

Ukrainian Academy of Sciences
Institute for Condensed Matter Physics

Preprint
IPCM-92-7E

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THERMODYNAMIC PROPERTIES OF THE BJH MODEL OF WATER FROM
COMBINING MD SIMULATIONS AND OPTIMIZED CLUSTER THEORY

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УДК 532; 537.226; 541.135

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Термодинамічні властивості ВЈН моделі води на основі об'єднання МД експерименту і оптимізованої кластерної теорії

Для опису рівноважних властивостей ВЈН моделі води застосовано підхід який базується на об'єднанні комп'ютерного експерименту, оптимізованої кластерної теорії і теорії інтегральних рівнянь. Даний підхід дозволяє уникнути труднощів обумовлених врахуванням далекодіючих елестростатичних взаємодій у комп'ютерному експерименті. Приведено результати для радіальної функції розподілу, міжмолекулярної середньої потенціальної енергії, тиску і ізотермічної стисливості які порівнюються з результатами комп'ютерного експерименту на основі сумування по Евальду і експериментальними даними.

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Thermodynamic properties of the ВЈН model of water from combining MD simulation and optimized cluster theory

An approach based on the combination of computer simulation, optimized cluster theory and the theory of integral equation for the description of the equilibrium properties of ВЈН model of water is applied. This approach avoids the difficulties connected with a proper treatment of the long-range electrostatic interaction in the computer simulation. The results for radial distribution functions, intermolecular mean potential energy, pressure and isothermal compressibility are presented and compared to the results obtained on the basis of Ewald summation method and to experimental data.

I. Introduction

In the Ref.1 we have considered the theoretical background of the method based on the combination of computer simulation, optimized cluster theory, and the theory of integral equations. Briefly, the computer simulation is carried out only for the short-range part of the interparticle interaction. Then, these results are used for the description of the reference system and for the renormalization of the long-range part of the interaction which is treated either by optimized cluster series or with the help of integral equations. This approach avoids the difficulties connected with a proper treatment of the long-range electrostatic interaction in the computer simulation and has been developed in order to calculate properties of aqueous electrolyte solutions which are sensitive to the long-range asymptotic behavior of the total interparticle interactions. These properties are difficult to evaluate from computer simulations alone.

This paper we start with the pure polar solvent by employing the Bopp-Janco-Heinzinger (BJH) model for water [2]. In the sections 2,3 the specific way of carrying out the computer simulation for the short-range potential is sketched and the results describing the reference system are discussed. In section 4 is demonstrated how the long-range contributions are taken into account on the basis of the renormalized electrostatic interactions. In section 5, the method is then applied to calculate the radial distribution functions (RDF) and some thermodynamical properties of liquid water. The results are compared to experimental data and to the results obtained on the basis of previous theoretical approaches.

2. Potentials and details of simulations

The BJH model [2] has been chosen for the description of the water-water interactions. The intermolecular interactions are pairwise additive, whereas the intramolecular part contains three-body contributions. The water molecules can be regarded as an assembly of partially charged oxygen and hydrogen atoms, which form water molecules because of a very short-ranged three-body

interaction. In this way, the techniques developed for the solution of the integral equations for ionic melts, which has been elaborated in detail [3,4], can be employed for the aqueous electrolyte solutions, too[5]. The existence of the three-body interactions poses no problem for the solution of the integral equations, as will be shown below. We will not discuss the problems connected with the separation and truncation of the site-site potentials $U_{ij}(r)$ but will use the "shifted-force potential" method [6]. In accordance with this method, the shifted force (SF) potentials $\varphi_{ij}^{SF}(r)$ constructed from the Central Force (CF) model[7] can be considered as reference system:

$$\begin{aligned} \varphi_{ij}^{SF}(r) &= U_{ij}^{CF}(r) - U_{ij}^{CF}(r_0) + F_{ij}(r_0)(r - r_0), \quad r < r_0 \\ &= 0, \quad r > r_0 \end{aligned} \quad (1)$$

In this way we have vanishing forces $F_{ij}(r) = -\partial\varphi_{ij}^{SF}(r)/\partial r$ and zero potentials $\varphi_{ij}^{SF}(r)$ at and beyond the cut-off radius $r_0 = L/2$. For the BJH model [2], the intermolecular part of the potentials $\varphi_{ij}^{SF}(r)$ and $U_{ij}(r)$ are compared in Fig.1. The main difference between is due to the long-range Coulomb interactions in the $U_{ij}(r)$ which will increase with decreasing r_0 .

In order to estimate the effects of the long-range interactions on the structural properties of water, MD simulation runs with the reference and the total potentials have been performed. In the latter case the Ewald Method was employed. In both runs the basic periodic cube contained 200 water molecules at 292 K and a density of 0.9718 g/cm³, leading to a sidelength of the unit-cell of 18.17 Å. For the total potential functions the BJH model [2] is used here. In this model the total potential energy is separated into an intermolecular and an intramolecular contribution. The intermolecular part is assumed to be the sum of the slightly modified version of the CF potentials $U_{ij}^{CF}(r)$ [7]: $U_{OO}^{CF}(r)$ and $U_{OH}^{CF}(r)$ do not change but $U_{HH}^{CF}(r)$ is used only in the range of the intermolecular distances (approximately $r_{OH} > 1.35$ Å) while the H-H intermolecular part $U_{HH}^{CF}(r)$ was slightly modified [8] and its use restricted to intermolecular H-H distances (approximately $r_{HH} > 2.0$ Å). The intramolecular part is formulated

in terms of a power series in the internal coordinates r_{ij} and contains pair $U_{ij}^{intra}(r)$ as well as three-body $U_{ijk}^{intra}(r_{ij}, r_{ik}, r_{jk})$ contributions. Both potential forms are given by:

$$\begin{aligned} U_{OH,1,2}^{intra}(r_{OH,1,2}) &= L_{11}q_{1,2}^2 + L_{111}q_{1,2}^3 + L_{1111}q_{1,2}^4 \\ U_{HH}^{intra}(r_{HH}) &= L_{33}q_3^2 \end{aligned} \quad (2)$$

