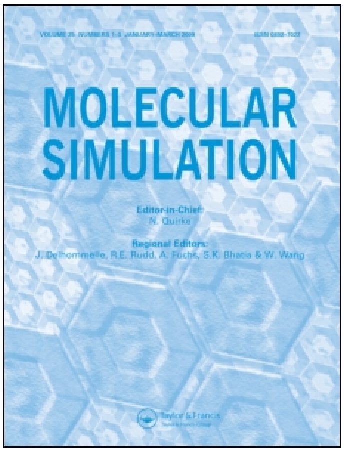
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Monte Carlo Simulation of Liquid Water and an Evaluation of Thermodynamic Properties

Kazuhiko Honda[a]; Kazuo Kitaura[b]; Kichisuke Nishimoto[a]
[a] Department of Chemistry, Osaka City University, Osaka, Japan [b] Institute for Molecular Science, Okazaki, Japan

To cite this Article Honda, Kazuhiko , Kitaura, Kazuo and Nishimoto, Kichisuke(1991) 'Monte Carlo Simulation of Liquid Water and an Evaluation of Thermodynamic Properties', Molecular Simulation, 6: 4, 275 — 289

To link to this Article: DOI: 10.1080/08927029108022436

URL: http://dx.doi.org/10.1080/08927029108022436

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 1991, Vol. 6, pp. 275–289
Reprints available directly from the publisher
Photocopying permitted by license only

MONTE CARLO SIMULATION OF LIQUID WATER AND AN EVALUATION OF THERMODYNAMIC PROPERTIES

KAZUHIKO HONDA*, KAZUO KITAURA** and
KICHISUKE NISHIMOTO*

**Department of Chemistry, Osaka City University, Sumiyosi-Ku, Osaka 558, Japan*
***Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

(*Received May 1990, accepted October 1990*)

Monte Carlo simulations were performed on liquid water using a new intermolecular potential function. For the evaluation of the thermodynamic properties of liquid water, simple expressions were proposed for the energies and the partition function, which reproduces the results of simulations reasonably. Various thermodynamic properties including heat capacities and compressibility were obtained from the partition function. The anomalous properties of liquid water were well reproduced by the calculation.

KEY WORDS: Liquid water, thermodynamic properties, partition function, Monte Carlo simulation.

1. INTRODUCTION

In a previous paper [1], we have proposed a new intermolecular potential function which is expressed in terms of intermolecular overlap integrals over localized orbitals of constituent molecules and electrostatic potentials between fractional point charges on the atoms in these molecules. In this paper, the potential function is applied to Monte Carlo simulations of liquid water.

Many statistical mechanical models have been proposed for liquid water [2,3,4,5]. The Monte Carlo (MC) and molecular dynamics (MD) techniques have been also applied to liquid water. A few of them, however, have been concerned with the thermodynamic properties because of difficulties in the numerical calculation of these properties. Recently Kataoka and his coworkers have succeeded in reproducing the characteristic futures of thermodynamic properties of liquid water using the results of MC and MD simulations [6]. They have carried out computations at various temperatures and densities and obtained an equation of state, from which various thermodynamic properties have been evaluated.

In the present paper, we propose a simple expression of partition function which involves some parameters to be evaluated using the results of MC simulation. From the partition function, the thermodynamic properties are derived.

2. INTERMOLECULAR POTENTIAL FUNCTION

The potential function between H_2O molecules, $V_{H_2O,\ H_2O}$, is expressed by intermolecular overlap integrals and intermolecular electrostatic interactions as follows;

$$
\begin{aligned}
V_{H_2O,H_2O} = {} & C_{OH,OH} \sum_{\substack{i\in OH\\ j\in OH}} S_{ij}^2 + C_{OH,\sigma L} \sum_{\substack{i\in OH\\ l\in \sigma L}} S_{il}^2 + C_{OH,\pi L} \sum_{\substack{i\in OH\\ n\in \pi L}} S_{in}^2 \\
& + C_{\sigma L,\sigma L}\, S_{\sigma L,\sigma L}^2 + C_{\sigma L,\pi L} \sum_{\substack{k\in \sigma L\\ n\in \pi L}} S_{kn}^2 + C_{\pi L,\pi L}\, S_{\pi L,\pi L}^2 \qquad (1)\\
& + C_{OH^*,OH} \sum_{\substack{i^*\in OH\\ J\in OH}} S_{i^*j}^2 + C_{OH^*,\sigma L} \sum_{\substack{i^*\in OH\\ l\in \sigma L}} S_{i^*l}^2 + C_{OH^*,\pi L} \sum_{\substack{i^*\in OH\\ n\in \pi L}} S_{i^*n}^2 \\
& + \sum \frac{Q_r Q_s}{R_{rs}}
\end{aligned}
$$

