

An improved thermodynamic perturbation theory for Mercedes-Benz water

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We previously applied Wertheim's thermodynamic perturbation theory for associative fluids to the simple Mercedes-Benz model of water. We found that the theory reproduced well the physical properties of hot water, but was less successful in capturing the more structured hydrogen bonding that occurs in cold water. Here, we propose an improved version of the thermodynamic perturbation theory in which the effective density of the reference system is calculated self-consistently. The new theory is a significant improvement, giving good agreement with Monte Carlo simulations of the model, and predicting key anomalies of cold water, such as minima in the molar volume and large heat capacity, in addition to giving good agreement with the isothermal compressibility and thermal expansion coefficient. © 2007 American Institute of Physics. [DOI: 10.1063/1.2784124]

I. INTRODUCTION

A key goal of liquid-state statistical thermodynamics is to develop quantitative theories for water and aqueous solutions. There has been much progress in this field (for reviews see Refs. 1–10). Among the most important properties in which pure water differs from other liquids are a temperature of maximum density in the liquid phase, a minimum in the isothermal compressibility, a negative thermal expansion coefficient in the liquid range, and a large heat capacity. Such theories strive to explain these properties. These anomalies appear to be related to the ability of water molecules to form tetrahedrally coordinated hydrogen bonds.

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 in Ref. 8). Such approaches can depend critically on the force field used in the calculation,^{11,12} and are computationally expensive, and so they are challenging to sample in enough detail to explore subtle properties, such as heat capacity and phase diagram.

Many properties of water and aqueous solutions can be captured by simpler and less detailed models.^{13–15} One class of such models has been developed by Nezbeda and co-workers.^{16–18} One of the simplest model for water is the so-called Mercedes-Benz (MB) model,^{19–24} originally proposed by Ben-Naim in 1971.^{25,26} This is a two-dimensional model, which captures the main aspects of water physics in a simple way: the long-ranged attractions and short-ranged repulsions are treated through Lennard-Jones interactions, and

hydrogen bonding is treated through an orientation-dependent interaction. Each water molecule is modeled as a disk that interacts with others such as 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.

The advantages of the MB model, compared to more realistic water models, are (i) the computer simulations of thermodynamic properties can be obtained in reasonable amounts of computer time and (ii) the underlying physical principles can be more readily explored and visualized in two dimensions. As a validation of the model, *N-P-T* Monte Carlo simulations have shown that it predicts qualitatively the density anomaly, the minimum in the isothermal compressibility as a function of temperature, the large heat capacity, and the experimental trends for the thermodynamic properties of solvation of nonpolar and ionic solutes.^{19–24}

Even though such computer simulations play an important role in understanding the properties of liquids, it is equally important, in our opinion, to develop simplified, more analytical theoretical approaches. One such approach in the theory of liquids is known as perturbation theory.²⁷ It is based on idea that the intermolecular pair potential can be separated into short-ranged and long-ranged parts. Such an approach is applicable for dense systems, where the structure of the liquid is largely determined by the packing of the molecules. About 20 years ago Wertheim^{28–31} proposed his statistical-mechanical approach for strongly associating systems of molecules and a corresponding thermodynamic perturbation theory.

In previous work,^{32–36} we applied Wertheim's theory for associating fluids^{28,29} to the MB model through both a thermodynamic perturbation theory (TPT) and orientationally averaged and angle-dependent integral equation theories

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(IETs). We found that both TPT and IET approaches gave good quantitative agreement with N - P - T Monte Carlo results for the molar volume, isothermal compressibility, and other thermodynamic properties as a function of temperature. However, we found that while the model gave quantitative agreement with the MC simulations for “hot” liquid water, it did not predict the properties of cold water equally well.^{32–34}

In particular, we found that those two theories were good for situations involving waters in hard-sphere contact, but less satisfactory when association leads to interwater separations smaller than hard core distances³⁷ (where the bonding distance is less than the contact distance) or when the waters are further apart. In short, it appeared that the previous work did not adequately handle changes in free volume. An accurate calculation for the reference system is a key component of a successful perturbation theory. Here we propose an improved version of Wertheim’s thermodynamic perturbation theory in which we treat the density of the reference system self-consistently. We find that this significantly improves the accuracy of the approach; it predicts the maximum of the molar volume and other anomalous properties of water in excellent agreement with previous computer simulations.