$$\begin{aligned} U_{OH_1H_2}^{intra}(r_{OH_1}, r_{OH_2}, r_{H_1H_2}) &= L_{12}q_1q_2 + L_{13}(q_1 + q_2)q_3 + \\ &L_{112}(q_1 + q_2)q_1q_2 + L_{113}(q_1^2 + q_2^2)q_3 + \\ &L_{1112}(q_1^2 + q_2^2)q_1q_2 + L_{1113}(q_1^3 + q_2^3)q_3 \end{aligned}$$

where

$$\begin{aligned} q_{1,2}(r_{OH,1,2}) &= (r_{OH,1,2} - r_E)/r_{OH,1,2} \\ q_3(r_{HH}) &= 2\alpha \cos(\theta_{HH}) - \theta_E \end{aligned} \quad (3)$$

with an equilibrium O-H distance $r_E = 0.9572$ Å and equilibrium bond angle $\theta_E = 1.8242$ rad. The potential functions $U_{ij}^{intra}(r)$ and $U_{ijk}^{intra}(r_{ij}, r_{ik}, r_{jk})$ with other combinations of the indexes i, j and k are assumed to be zero. The parameter set is given in Ref.[2].

3. Shifted force potential system

From the simulation with the shifted force potential we get the radial distribution function $g_{ij}^{CS}(r)$ for distances $0 < r < L/2$. From other side the reference system pair $h_{ij}^0(r)$ and direct $c_{ij}^0(r)$ correlation functions are connected by a system of Ornstein-Zernike integral equations:

$$h_{1j}^0(r_{12}) - c_{1j}^0(r_{12}) = \sum_k \int d\vec{r}_3 h_{1k}^0(r_{13}) c_{kj}^0(r_{32}) . \quad (4)$$

In order to close these equations we have used conditions [1]:

$$h_{1j}^0(r) = h_{1j}^{CS}(r), \quad r \leq L/2, \quad (5A)$$

$$c_{1j}^0(r) = F[h_{1j}^0(r)], \quad r > L/2. \quad (5B)$$

In the general case Eq.(4) with the conditions (5) can be solved numerically, e.g. using the method suggested by Labik, Malijevisky and Vonka [9]. In accordance with this scheme the function

$$\tau_{1j}^0(r) = h_{1j}^0(r) - c_{1j}^0(r) \quad (6)$$

has been introduced and the closure conditions (5) rewritten:

$$\begin{aligned} c_{1j}^0(r) &= g_{1j}^{CS}(r) - 1 - \tau_{1j}^0(r), \quad r \leq L/2 \\ &= f[\tau_{1j}^0(r)], \quad r > L/2 . \end{aligned} \quad (7)$$

Assuming for F in (5) the PY approximation

$$f[\tau_{1j}^0(r)] = (\exp[-\beta\phi_{1j}^{SF}(r)] - 1)(\tau_{1j}^0 + 1) \quad (8)$$

or HNC approximation

$$f[\tau_{1j}^0(r)] = \exp[-\beta\phi_{1j}^{SF}(r) + \tau_{1j}^0(r)] - \tau_{1j}^0(r) - 1 \quad (9)$$

the algorithm of Ref.[9], has been extended to a two-component system. For the solution of Eq.(4) a running parameter $d_{1j} \leq r_s < L/2$ has been introduced into the closure condition (7) instead of

fixed value $L/2$. The convergence of this solution is very fast. As initial estimate the ideal gas approximation is used ($\tau_{1j}^0(r) = 0$) and finally an approximate solution for $r_s \approx 3(L/2)/4$ is sufficient. The calculation was performed with 1024 grid points and with a grid of 0.02 Å.

The calculated $g_{1j}^0(r)$ according to (5) coincide with the simulated $g_{1j}^{CS}(r)$ for $r \leq L/2$ but extend to larger r . In this region $g_{1j}^0(r)$ are weakly oscillating functions around unity. Figure 2 shows the direct correlation functions $c_{1j}^0(r)$ for the SF system with HNC closure (9). In the present case, $c_{1j}^0(r)$ are not sensitive to the choice of the closure approximation f and decay very vast with distance just as for the Lennard-Jones fluid [10]. The first sharp peaks in $c_{1j}^0(r)$ are caused by the intramolecular part of the functions $h_{OH}^0(r)$ and $h_{HH}^0(r)$ and the next ones are connected with the first maxima in the intermolecular part of the $g_{1j}^0(r)$.

Knowing the functions $h_{1j}^0(r)$ and $c_{1j}^0(r)$ from the exact relation [11]

$$g_{1j}^0(r) = \exp[-\beta\phi_{1j}(r) + h_{1j}^0(r) - c_{1j}^0(r) + E_{1j}^0(r)], \quad (10)$$

the bridge functions of the SF system can be calculated:

$$E_{1j}^0(r) = \ln[g_{1j}^0(r)] + \beta\phi_{1j}(r) + h_{1j}^0(r) - c_{1j}^0(r) . \quad (11)$$

These functions play an important role in the theory of integral equations. A popular approach is based on the hypothesis of the universality of the bridge functions. It is assumed that they have the same form regardless of the potential. For example, in the RHNC theory [12,13] the bridge function for the hard sphere system was used with the diameter as adjustable parameter.

Figure 3 shows the bridge functions for the shifted force potential system in the region $r > d_{1j}$ derived from (11). For the

region $r < d_{1j}$, we must use instead of (11) the definition:

$$E_{1j}^0(r) = \ln[Y_{1j}^0(r)] - \tau_{1j}^0(r) \quad (12)$$

where the $Y_{1j}^0(r) = \exp[\beta\phi_{1j}(r)]g_{1j}^0(r)$ are the cavity distribution functions.