A H_2O molecule has six localized orbitals; two O–H bonding (OH), two O–H antibonding (OH•), and two lone pair (σL and πL) orbitals. S_{ij} in Equation (1) refers to the intermolecular overlap integrals associated with localized orbitals, i and j. $C_{A,B}$ is the parameter for a given bond–bond pair which is determined to reproduce *ab initio* interaction energies with the least square technique. The values of C's are given in the previous paper [1]. The first six terms of Equation (1) expresses the exchange type repulsions, and the next three terms for charge transfer type interactions. the last term of Equation (1) is the electrostatic interaction potential, where Q_r means the fractional charge on the r-th atom. Details of this potential function is referred to the previous paper [1].

3. MONTE CARLO SIMULATION

Monte Carlo simulations [7] were performed in the standard manner using periodic boundary conditions and Metropolis sampling algorithm [8] for 125 molecules in the base cell. Equilibration was achieved after 10 K steps and additional 20 K steps were averaged, where one step means 125 attempted moves. The calculations were carried out at various temperatures and densities including rather high temperatures and low densities (see Table 1). Large fluctuation of configurational energies, which suggests that the system was not mechanically stable, was not found in all calculations.

In the Monte Carlo simulation, the potential functions for molecular pairs must be calculated more than 10^8 times. The most time consuming part of our potential functions is the calculations of overlap integrals. In order to save the computation time, we tabulated the diatomic overlap integrals and interpolated them to obtain required integrals in the simulation. This makes the calculations ten times as faster than that of the analytical evaluation. The detail of computational procedure is given in Appendix.

4. PARTITION FUNCTION

Our simple model of liquid water is based on the following assumptions;

1) A base cell includes m molecules, which is statistically independent assembly.
2) A rigid body approximation of H_2O molecule is employed and only six degrees of freedom, three translations and three rotations, are taken into account.
3) All 6 m degrees of freedom are assigned to harmonic oscillators [9], except only

one degree of freedom which is regarded as a "reaction coordinate" [10]. The "reaction coordinate" allows the system to rearrange hydrogen bonds.

Our model is almost the same with the usual harmonic oscillator models of liquids [6]. However, the assumption 3) improves the usual harmonic oscillator model, since it takes the conformational energy change due to the rearrangements of hydrogen bonds into account. This model may be applied to other hydrogen bonding liquids such as liquid hydrogen fluoride.

By the assumption 1), a partition function for a system consisting of N molecules, $Z(N,T,V)$, is expressed by that of m molecules, $Z(m,T,V)$;

$$Z(N,T,V) \propto \{z(m,T,V)\}^{N/m} \tag{2}$$

The energy of base cell, E^T, is given by the assumptions 2) and 3), as follows,

$$E^T = E^H + \sum_{j=1}^{6m\text{-}1} \left(n_j + \frac{1}{2}\right) h\nu_j \tag{3}$$

The first term of the right hand side of Equation (3) represents the energy associated with hydrogen bonds, and the second expresses that of harmonic oscillators. E^H is assumed to be written as a function of the number of hydrogen bonds, n_H:

$$E^H = E^K + E_H n_H + E_0 \tag{4}$$

where the first term gives the contribution from kinetic energy. The second term is proportional to the number of hydrogen bonds and is associated with a conformational energy change due to hydrogen bond rearrangements. E_H in Equation (4) measures an energy per one hydrogen bond. This term is referred to as "bond", hereafter. The third term does not depend on the number of hydrogen bonds. This term is referred to as "potential". Note that E_H and E_0, are the function of the density of base cell. This will be discussed in section 6.

