high heat capacity. Moreover, the temperature dependence of the heat capacity of MB water is similar to that found experimentally. All theories have similar trends, only lattice model shows a drop in C_p^* as the temperature is reduced, whereas

the MB model does not. We think that this is a consequence of the water-cage cooperativity that we have included here, which was not included in the MB model.

Figure 9 shows the averaged number of hydrogen bonds as a function of temperature. Results are shown for a reduced pressure of $p^* = 0.19$. The present theories give good agreement with the Monte Carlo simulation results³⁹. Even so, the agreement is not perfect. The simulations still underpredicts hydrogen bonding compared to the theories. However, we believe this is for the trivial reason that the MB simulations use a tighter definition for the range of angles that define a hydrogen bond.

2. 3D MB model—Next figures compare density (Figure 10), heat capacity (Figure 11), isothermal compressibility (Figure 12), and thermal expansion coefficient (Figure 13) versus temperature at a reduced pressure of $p^* = 0.19$ for 3D MB model^{47,48}. All the state points presented on the graphs apply to the liquid phase. We can see that the computer simulations successfully predict maxima in the density with temperature, as is found in real water. In contrast to the computer simulation results, the analytical theories (original TPT and orientational averaged IET) do not predict this minimum. At higher temperatures, both TPT and IET have a good agreement with the MC data. For other quantities we have similar agreement between theories and simulation data. Both theories predict well heat capacity, the compressibility and the expansion coefficient at higher temperatures, but are much less successful at low temperatures. As expected, the predictions of the integral equation theory are superior to the TPT approach. The model correctly predicts that the thermal expansion coefficient is negative at low temperatures, changing sign for the temperature where the molar volume of the model water has its minimum. Negative values of expansion coefficient are very small.

B. Structure

1. 2D MB model—Figure 14 shows the water-water radial distribution functions, $g(r^*)$, calculated for different state points (T^* and p^*) for 2D MB model. In particular we compare the new results by orientational averaged IET⁵⁰, angle dependent IET⁵² and Monte Carlo computer simulations³⁹. The calculations are applied at the reduced reduced pressure $p^* = 0.19$ for three different temperatures. At lowest temperature MB model water exhibits a minimum in the molar volume in MC computer simulations. This figure shows that inclusion of the explicit angular dependence in the integral equation theory improves the predicted pair distribution function. As expected, the improved theory predicts more structure, seen as higher peaks, in the second and third solvation shells, in better agreement with the Monte Carlo results. Figure 15 shows typical structures present in liquid state of 2D MB model of water. In general, the IET results overestimates the LJ part of the interaction (Figure 15(a)). The theory also predicts a second peak that is too low (Figure 15(b)). There are three main peaks in the correlation functions. The first peak at 0.7 is a consequence of the Lennard–Jones interaction, and the second one at 1.0 is a result of the hydrogen-bond interaction, the third peak at 1.72 is a result of two hydrogen bonds. At low temperatures, the hydrogen bonding peak is large relative to the van der Waals peak.

2. 2D MB model—Figure 16 shows the water-water radial distribution functions, $g(r^*)$, calculated for different state points (T^* and p^*) for 3D MB model. Like in 2D, there are two main peaks in this plot. The first peak at 0.7 is a consequence of the Lennard–Jones interaction, and the second one at 1.0 is a result of the hydrogen-bond interaction. At low temperatures, the hydrogen bonding peak is large relative to the van der Waals peak. The peak at distance $r = 1.6$, can be understood by two hydrogen bonds formation like in 2D. In general, the orientational averaged IET results are in good agreement with the MC simulations, although at lower temperatures, the integral equation theory slightly overestimates the LJ part of the interaction. The theory also predicts a second peak that is too low.