It is seen from Fig.3 that the bridge functions are monotonous. The negative value of $E_{OH}^0(r)$ is connected with the strong attractive OH interaction at small distances and cannot be obtained from the hard sphere model using the assumption of the universality. $E_{OO}^0(r)$ is larger than $E_{HH}^0(r)$ because of the more intensive repulsion between OO compared with HH. As r_0 is larger compared with the diameter of the water molecule, we can hope that the bridge function calculated for $\phi_{1j}(r)$ are very close to those for $U_{1j}(r)$ and thus $\Delta E_{1j}(r) = E_{1j}(r) - E_{1j}^0(r) = 0$ will be a good approximation. A similar behavior of $E_{1j}^0(r)$ was obtained also for the 2-2 ionic system [14].

4. Renormalization of the long-range interaction

In accordance with Ref.[1] renormalization of the long-range interaction can be obtained from the solution of the Ornstein-Zernike equation for functions $H_{1j}(r)$ and $C_{1j}(r)$:

$$H_{1j}(r) = h_{1j}^0(r) + G_{1j}(r), \quad (13)$$

$$C_{1j}(r) = c_{1j}^0(r) - \beta\phi_{1j}(r). \quad (14)$$

with the closure:

$$H_{1j}(r) = h_{1j}^{CS}(r), \quad r \leq d_{1j} \quad (15A)$$

$$C_{1j}(r) = c_{1j}^0(r) - \beta\phi_{1j}(r), \quad r > d_{1j}. \quad (15B)$$

With this aim special techniques, that have been developed in the theory of integral equations, have to be adopted in order to overcome the difficulties associated with the long-range part of the Coulomb potential. The traditional way combines the method introduced by Gillan [3] and improved by Malijevsky, Labik, Vonka [9] with the renormalization methods of Allnatt [15] and Rossky and Friedman [16], generalized for the many component Coulomb systems Ichiye and Haymet [5]. In the present paper we develop it for the long-range interaction $\phi_{1j}(r)$ which is Coulombic at large distances but not so $r < r_0$.

In accordance with the general scheme of the traditional renormalization procedure the functions $H_{1j}(r)$ and $C_{1j}(r)$ from (13), (14) are written in the form:

$$H_{1j}(r) = H_{1j}^S(r) + Q_{1j}(r), \quad (16)$$

$$C_{1j}(r) = C_{1j}^S(r) - \beta\phi_{1j}(r), \quad (17)$$

where $Q_{1j}^E(r)$ is the point renormalized potential determined from equation:

$$Q_{1j}(r_{12}) = -\beta\phi_{1j}(r_{12}) + \sum_k \rho_k \int d\vec{r}_3 Q_{1k}(r_{13})\phi_{kj}(r_{32}). \quad (18)$$

The solution of this equation in k-space has the form:

$$Q_{1j}^E(k) = \frac{\beta\phi_{1j}^E(k)}{1 + \beta\sum_1 \rho_1 \phi_{11}^E(k)} \quad (19)$$

The function $\phi_{1j}^E(r)$, which contain the Coulomb interactions, approximate $\phi_{1j}(r)$ quite well if we write:

$$\phi_{1j}^E(r) = Z_1 Z_j (1 - \exp[-tr])/r$$

They are depicted in Fig.4 for the value $t = 0.25\text{\AA}^{-1}$. The Fourier transform

$$\tilde{\Phi}_{1j}^E(k) = -4\pi\beta Z_1 Z_j t^2 / [k^2(k^2 + t^2)]. \quad (21)$$

decays rapidly with $k \rightarrow \infty$ and therefore numerical Fourier algorithms can be used successfully without the need of a very large integration range.

Taking into account (21) we get

$$\tilde{q}_{1j}^E(k) = \frac{4\pi\beta Z_1 Z_j t^2}{k^2(k^2 + t^2) + \alpha^2 t^2}, \quad (22)$$

where $\alpha^2 = 4\pi\beta \sum_0 Z^2$. After inverse Fourier transform an analytical expression for $q_{1j}^E(r)$ is obtained:

$$q_{1j}^E(r) = -\frac{\beta Z_1 Z_j t^2}{2ab} \frac{e^{-br} \sin ar}{r} \quad (23)$$

where

$$a = \frac{t}{2} \left[\frac{2\alpha}{t} - 1 \right]^{1/2}, \quad b = \frac{t}{2} \left[\frac{2\alpha}{t} + 1 \right]^{1/2}. \quad (24)$$

The parameter t in (24) is less unity and α^2 is large ($\sim 10^2$). It caused the peculiarity our application this renormalized procedure. The function $q_{1j}^E(r)$ in form (23) is different from the same one when $\Phi_{1j}^E(r)$ is Coulombic for all distances: $-\beta Z_1 Z_j e^{-\alpha r} / r$, which is in our case only correct for $t \rightarrow \infty$.

Subtracting (18) from the Ornstein-Zernike equation which connects $H_{1j}(r)$ and $C_{1j}(r)$ and with:

$$T_{1j}^S(r) = H_{1j}^S(r) - C_{1j}^S(r) \quad (25)$$

we write at equation:

$$\begin{aligned} T_{1j}^S(r_{12}) &= \sum_k \rho_k \int dr_3 [T_{1k}^S(r_{13}) + C_{1k}^S(r_{13}) + q_{1k}(r_{13})] C_{kj}^S(r_{32}) \\ &+ \sum_k \rho_k \int dr_3 C_{1k}^S(r_{13}) q_{kj}(r_{32}) \\ &+ \sum_{kl} \rho_k \rho_l \int \int dr_3 dr_4 [T_{1k}^S(r_{13}) + C_{1k}^S(r_{13}) + q_{1k}(r_{13})] C_{kl}^S(r_{34}) q_{lj}(r_{42}). \end{aligned} \quad (26)$$

Taking into account (16) and (5A), the closure of this equation, different from Ref.[5], is:

$$\begin{aligned} C_{1j}^S(r) &= -q_{1j}^E(r) + h_{1j}^{CS}(r) - T_{1j}^S(r), \quad r \leq d_{1j} \\ &= G_{1j}^O(r), \quad r > d_{1j}. \end{aligned} \quad (27)$$