Using Equation (3), the partition function of base cell is written straightforwardly by

$$Z(m,T,V) = Z^{\mathrm{H}} \cdot Z^U \tag{5}$$

where Z^H is a partition function associated with the hydrogen bond term and Z^U is that associated with harmonic oscillator term. Z^H is written from Equation (4) as,

$$Z^H = Z^K \cdot Z^B \cdot Z^P \tag{6}$$

Z^K is a partition function corresponding to E^K in Equation (4). Z^B and Z^P are the "bond" and the "potential" terms, respectively, and are expressed as follows;

$$Z^B = \sum_{n_H=0}^{n_H\max} g(n_H)\exp\{-E_H n_H/k_B T)\} \tag{7}$$

$$Z^P = \exp\{-E_0/k_B T)\} \tag{8}$$

where $g(n_H)$ means the density of states of base cell having n_H hydrogen bonds. $n_H$max is the maximum number of hydrogen bonds in the system with m molecules. The summation in Equation (7) may be replaced by the following integral;

$$Z^B = \int_{n_H=0}^{n_H\max} g(n_H)\exp\{-E_H n_H/(k_B T)\} dn_H \tag{9}$$

Z^U in Equation (5) can be expressed as

$$Z^U = \prod_j^{6m-1} \frac{1}{2\sinh\{h\nu_j/(2k_BT)\}}, \tag{10}$$

where each oscillator is assumed to be independent.

The partition function of the whole system is, therefore, expressed as

$$\ln Z(N,T,V) = \frac{N}{m}(\ln Z^K + \ln Z^B + \ln Z^P + \ln Z^U) \tag{11}$$

In Equation (11), the constant term for T and V was omitted. Hereafter $\ln Z^K$ is neglected because the term is small as compared with the other terms.

The parameters involved in the partition function of the present model will be determined using the results of the Monte Carlo simulations (see section 6).

5. DERIVATIONS OF THERMODYNAMIC PROPERTIES FROM THE PARTITION FUNCTION

All thermodynamic properties of a given system can be evaluated, using the partition function. In order to carry out numerical calculations, we should take further assumptions.

It is assumed that $\ln g(n_H)$ (Equation (9)) may be written by the following quadratic function:

$$\ln g(n_H) = an_H^2 + bn_H \tag{12}$$

Parameters a and b are determined using the results of Monte Carlo simulations. This assumption will be rationalized later in section 7 by the comparison of the distribution function of hydrogen bonds, P_{n_H}, obtained from the partition function with that from the Monte Carlo simulations. For the volume dependence of ν_j in the partition function of harmonic oscillator, Grüneisen approximation [11] is used. Namely,

$$\frac{d\ln\nu_j}{dV} = -\frac{\gamma}{V} \tag{13}$$

where V is the volume of system and γ is a parameter.

Various thermodynamic properties are evaluated straightforwardly from the partition function by the following manner.

1) Average number of hydrogen bonds, $\langle n_H \rangle$

The average number of hydrogen bond, $\langle n_H \rangle$, is an fundamental quantity in our model for representing other thermodynamic properties. $\langle n_H \rangle$ is defined as the expectation value of n_H,

$$\begin{aligned}\langle n_H \rangle &= \int_{n_H=0}^{n_h\max} n_H \cdot g(n_H)\exp\{-E_H n_H/(k_BT)\}dn_H/Z^B \\ &= \int_x^{x+n_H\max} (t-x)\cdot\exp(at^2)dt/Z^B \\ &= -x + \frac{1}{2a}\frac{\partial \ln A(x)}{\partial x}\end{aligned} \tag{14}$$

where

$$A(x) = \int_{x}^{x+n_H\max} \exp(at^2)dt,$$

$$x = \frac{b - E_H/(k_B T)}{2a} \tag{15}$$

2) Internal energy, $\langle E\rangle$

$$\langle E\rangle = \frac{N}{m}(E_H \langle n_H\rangle + \langle E_\theta\rangle + \langle E^U\rangle) \tag{16}$$

where

$$\langle E^U\rangle = \sum_{j}^{6m-1}{}' \left[\frac{hv_j}{2} + \frac{hv_j}{\exp\{hv_j/(k_B T)\} - 1}\right] \tag{17}$$