II. THE MODEL

Each water molecule is represented in the MB model as a two-dimensional Lennard-Jones disk with three arms separated by an angle of 120° .^{20,25} The interaction potential between two MB particles is a sum of a Lennard-Jones term and a hydrogen-bonding (HB) term

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

where r_{ij} is the distance between centers of particles i and j and \mathbf{X}_i denotes the vector representing the coordinates and the orientation of the i^{th} particle. The Lennard-Jones part of the potential is defined as

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

where ε_{LJ} is the well depth and σ_{LJ} is the contact parameter. The hydrogen bonding part of the interaction potential is

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

where U_{HB}^{kl} describes the interaction between two arms of different molecules,

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

Expressing the scalar products explicitly gives the following form of the HB potential:

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

where k and l stand for the different arms and $G(x)$ is an unnormalized Gaussian function

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

Further, $\varepsilon_{\text{HB}} = -1$ is an energy parameter and $r_{\text{HB}} = 1$ is a characteristic hydrogen bond length. \mathbf{u}_{ij} is the unit vector along \mathbf{r}_{ij} and \mathbf{i}_k is the unit vector representing the k^{th} arm of the i^{th} particle, where θ_i is the orientation of i^{th} particle. The strongest hydrogen bond occurs when an arm of one particle is colinear 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 $0.7r_{\text{HB}}$.

III. THERMODYNAMIC PERTURBATION THEORY

Here is a brief overview of Wertheim’s first order perturbation theory,^{28,38} which we used previously.³² The Helmholtz free energy for MB molecules can be expressed as a sum of an ideal term A_{id} , a reference term A_{LJ} , and a perturbation term A_{HB} . The latter takes into account the association of MB molecules into hydrogen bond networks,

$$\frac{A}{Nk_B T} = \frac{A_{\text{id}}}{Nk_B T} + \frac{A_{\text{LJ}}}{Nk_B T} + \frac{A_{\text{HB}}}{Nk_B T}, \quad (7)$$

where N is the number of particles, T is temperature, and k_B is Boltzmann’s constant. The term A_{LJ} is calculated using the Barker-Henderson perturbation theory.^{27,32} The use of other perturbation methods for the Lennard-Jones part did not improve the results. As our reference system, we previously used hard disks, i.e.,

$$\frac{A_{\text{LJ}}}{Nk_B T} = \frac{A_{\text{HD}}}{Nk_B T} + \frac{\rho^{\text{ef}}}{2k_B T} \times \int_{\sigma_{\text{LJ}}}^{\infty} g_{\text{HD}}(r, \eta^{\text{ef}}) u_{\text{LJ}}(r) dr, \quad (8)$$

where A_{HD} is the hard-disk part of the Helmholtz free energy, ρ^{ef} is the effective number density of particles, η^{ef} is the effective packing fraction, and $g_{\text{HD}}(r, \eta^{\text{ef}})$ is pair distribution function of hard-disk reference fluid.³² For the contribution of hydrogen bonding to the Helmholtz free energy we used

$$\frac{A_{\text{HB}}}{Nk_B T} = 3 \left(\log x - \frac{x}{2} + \frac{1}{2} \right), \quad (9)$$

where x is the fraction of molecules not bonded at one particular arm. x is obtained from the mass-action law²⁸ in the form

$$x = \frac{1}{1 + 3\rho^{\text{ef}} x \Delta}. \quad (10)$$

Finally, Δ is defined by^{28,38}

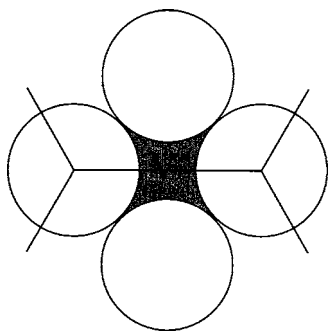


FIG. 1. Excluded volume.

$$\Delta = 2\pi \int g_{LJ}(r, \rho^{ef}) \bar{f}_{HB}(r) r dr, \quad (11)$$

where $\bar{f}_{HB}(r)$ is an orientationally averaged Mayer function for the hydrogen-bonding potential of one site. The pair distribution function $g_{LJ}(r, \rho^{ef})$ is obtained by solving the Percus-Yevick equation for Lennard-Jones disks.

Up to this point [Eqs. (7)–(11)], this overview of our previous TPT treatment³² also describes our present treatment. The basic difference here is that we now use ρ^{ef} in Eqs. (7)–(11) as an effective density, which is calculated as explained below. The logic for using such an effective density, rather than the particle density that we used before, is the following: when two water molecules form a hydrogen bond, it sterically occludes space, which becomes inaccessible to any other molecule (see Fig. 1). We calculate the effective particle volume as

$$V^{ef} = \frac{1}{\rho} - \frac{\bar{n}V'}{2}, \quad (12)$$

where V' is the volume not accessible to other molecules when two molecules form a hydrogen bond. This excluded volume can be approximated by simple geometry. Two water molecules that form a hydrogen bond are separated by a distance of 1. If the hard core has diameter d of HD molecules in Barker-Henderson perturbation, V' can be approximated as

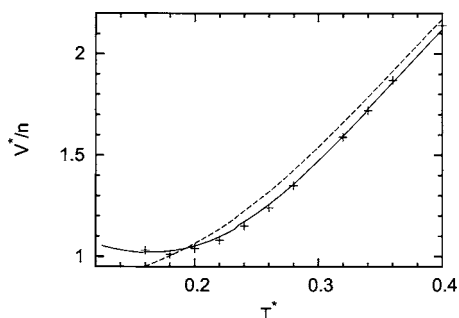


FIG. 2. Temperature dependence of the molar volume at $P^* = 0.19$ as obtained by the Monte Carlo simulation (symbols), the improved thermodynamic perturbation theory (continuous line), and original thermodynamic perturbation theory (dashed line).