Having solved Eq.(26) for the optimized renormalized potentials $G_{1j}(r)$ we obtain:

$$G_{1j}(r) = \Delta G_{1j}(r) + q_{1j}^E(r), \quad (28)$$

where

$$\Delta G_{1j}(r) = H_{1j}^S(r) - h_{1j}^O(r), \quad (29)$$

and, particularly, $\Delta G_{1j}(r) = -q_{1j}^E(r)$ for $r \leq d_{1j}$. The function $\Delta G_{1j}(r)$ for $r > d_{1j}$ is short-range, because $H_{1j}^S(r)$ and $h_{1j}^O(r)$ are short-range functions. At large values of the parameter r_c the functions $H_{1j}^S(r)$ and $h_{1j}^O(r)$ are very similar for $r > d_{1j}$ and we can assume that $\Delta G_{1j}(r) = 0$, which means:

$$G_{1j}(r) = q_{1j}^E(r), \quad r > d_{1j}. \quad (30)$$

Some words about choice of the parameter d_{1j} in this case. The RDFs for the flexible models of water can be subdivided into intramolecular and intermolecular parts:

$$g_{ij}(r) = g_{ij}^{intra}(r) + g_{ij}^{inter}(r) . \quad (31)$$

From our private MD simulations one concludes that intramolecular parts depend only weakly on the parameter r_c , and are at $r_c = L/2$ exactly the same as for the MD simulation with the Ewald method. Therefore, we included the intramolecular parts $g_{ij}^{intra}(r)$ into the optimize region and the parameters d_{ij} are chosen to be: $d_{OO} = 2.48\text{\AA}$, $d_{HH} = 2.08\text{\AA}$, $d_{OH} = 1.540\text{\AA}$.

5. Results and discussion

a. Structure

The radial distribution functions $g_{ij}(r)$ calculated by this approach are given in the simplest approximation by:

$$g_{ij}(r) = g_{ij}^O(r) + G_{ij}(r) \quad (32)$$

For $r \leq L/2$ they are the same as the ones calculated from the simulation with the Ewald method within the limits of statistical uncertainty: distance $\pm 0.02 \text{\AA}$, peak heights ± 0.1 (see Table I). The simulation does not provide the RDFs for $r > L/2$, but the $g_{ij}(r)$ can be calculated from the procedure given above for all distances. This information is not very important as far as the structure is concerned but it allows to calculate various thermodynamic, dielectric and kinetic properties in spite of the small basic box size used in the simulations.

b. Energy and pressure

This section contains the results for three thermodynamic quantities calculated by equations relating the thermodynamic properties to the pair and direct correlation functions.

The first is relation between the energy and the radial distribution functions from which the intermolecular mean potential

energy per molecule is given by:

$$\langle U \rangle = U^{CS} + U^\Phi + U^{\Delta g} \quad (33)$$

with

$$U^{CS} = \frac{1}{2\rho_w} \sum_{ij} \rho_i \rho_j \int_0^{r_c} g_{ij}^{CS,inter}(r) \phi_{ij}^{SF}(r) 4\pi r^2 dr , \quad (34)$$

$$U^\Phi = \frac{1}{2\rho_w} \sum_{ij} \rho_i \rho_j \int_0^\infty g_{ij}^{O,inter}(r) \phi_{ij}(r) 4\pi r^2 dr , \quad (35)$$

$$U^{\Delta g} = \frac{1}{2\rho_w} \sum_{ij} \rho_i \rho_j \int_0^\infty \Delta g_{ij}(r) U_{ij}(r) 4\pi r^2 dr . \quad (36)$$

for $R \rightarrow \infty$. Where $\Delta g_{ij}(r) = g_{ij}(r) - g_{ij}^O(r)$ and the indices 1 and j stand for O and H with the number densities $\rho_w = \rho_O = \rho_H/2 = 0.0335 \text{\AA}^{-3}$.

A similar relationship exists between the thermodynamic pressure P of the system and the radial distribution functions from which the compressibility factor can be calculated according to:

$$Z = \beta P / \rho_w = 3 + Z^{CS} + Z^\Phi + Z^{\Delta g} . \quad (37)$$

where

$$Z^{CS} = -\frac{\beta}{6\rho_w} \sum_{ij} \rho_i \rho_j \int_0^{r_c} g_{ij}^{CS,inter}(r) \frac{\partial \phi_{ij}^{SF}(r)}{\partial r} 4\pi r^3 dr .$$

$$+ \frac{\beta}{6\rho_w} \sum_{ij} \rho_i \rho_j \int_0^R g_{ij}^{CS,intra}(r) \frac{\partial U_{ij}^{intra}(r)}{\partial r} 4\pi r^3 dr$$

$$+ \frac{-\beta}{18\rho_w} \rho_O \rho_{H_1} \rho_{H_2} 8\pi^2 \int_0^R r_{OH_1} dr_{OH_1} \int_0^R r_{OH_2} dr_{OH_2}$$

$$r_{OH_1}^{+r_{OH_2}} \int dr_{H_1 H_2} r_{H_1 H_2} g_3^{intra}(r_{OH_1}, r_{OH_2}, r_{H_1 H_2}) v_3^{intra}(r_{OH_1}, r_{OH_2}, r_{H_1 H_2})$$

$$r_{OH_1}^{-r_{OH_2}}$$

$$Z^\phi = \frac{-\beta}{6\rho_w} \sum_{ij} \rho_i \rho_j \int_0^R g_{ij}^o(r) \frac{\partial \phi_{ij}(r)}{\partial r} 4\pi r^3 dr. \quad (39)$$

$$Z^{\Delta g} = \frac{-\beta}{6\rho_w} \sum_{ij} \rho_i \rho_j \int_0^R \Delta g_{ij}(r) \frac{\partial U_{ij}(r)}{\partial r} 4\pi r^3 dr. \quad (40)$$

The last term in (38) deals with the presence of the three-body interactions in the intramolecular part of the BJH potential. Instead of the three-body distribution function $g_3^{intra}(r_{12}, r_{13}, r_{32})$ the superposition approximation is used. $v_3^{intra}(r_{12}, r_{13}, r_{32})$ is a virial function which arises from the three-body intramolecular forces and is given by:

$$v_3^{intra}(r_{OH_1}, r_{OH_2}, r_{HH}) = \quad (41)$$

$$(r_{OH_1} \frac{\partial}{\partial r_{OH_1}} + r_{OH_2} \frac{\partial}{\partial r_{OH_2}} + r_{H_1 H_2} \frac{\partial}{\partial r_{H_1 H_2}}) v_3^{intra}(r_{OH_1}, r_{OH_2}, r_{H_1 H_2})$$

The indexes i and j in the second term of (38) stand for O, H₁ and H₂ with the number densities $\rho_{H_1} = \rho_{H_2} = \rho_w$.