3) Heat capacity at constant volume, C_v

$$C_v = \frac{N}{m}(C_v^B + C_v^U) \tag{18}$$

where

$$\begin{aligned} C_v^B &= E_H \frac{\partial\langle n_H\rangle}{\partial T} \\ &= - \frac{E_H^2}{2ak_B T^2}\left\{- \frac{1}{2a}\frac{\partial^2 \ln A(x)}{\partial x^2} + 1\right\} \end{aligned} \tag{19}$$

$$C_v^U = k_B \sum_{j}^{6m-1}{}' \frac{\exp\{hv_j/(k_B T)\}}{[\exp\{hv_j/(k_B T)\} - 1]^2}\{hv_j/(k_B T)\}^2 \tag{20}$$

4) Pressure, P

$$P = \frac{N}{m}\left(- \langle n_H\rangle \frac{\partial E_H}{\partial V} - \frac{\partial E_0}{\partial V} + \gamma\frac{\langle E^U\rangle}{V}\right) \tag{21}$$

5) Isothermal compressibility, κ_T

$$\kappa_T = \frac{1}{-\frac{N}{m}V\left(- \langle n_H\rangle\frac{\partial^2 E_H}{\partial V^2} - \frac{\partial\langle n_H\rangle}{\partial V}\frac{\partial E_H}{\partial V} - \frac{\partial^2 E_0}{\partial V^2} + \frac{\gamma^2 C_v^U T - \gamma\langle E^U\rangle - \gamma^2\langle E^U\rangle}{V^2}\right)} \tag{22}$$

where

$$\frac{N}{m}\frac{\partial\langle n_H\rangle}{\partial V} = - \frac{C_v^B T}{E_H^2}\frac{\partial E_H}{\partial V} \tag{23}$$

6) Coefficient of thermal expansion, α_p

$$\alpha_p = \frac{N}{m}\left(- \frac{\partial\langle n_H\rangle}{\partial T}\frac{\partial E_H}{\partial V} + \gamma\frac{C_v^U}{V}\right)\kappa_T \tag{24}$$

where

$$\frac{N}{m}\frac{\partial\langle n_H\rangle}{\partial T} = \frac{C_v^B}{E_H} \tag{25}$$

7) Heat capacity at constant pressure, C_p

$$C_p = C_v + \frac{\alpha_p^2 VT}{\kappa_T} \tag{26}$$

Since the molecules are weakly bound each other, an approximation of $h\nu_j \ll k_B T$ can be used. In this case, Equation (17) is redued to

$$\langle E^L\rangle \simeq \sum_j^{6m-1} \frac{h\nu_j}{\exp\{h\nu_j/(k_B T)\} - 1} \simeq \sum_j^{6m-1} \frac{h\nu_j}{1 + \{h\nu_j/(k_B T)\} - 1}$$
$$= \sum_j^{6m-1} k_B T \simeq 6\mathrm{m}k_B T$$

This is the classical harmonic oscillator approximation. In Equation (27), the contribution from the "reaction coordinate" is neglected because it is very small compared with that of $6m$ ($6m \gg 1$). This neglection may be partly canceled with the neglection of E^k in Equation (4).

6. EVALUATION OF PARAMETERS

All parameters involved in the partition function were determined using the results of Monte Carlo simulations. Figure 1 shows the plots of averaged configurational energies, E_z's, versus the number of hydrogen bonds, n_H, at various temperatures. Since E_H is the configurational energy change associated with the formation or breaking of one hydrogen bond, it is given by $m \times \partial E_z/\partial n_H$ in Figure 1. The number of hydrogen bonds in a given configuration obtained by Monte Carlo simulations is

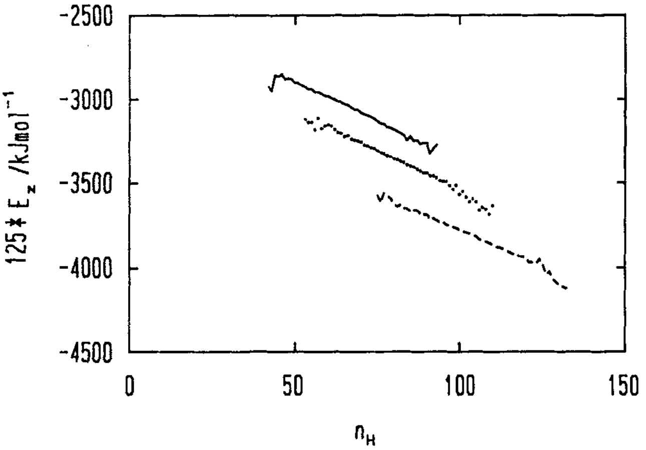


Figure 1 Plots of average configurational energy, E_z, against number of hydrogen bonds, n_H, in 125 molecular systems at 450 K (solid line), 400 K (dotted line) and 350 K (dashed line), respectively. Density is $1.0\,\mathrm{gcm^{-3}}$.