C. Phase diagram of the 2D model

We calculated liquid part of phase diagram by performing Monte Carlo simulations in the grand canonical ensemble⁵⁹. We varied chemical potential and calculate equilibrium density at constant temperature. We determined liquid part of phase diagram also by original TPT and improved TPT⁵⁹. Gas-liquid coexistence lines are plotted in Figure 17. This figure shows a comparison of the gas-liquid equilibria curves calculated by MC and both TPT methods. The critical point for the gas-liquid transition by MC is $T_c^* = 0.18$, $p_c^* = 0.016$, $\mu_c^* = -0.56$ and $\rho_c^* = 0.433$, by standard TPT is $T_c^* = 0.14$, $p_c^* = 0.0036$, $\mu_c^* = -0.625$ and $\rho_c^* = 0.150$ and by improved TPT is $T_c^* = 0.179$, $p_c^* = 0.017$, $\mu_c^* = -0.533$ and $\rho_c^* = 0.370$. From the results it can be seen that the improved TPT predicts the correct critical point well, while the original TPT predicts it at a lower temperature, density and pressure. We tried to determine a liquid-liquid phase transition of the model, but due to crystallization issues we cannot calculate this with the current version of the MC method, also both TPT methods fail to detect any liquid-liquid phase transition. Figure 18 shows our data for liquid-gas coexistence and phase diagram proposed by Silverstein et al.⁴⁰. They reported a rough sketch of the PT phase diagram including solid-liquid transition which has similar shape as in real water. At higher pressure melting temperature decreases. In our calculations we also determined the percolation line. We checked how the system is connected by hydrogen bonds. We performed cluster analysis and checked the fraction of water molecules belonging to the biggest cluster in the system by MC computer simulations. Results for this are plotted in Figure 19. At constant temperature, the fraction of molecules belonging to the biggest cluster connected by hydrogen bonds increases with density, reach a maximum and then, due to high packing, starts to decrease. This happens at densities higher than the perfect hexagonal crystal. In MC, the percolation line was determined as density at which at least 50% of water particles were part of one big cluster connected by hydrogen bonds. In TPT, we followed Bianchi et al.⁸⁴ where the ratio of non-bonded particles at a particular arm at percolation x_p is equal to 0.5. Percolation curves determined with these methods are presented in Figure 19 for MC simulations and both versions of TPT. Since the calculation in TPT is based on ratios of free particles, and since agreement with MC was not good for high temperatures⁵⁹, the TPT curves deviate from MC results in that region. The TPT is predicting a connected system at lower temperatures than MC⁸⁵.

D. Anomalies in the 2D model

To observe density anomaly we can calculate of density as function of temperature and observe density maximum at certain pressures. This was done for selected pressures before³⁹. An alternative way to determine temperature of maximum density is to calculate pressure as function of density at constant density. Where density anomaly is present we observe minimum in pressure. Several isochores are presented in Figure 20 as well as temperature of maximum density. For the model we observe density anomaly for the temperatures lower than 0.18 and for the densities between 0.8 and 1.1 and for the pressures between 0.05 and 0.3. The pseudo diffusion coefficient is determined by the displacement of water molecules in the MC steps. For normal fluids diffusivity decreases monotonically with increasing density at constant temperature. For 2D MB model this is observed only for temperatures higher than 0.175. For temperatures lower than 0.175 diffusion has anomalous behavior. The region between the minima and the maxima is so-called anomalous diffusion region and is presented in Figure 20. To study the structural behavior we calculated three quantities, the translational order parameter t and two orientational order parameters q_3 (with three fold axis) and q_6 (with six fold axis). For normal fluids translational order parameter monotonically increases with density. If a different behavior is observed in a certain density range, the fluid is said to exhibit a structural anomaly. For the 2D MB model we found this monotonic behavior only for the temperatures higher than 0.19 (see Figure 20). For lower temperatures we observe that the t has a maximum, decreases up to a minimum and recovers the normal increasing behavior after the minimum. The region between the minima and maxima is called the anomalous structure region. Figure 21 shows distribution of both orientational order parameters for low and high temperatures for different densities. We can see huge peak for both. Our study reveals the anomalous behavior also for both orientational order parameters. For the temperatures higher than 0.16 both parameters decrease with increase of density. For temperatures lower than 0.16 we can observe maxima close to density of low density ice phase. In Figure 20 we plotted pair entropy as function of density and temperature and we observed anomalous region.

In Figure 22 we plotted the relation between the several anomalies presented for the 2D MB model of water. The temperature of maximum density line lies between diffusion and entropy anomaly. There is difference between position of structure and entropy anomaly. Hierarchy of anomalies found here is different that reported for the SPC/E water and other two-scale potentials^{16,86–88}.

V. CONCLUSIONS

In this work we have reviewed 2D and 3D MB model of water and the insights they give into water, including its thermal properties, phase diagram, volumetric anomalies. Monte Carlo simulations of MB water have data that can be compared when applying more analytical theories for description of properties of this model, like thermodynamics perturbation theory, integral equation theory and Lattice model, that can be used for orientational liquids such as water. These models suggest that many of the qualitative and global properties of waterwaters thermodynamics, its volume anomalies, may not depend strongly on atomic details or on waters tetrahedrality per se; rather, they depend on waters fixed angular

interactions owing to its hydrogen bonding geometry. One long-term goal of simplified modeling is to develop more computationally efficient ways to understand pure water and aqueous solvation.

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FIG. 1:
The MB particles in 2D.

FIG. 2:
The MB particles in 3D.