The U^{CS} and Z^{CS} are obtained directly from the computer simulation results and give the mean intermolecular potential energy $\langle U^{SF} \rangle$ and together with the ideal gas contributions the compressibility factor Z^{SF} for the SF system, respectively. The U^ϕ and Z^ϕ result from the long-range part of the potential, $\phi_{ij}(r)$, while $U^{\Delta g}$ and $Z^{\Delta g}$ describe the contributions to the energy and pressure from the difference function $\Delta g_{ij}(r)$. The three contributions to the mean intermolecular potential energy $\langle U \rangle$ and

the compressibility factor Z are depicted separately in Figs.5 and 6, respectively. The Eqs. (34)-(36) and (38)-(40) are correct in principle only for $R \rightarrow \infty$. But it can be seen from both figures that for all practical purposes in our case R is infinity already beyond about 15 Å.

The intermolecular mean potential energy per molecule $\langle U \rangle$ does not depend on the intramolecular part of the potential. Therefore, the flexibility of the BJH model is not of relevance here and, consequently, the results for the energy obtained from different models are very close [17]. The pressure, in contrast to the intermolecular mean potential energy, is determined according to (38)-(40) by two contributions: the behavior of the intermolecular part of the potentials (similar as for the energy) and the form of the intramolecular part of the RDFs (where the derivatives of the potentials change very rapidly with r). Both contributions are large and of opposite sign. This can be a source of considerable errors and result can strongly depend on the choice of the water model as well as on the method [17]. The resulting difference should compensate the ideal gas contribution.

Since, in our case, the intramolecular part of the RDF's does not depend on the long-range interactions, the intramolecular contribution to the pressure is calculated practically exactly. The error caused by the superposition approximation for the three-body RDF $g_3^{intra}(r_{12}, r_{13}, r_{32})$ can be ignored due to the small contribution from the last integral in (38), which amount to only 0.3% of the two-body contribution. For the same reason this integral may also be approximated by representing the intramolecular parts of the oxygen-hydrogen and hydrogen-hydrogen RDF's by Dirac delta functions with the positions of the maxima at $a_{OH} = 0.9753 \text{ \AA}$ and $a_{HH} = 1.5 \text{ \AA}$. Then, three-body interactions can be calculated analytically. In this case the three-body contributions amount to 0.2% of the two-body contribution. While this approximation would be acceptable here, it may not be useful for other properties or other liquids.

In Tables II and III, our results are compared with those calculated from simulations of Stillinger and Rahman (Ewald summation)[7] and of Andrea et al. (truncation by switching

function) [18] with the same CF model of water in both cases as well as with experimental data. It can be seen that Ewald summation as well as the truncation at sufficiently large distances lead to fair agreement with the experimental values for both energy and pressure. The same is true for the results achieved here. The shifted force potential by itself would give rather poor results, which lie outside the region between Ewald summation and truncation. But the way to calculate the long-range correction via renormalized potentials leads to a significant improvement.

The calculation of the intermolecular contribution to energy and pressure can be improved by more precise calculations of the renormalized potentials $G_{ij}(r)$ and, of course, by using of higher order approximations for the radial distribution function $g_{ij}(r)$. This will be investigated in a future communication.

c. Isothermal compressibility

Finally, a third relation between thermodynamics and the correlation functions allows us to calculate the isothermal compressibility of the liquid. In our case, this relation can be written conveniently in terms of the direct correlation functions $c_{ij}(r)$. Assuming for this function approximation $c_{ij}(r) = c_{ij}^0(r) - \beta\phi_{ij}(r)$ for all distances, not just for $r > d_{ij}$, thus neglecting the contribution from the optimization procedure, we obtain for the isothermal compressibility:

$$k_T = \frac{1}{\rho_w kT} \left[1 - 4\pi \sum_{i=O,H} \rho_i \int c_{O1}^0(r) r^2 dr \right]^{-1}, \quad (42)$$

where the $c_{ij}^0(r)$ are the direct correlation functions for the reference system as depicted in Fig.2. These correlation functions cannot be separated into inter- and intramolecular parts like the RDFs. Therefore, different from the calculation of the mean

interaction energy and the compressibility factor, Eq.(42) cannot be employed directly for the calculation of the isothermal compressibility in the case of rigid models.

There is good agreement between the value for k_T calculated with this procedure and the experimental one as can be seen from Table IV where the results for k_T from three other simulations are listed additionally. In two of these simulations, k_T was calculated from the density fluctuations [19,20], while in the third case the finite difference approximation $\Delta \ln \rho / \Delta P$ was employed [21]. Ruff and Diestler [19] pointed out that it is difficult to calculate a reliable value from the density fluctuations as the convergence of this procedure is very slow. This might be the reason why their data differ significantly from the value calculated by Jorgensen and Madura [20] and the experimental one. A much longer simulation time is expected to reduce this discrepancy. There is excellent agreement between our result and the value calculated by Motakabbir and Berkowitz [21] from $\Delta \ln \rho / \Delta P$. Although both methods lead to good agreement with the experimental result, the procedure proposed here has the advantage that the isothermal compressibility can be calculated from the RDFs of a single simulation, which can be relatively short as only structural properties are of relevance.

6. Summary and Conclusions

In the present paper the scheme of combining computer simulation methods, optimized cluster theory and theory of integral equations to describe the properties aqueous electrolyte solutions with the BJH model of water is presented. It contains the following steps:

- (a) separation of the total interaction potential into short- and long-range parts;
- (b) computer simulation of the subsystem with the short-range part (reference system);

- (c) description of the reference system;
- (d) renormalization and optimization of the long-range part;
- (e) correction of the results for the reference system.