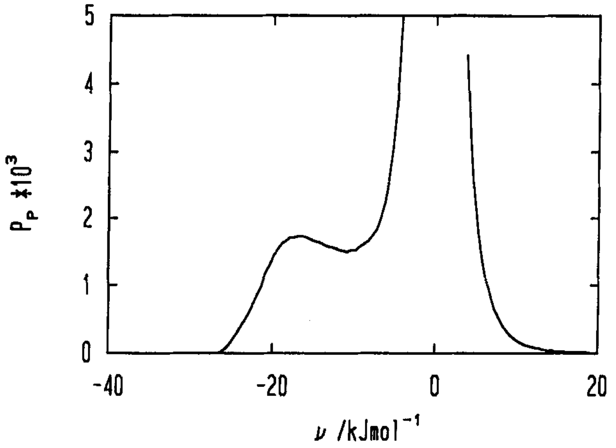


Figure 2 Pair energy distribution function at 400 K, 1.0 gcm^{-3}.

counted using a threshold energy of $-16.0\,\mathrm{kJmol^{-1}}$ referring the pair energy distribution function shown in Figure 2. We counted n_H's of more than 20 K configurations, and calculate each energy of configurations having the same number of n_H.The calculated configurational energies are roughly proportional to the number of hydrogen bonds. This result provides an evidence of the reasonableness of our assumption that the energy is written by Equation (4). At the both sides of each line E_z versus n_H in Figure 1, there are zigzags because of large statistical error due to the small frequency of occurrence.

Figure 3 shows the density dependence of E_H. In order to reduce the statistical errors, Monte Carlo simulations were carried out at rather high temperature, 650 K. 650 K is nearly the critical temperature of liquid water [12]. E_H's are obtained using

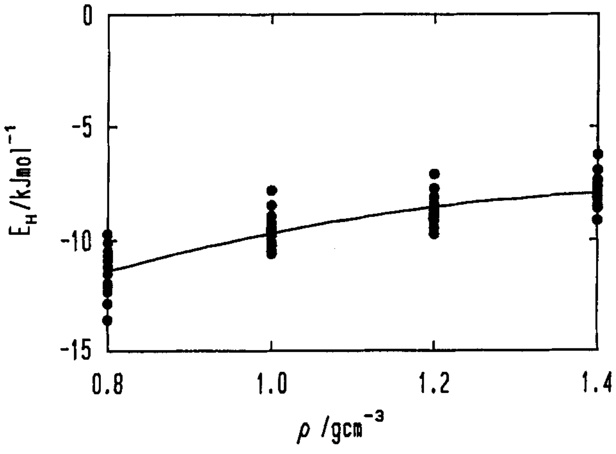


Figure 3 Density dependence of E_H at 650 K. Each circle corresponds to the value for pair energy threshold (-8, -9, . . . $-19\,\mathrm{kJmol^{-1}}$). The solid line shows the result obtained by the least square fitting using Equation (28).

the different threshold energies of -8.0 to $-19.0\,\mathrm{kJmol^{-1}}$ for counting the number of hydrogen bonds. As seen from Figure 3, E_H does not depends largely on the threshold energy used. When we use the threshold energy of $-16.0\,\mathrm{kJmol^{-1}}$ at 400 K, $1.0\,\mathrm{gcm^{-3}}$, then the average number of hydrogen bonds per molecule, $\langle n_H \rangle / m$, is calculated to be 0.636. This value is comparable with that of the Stillinger's estimation [13].