FIG. 3:
The lattice of the model showing both the hexagon of the icelike structure and showing illustrating a pair interaction used for bookkeeping to avoid triple counting.

FIG. 4:
The three model states: (1) hydrogen bonded, (2) vdW bonded, and (3) nonbonded.

FIG. 5:

Temperature dependence of the density at $p^* = 0.19$ for 2D MB model. Monte Carlo simulation is plotted with black symbols, original TPT with green line, modified TPT with red line, orientationally averaged IET with grey line, angle dependent IET with yellow line and results from lattice model by orange line.

FIG. 6:
Temperature dependence of the heat capacity at $p^* = 0.119$ for 2D MB model. Legend same as in 5.

FIG. 7:
 Temperature dependence of the isothermal compressibility at $p^* = 0.19$ for 2D MB model.
 Legend same as in 5.

FIG. 8:
Temperature dependence of the thermal expansion coefficient at $p^* = 0.19$ for 2D MB model. Legend same as in 5.

FIG. 9: Temperature dependence of the averaged number of hydrogen bonds at $p^* = 0.19$ for 2D MB model. Legend same as in 5.

FIG. 10: Temperature dependence of the density at $p^* = 0.19$ for 3D MB model. Monte Carlo simulation is plotted with black symbols, original TPT with blue line and orientationally averaged IET with red line.

FIG. 11: Temperature dependence of the heat capacity at $p^* = 0.19$ for 3D MB model. Legend same as in 10.

FIG. 12:
Temperature dependence of the isothermal compressibility at $p^* = 0.19$ for 3D MB model.
Legend same as in 10.

FIG. 13:
Temperature dependence of the thermal expansion coefficient at $p^* = 0.19$ for 3D MB model. Legend same as in 10.

FIG. 14: The waterwater radial distribution function, $g(r^*)$, at $p^* = 0.19$ and (a) $T^* = 0.18$, (b) $T^* = 0.24$ and (c) $T^* = 0.28$. The MB model Monte Carlo results³⁹ are presented by symbols and the results by orientational average IET by red line and by angle dependent IET by blue line.

FIG. 15:
Typical short range structures for 2D MB model of water.

(a)

(b)

FIG. 16: The waterwater radial distribution function, $g(r^*)$, at $p^* = 0.19$ and (a) $T^* = 0.15$, (b) $T^* = 0.30$. The MB model Monte Carlo results^{47,48} are presented by symbols and the results by orientational average IET by red line.

FIG. 17:

Vapour-liquid equilibria from MC and TPT. Results from computers simulations are plotted with black symbols, from TPT with a red solid line and from improved TPT with a blue dashed line. In (a) there is $T^* - \rho^*$ liquid-gas coexistence, in (b) $T^* - p^*$ coexistence and in (c) $T^* - \mu^*$ coexistence.

FIG. 18:
 $T^* - p^*$ phase diagram from MC simulations. Black curve are our results for gas-liquid coexistence in comparison with prediction of phase diagram by Silverstain et al.⁴⁰ which is plotted by green line.

FIG. 19:

(a) Fraction of molecules belonging to the biggest cluster as a function of density for different temperatures. Points are the results from Monte Carlo computer simulations. Black color is for high temperature $T^* = 0.4$, red for $T^* = 0.3$, blue for $T^* = 0.2$, yellow for low temperature $T^* = 0.18$, and green for low temperature $T^* = 0.15$. (b) Percolation line from MC and TPT. Results from computers simulations are plotted with black symbols and from TPT with a red solid line and from improved TPT with a blue dashed line.

FIG. 20:

(a) The pressure as a function of temperature for different densities. Red lines correspond to isochores from bottom up for densities 0.8, 0.825, 0.85, 0.875, 0.9, 0.925, 0.95, 0.975, 1.0, 1.025, 1.05, 1.075, 1.1. (b) The pseudo diffusion coefficient as a function of the density for several isotherms. (c) The translational order parameter as a function of the density for several isotherms. (d) The pair entropy as a function of the density for several isotherms. Black lines connects points with maximum and minimum of the parameter.

FIG. 21:
Density dependence of (a) the orientational order parameter with three fold symmetry and (b) the orientational order parameter with six fold symmetry for several isotherms.

FIG. 22:

(a) The temperature-density plane containing all the anomalies found for the 2D MB model of water. A grey line is the line of the density anomaly, a red is the diffusion anomalous region, a black is the anomalous region to the translation order parameter, a green is the anomalous region of the pair entropy. An orange and a yellow lines show the position of the maximum of the orientational order parameters. (b) Same as in (a) but for pressure temperature plane.