Step (a) is in general not unique. However, the final outcome should not depend on this point. By the interplay of steps (b) and (e) an optimal separation can be found. The reference potentials should be sufficiently short-ranged to perform computer simulations without Ewald summation or other elaborate methods (b) but step (e) requires to include into the reference system the range of the potential minimum. The description of the reference system (c) means that the simulated pair correlation function $h_{ij}^{CS}(r)$ has to be extended to large r in order to deduce the direct correlation function $c_{ij}^O(r)$. It is suggested that the Ornstein-Zernike equation is employed for this procedure. In step (d) we used the traditional renormalization technique for the long-range interaction which is Coulombic for long distances. For the correction procedure (e) the development of the cluster series or the solution of the integral equation are suggested.

The usefulness of the proposed scheme for the calculation of structural and thermodynamic properties of pure water has been demonstrated for the case where the water-water interactions are described by a BJH model.

Acknowledgements

We are indebted to I.R.Yukhnovskij, P.Bopp and A.D.J.Haymet for helpful discussions. Financial support by the Ukrainian Academy of sciences and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- [1] Holovko, M.F. and Trokhymchuk, A.D., 1989, Preprint Inst. for Theoretical Physics # 47E, (Kyiv).
- [2] Bopp, P., Janoso, G., Heinzinger, K., 1983, Chem. Phys. Lett., **98**, 129.

- [3] Gillan, M.J., 1979, Molec. Phys., **38**, 1781.
- [4] Larsen, B., 1978, J. Chem. Phys., **68**, 4511. Larsen, B., and Rogde, S.A., 1980, J. Chem. Phys., **72**, 2578.
- [5] Ichiye, T. and Haymet, A.D.J., 1988, J. Chem. Phys., **89**, 4315.
- [6] Street, W.B., Tildesley, D.J., and Saville, G., 1978, ACS Symp. Series, **86**, 144.
- [7] Stillinger, F.H., and Rahman, A., 1978, J. Chem. Phys., **68**, 666.
- [8] Janoso, G., Bopp, P. and Heinzinger, K., 1984, Chem. Phys., **85**, 377.
- [9] Labik, S., Malijevsky, A., Vonka, P., 1985, Molec. Phys., **56**, 709.
- [10] Allen, M.P., and Tildesley, D.J., 1987, *Computer Simulation of Liquids* (Clarendon Press).
- [11] Hansen, J.P., and McDonald, I.R., 1976, *Theory of Simple Liquids* (Academic Press)
- [12] Rosenfeld, Y., and Ashcroft, N.W., 1979, Phys. Rev., **A20**, 1208.
- [13] Lado, F., Poiles, S.M., and Ashcroft, N.W., 1983, Phys. Rev., **A28**, 2374.
- [14] Ichiye, T., and Haymet, A.D.J., 1990, J. Chem. Phys., **93**, 8954.
- [15] Allnatt, A.R., 1964, Molec. Phys., **8**, 533.
- [16] Rossky, P.J., and Friedman, H.L., 1980, J. Chem. Phys., **72**, 5694.
- [17] Reimers, J.R., Watts, R.O., and Klein, M.L., 1982, Chem. Phys., **64**, 95.
- [18] Andrea, T.A., Swope, W.C., and Andersen, H.C., 1983, Molec. Phys., **79**, 4576.
- [19] Ruff, I., and Diestler, D.J., 1990, J. Chem. Phys., **93**, 2032.
- [20] Jorgensen, W.L., and Madura, J.D., 1985, Molec. Phys., **56**, 1381.
- [21] Kotakabir, K.A., and Berkowitz, M., 1990, J. Phys. Chem., **94**, 8359.

Received April 20, 1992

TABLE I. Numerical comparison of atom-atom radial distribution functions for pure water

	Ewald	calcul.	expt ^c
g_{OO} first maximum:			
height	3.208	3.113	2.3
position, Å	2.825	2.850	2.85
g_{HH} first maximum:			
height	1.632	1.637	1.42
position, Å	2.325	2.325	2.4
g_{OH} first maximum:			
height	1.543	1.486	1.19
position, Å	1.900	1.925	1.97

^aref. [7]TABLE II. Intermolecular mean potential energy per molecule $\langle U \rangle$ in kJ/mol

MD ^a	MD ^b	SF ^c	calc. ^c	expt ^d
-39.70	-41.25	-34.40	-40.63	-41.42

^a CF model and Ewald summation at 304 K [7]^b CF model and truncation by switching function at 304 K [18]^c this work^d ref. [21]TABLE III. Compressibility factor $Z = \beta P/\rho_w$

MD ^a	MD ^b	SF ^c	calc. ^c	expt ^d
0.1±0.1	2.36±0.06	2.7	1.3	0.07

^a CF model and Ewald summation at 304 K [7]^b CF model and truncation by switching function at 304 K [18]^c this work^d ref. [18]TABLE III. Isothermal compressibility k_T (in 10^{-11}Pa^{-1})

MD ^a	MC ^b	MD ^c	calc. ^d	expt ^e
33.00	67±13	41.4±2.0	41.36	45.25

^a CF model and Ewald summation at 304 K [19]^b TIP4 model and truncation at $r_o = 8.5 \text{ Å}$ and 298 K [20]^c SPC/E model and reaction field at 298 K [21]^d this work^e ref. [21]

Figure Captions

Fig. 1 Total (—) and shifted force (---) potentials for the intermolecular part of the BJH model of water.

Fig. 2 The direct correlation functions $c_{ij}^O(r)$ for the shifted force potential used as a reference system. These functions are obtained from the solution of Eq.(4) with the closure conditions (5).

Fig. 3 Bridge function for the shifted force potential used as a reference system.

Fig. 4 The long-range part of the pair potential for the BJH model of water (—) and its approximation (---).

Fig. 5 The contributions of the integrals (34) - (36) to the intermolecular mean potential energy per molecule $\langle U \rangle$ as a function of their upper limits: U^{CS} (—), U^{Φ} (---) and $U^{\Delta g}$ (.....).