The density dependence of E_H is found to be expressed by quadratic equation of the density (0.8–$1.4\,\mathrm{gcm^{-3}}$):

$$E_H = a_H(\rho - \rho_H)^2 + b_H \tag{28}$$

E_H is calculated to be $-9.7\,\mathrm{kJmol^{-1}}$ at the density of $1.0\,\mathrm{gcm^{-3}}$. This value is surprisingly small compared with the hydorgen bond energy of H_2O dimer in gas phase ($-26.4\,\mathrm{kJmol^{-1}}$ [1]). It is noted that E_H measures the energy associated with the conformational change caused by a hydrogen bond formation or hydrogen bond breaking in the liquid phase, but does not measures the usual hydrogen bond energy. A part of usual hydrogen bond energy is involved in E_0 in the liquid phase.

The parameters a and b of the density of states, $g(n_H)$ in Equation (12) are evaluated using the values of $\langle n_H \rangle$, (Equations (14)), and C_v^B, (Equations (19)). $\langle n_H \rangle$ and C_v^B are obtained from the results of Monte Carlo simulations. Furthermore the value of $n_H\max$ is needed for the calculation of the function $A(x)$ (Equation (15)) which is appeared in Equations (14) and (19). Each H_2O molecule can have four hydrogen bonds at maximum. Therefore n_H max in base cell is reasonably assumed to be

$$n_H \max = \frac{4\mathrm{m}}{2} \tag{29}$$

From Equation (18), C_v^B can be written by

$$\frac{N}{m} C_v^B = C_v - \frac{N}{m} C_v^u$$

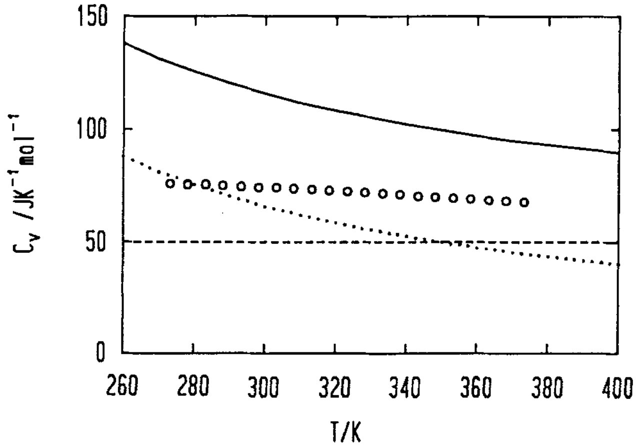


Figure 4 Temperature dependence of heat capacity at constant volume, C_v, at 0.1 MPa calculated by the partition function (solid line) with the contribution from the "bond" term (dotted line), and from oscillators (dashed line). Circles are experimental data [12].

$$= C_v - 6Nk_B \tag{30}$$

where

$$C_v^u = \frac{\partial\langle E^u\rangle}{\partial T} = 6mk_B \tag{31}$$

C_v at 400 K is estimated to be 86.3 $\mathrm{JK^{-1}\,mol^{-1}}$ from the plot of internal energies obtained by the Monte Carlo simulations (Table 1) against temperatures 350, 400, and 450 K at the density of 1.0 $\mathrm{gcm^{-3}}$. Using the values of $\langle n_H\rangle$ and C_v, the parameters a, b are calculated to be -0.0078 and -1.68, respectively (Table 2).

The remaining parameter to be determined is E_0. E_0 may depend on the density and is assumed to be written in the same manner as E_H:

$$E_0 = a_0(\rho - \rho_0) + b_0 \tag{32}$$

Substituting the values of E_H, $\langle n_0\rangle$, $\langle E^u\rangle$, and internal energies $\langle E\rangle$ at three different densities at 400 K into Equation (16), we obtained the parameters, a_0, ρ_0 and b_0. Parameters in the present partition function are summarized in Table 2.