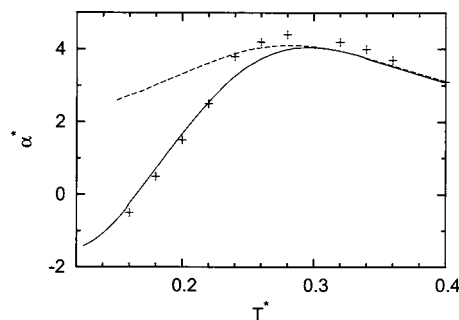


FIG. 3. Temperature dependence of the thermal expansion coefficient at $P^* = 0.19$; legend as for Fig. 2.

$$V' = \sqrt{d^2 - \frac{1}{2}} - \frac{\pi d^2}{4}. \quad (13)$$

In Eq. (12) \bar{n} is the average number of hydrogen bonds per molecule. Each molecule has three arms. The probability that a hydrogen bond is formed at one arm is $(1-x)$ where x is ratio of nonbonded molecules at one arm. We now get

$$\bar{n} = 3(1-x). \quad (14)$$

The effective particle density can now be calculated as

$$\rho^{ef} = \frac{1}{V^{ef}}. \quad (15)$$

Now, the set of Eqs. (10)–(15) 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 Eqs. (7)–(9) and with standard thermodynamic relations.²⁷

IV. RESULTS AND DISCUSSION

All our results reported below are shown in reduced units; the excess internal energy and temperature are normalized to the HB energy parameter ϵ_{HB} ($A^* = A/|\epsilon_{HB}|$, $T^* = k_B T/|\epsilon_{HB}|$) and the distances are scaled to the hydrogen bond characteristic length r_{HB} ($r^* = r/r_{HB}$).

In Fig. 2, we compare the molar volume V^*/n , obtained from the Monte Carlo simulations, with the results of both the present thermodynamic perturbation theory and the original version of the theory. The calculations were performed at

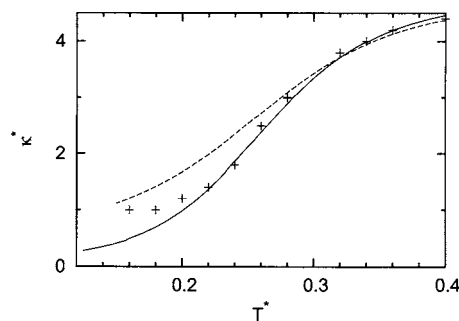


FIG. 4. Temperature dependence of the isothermal compressibility at $P^* = 0.19$; legend as for Fig. 2.

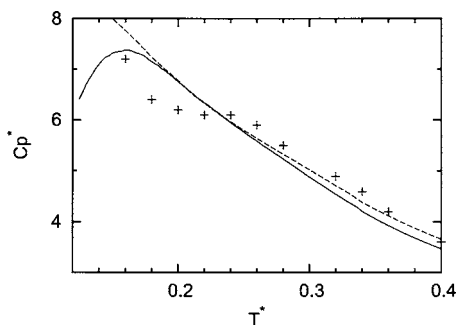


FIG. 5. Temperature dependence of the heat capacity at constant pressure at $P^*=0.19$; legend as for Fig. 2.

a reduced pressure of $P^*=0.19$. We find that the new version of the TPT, which is based on the use of an effective density, yields quite good agreement with the simulations. The new theory even 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 remaining figures show the temperature dependencies of the other thermodynamic quantities of interest: the isothermal compressibility κ_T^* (Fig. 3), the thermal expansion coefficient α^* (Fig. 4), and the heat capacity C_p^* (Fig. 5). We find that the new theory is in much better agreement with the Monte Carlo simulation data for all quantities than the original TPT does. Monte Carlo simulation of the MB water has a minimum in the isothermal compressibility versus temperature but it is not as pronounced as in experiment.²⁰ In contrast with this no minimum in κ_T^* has been observed in our old and new TPT calculations (Fig. 3).

V. CONCLUSIONS

We have shown here a simple way to improve upon a previous treatment of Wertheim's thermodynamic perturbation theory applied to the MB model of water. We have replaced the previous hard-disk reference system with a Lennard-Jones reference system. This approach treats the free volume more accurately, and leads to much improved agreement with Monte Carlo simulations of the same model. With this improvement, the theory correctly predicts such subtle properties as is the temperature of maximum density, and yields very good agreement with Monte Carlo simulation for the isothermal compressibility, the thermal expansion coefficient, and water's heat capacity. The advantages of the perturbation theory are that it gives insights into the physics of such complex hydrogen bonding liquids, and it is of orders of magnitude faster on computers than the corresponding Monte Carlo simulations of the same system.

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