Fig. 6 The contributions of the integrals (38) - (40) to the compressibility factor Z as a function of their upper limits: Z^{CS} (—), Z^{Φ} (---) and $Z^{\Delta g}$ (.....).

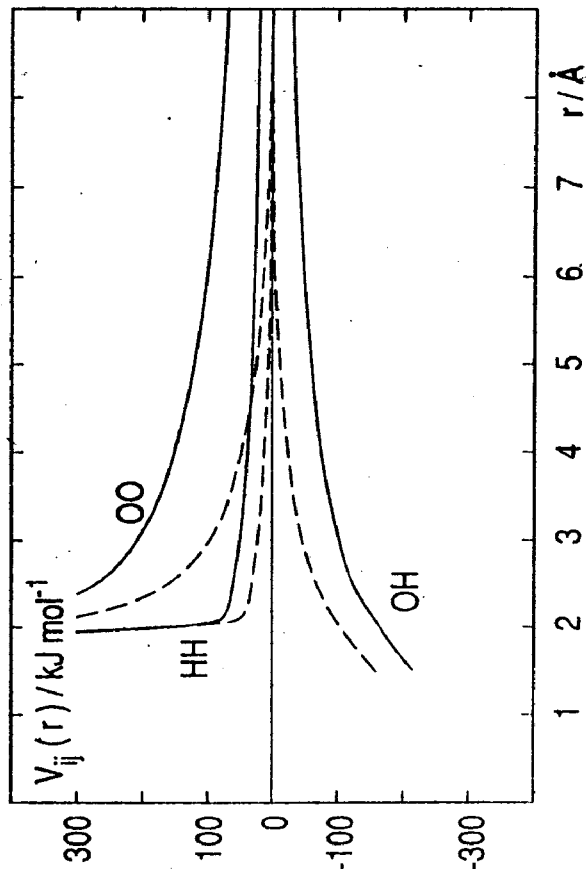


Fig. 1

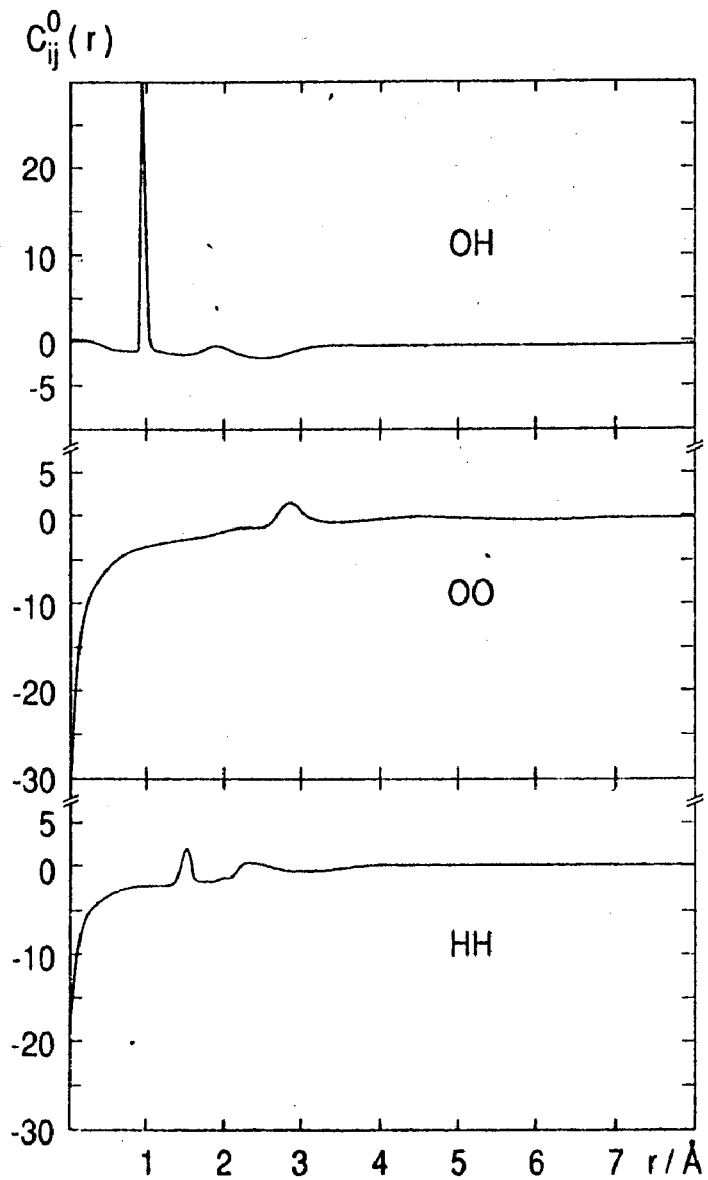


Fig. 2

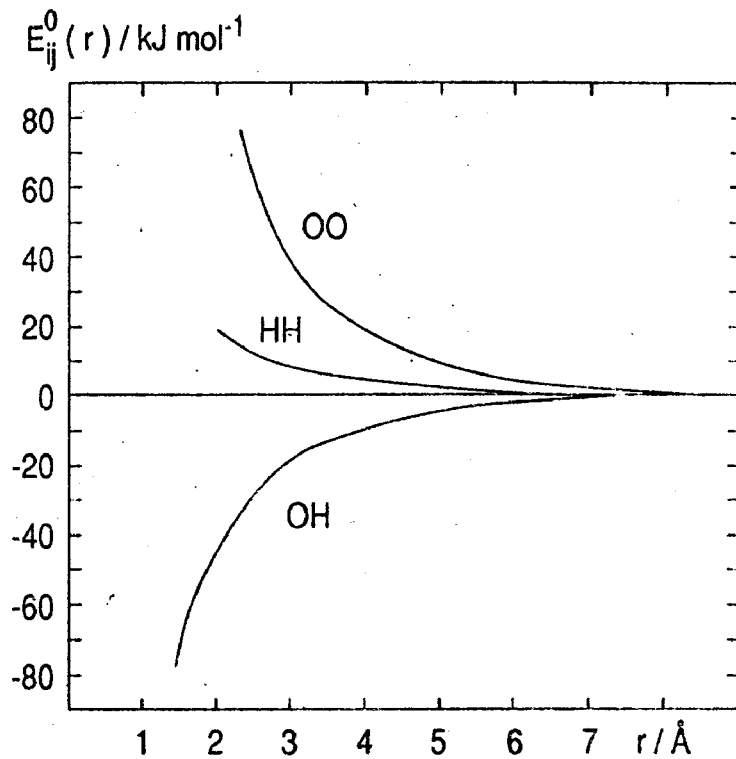


Fig. 3

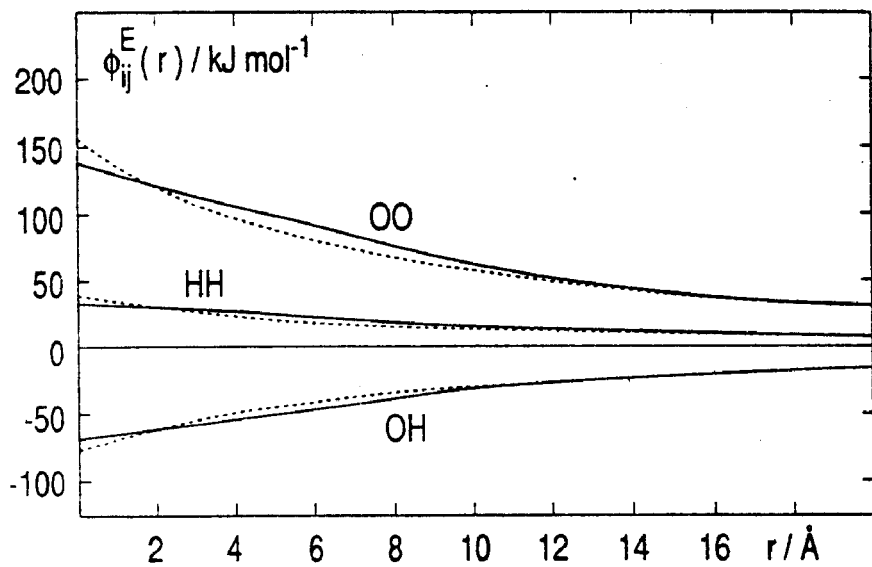


Fig. 4

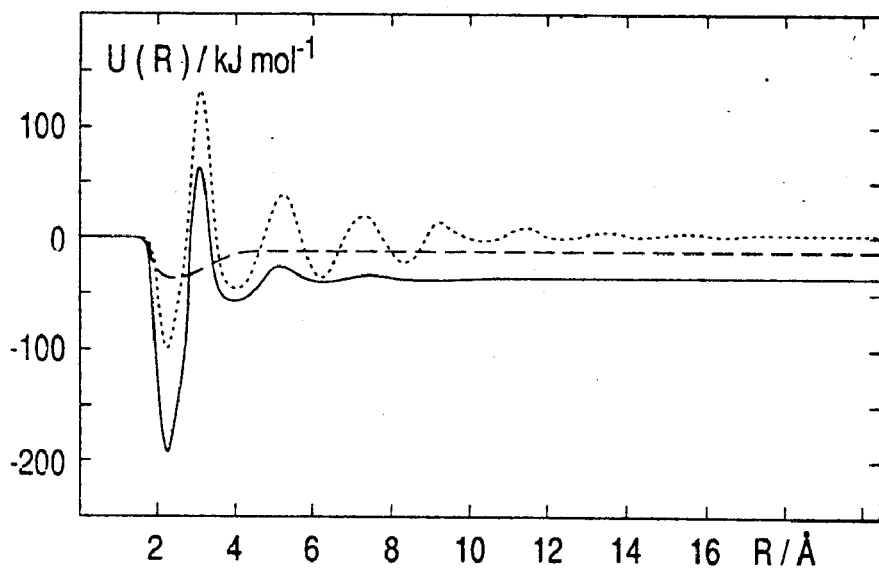


Fig. 5

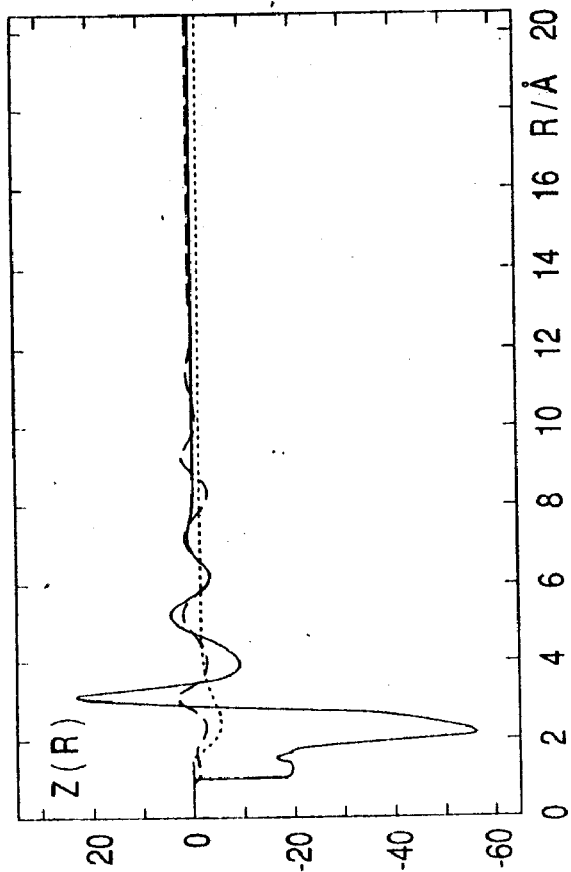


Fig. 6

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Затверджено до друку вченою радою ІФЖС АН України

Редактор А.О.Храброва Техн.редактор О.О.Бунькова
Зам. 134 Формат 60x84/16. Обл.-вид.арк. 1,63
Підписано до друку 30.04.1992 р. Тираж 100. Ціна 1 крб. 44 коп.
Поліграфічна дільниця Інституту теоретичної фізики АН України