7. RESULTS AND DISCUSSION

Heat Capacity at Constant Volume, C_v

The temperature dependence of C_v is calculated by our partition function at the pressure of 0.1 MPa and compared with the corresponding experimental data in Figure 4. In hydrogen bonded systems, C_v is known to be considerably larger than that of normal liquids [14]. The present model tells us that this is due to the contribution of the "bond" term. It has been known experimentally [15] that C_v of liquid water decreases with the increase of temperature. The calculated C_v reproduces this tendency. It should be noted that this tendency is realised by the contribution of the "bond" term, since the contribution of the harmonic oscillator term remains a

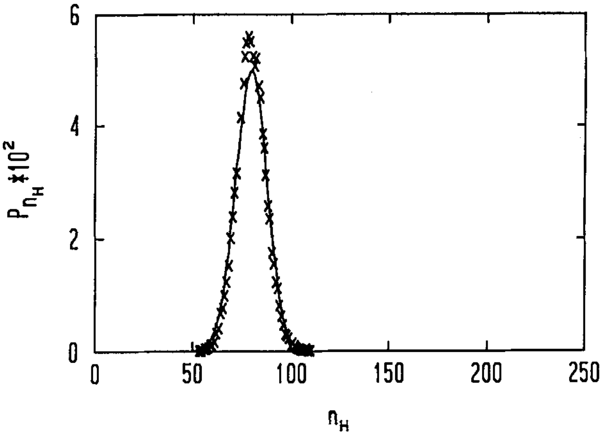


Figure 5 Distribution function of n_H. The solid line is the distribution function of n_H calculated by $\exp(an_H^2 + bn_H)\cdot\exp\{-E_Hn_H/(k_BT)\}$. The crosses are n_H's directly counted from Monte Carlo simulations.

constant. C_v of liquid hydrogen fluoride is also larger than that of normal liquid. The temperature dependence, however, is opposite with that of liquid water; C_v increases with the increase of temperature. This interesting feature of temperature dependence of C_v will be discussed elsewhere.

The function $A(x)$ (Equation (15)) can be calculated by the numerical integration. When the range of integration is large enough, the integration can be carried out from $t = -\infty$ to $t = \infty$, instead of $x \leqq t \leqq x + n_H$ max (see Figure 5). In this case, $A(x)$. is given by an analytical form,

$$A(x) = (-\pi/a)^{1/2}.$$

Then, Equation (19) can be reduced as follows;

$$\frac{N}{\mathrm{m}} C_v^B = -\frac{N}{m} \frac{E_H^2}{2ak_B T^2} \tag{33}$$

This is the case of liquid water. Equation (33) clearly shows that C_v decreases with the increase of temperature.

In Figure 5, the distribution functions of n_H calculated by the function, $\exp(an_H^2 + bn_H)\exp\{-E_H n_H/(k_B T)\}$, is compared with that calculated by the Monte Carlo simulations. As seen from this figure, the calculated result with the present partition function agrees satisfactorily with that directly obtained from the Monte Carlo simulations. This result suggests that our assumption for $g(n_H)$ given by Equation (12) is reasonable.

Equation of State

As shown in Figure 6, the "bond" and the harmonic oscillator term exert positive pressure and work to expand the volume, while that form the "potential" term exerts negative pressure and works to contract it.

Temperature Dependence of κ_T, α_p, ρ, and C_p

κ_T of normal liquid increases with the increase of temperature. However, it has been known experimentally [12,15] that a plot of κ_T of water against temperature has a

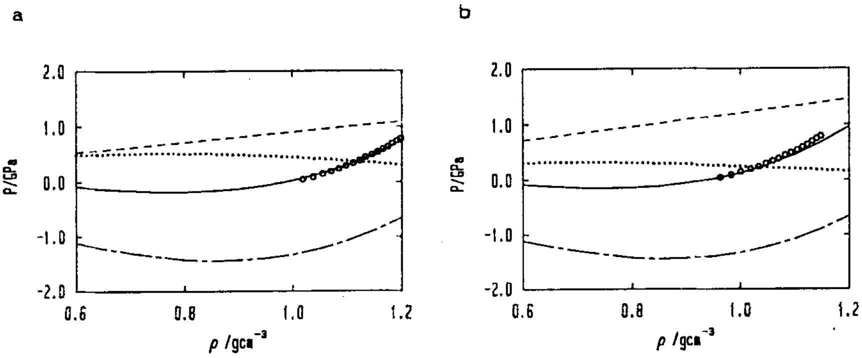


Figure 6 Density dependence of pressure at 298 K (a) and 398 K (b) calculated by the partition function (solid line) with the contribution form the "bond" term (dotted line), from oscillators (dashed line), and from the "potential" term (dash-dotted line), respectively. Circles are experimental data [12].

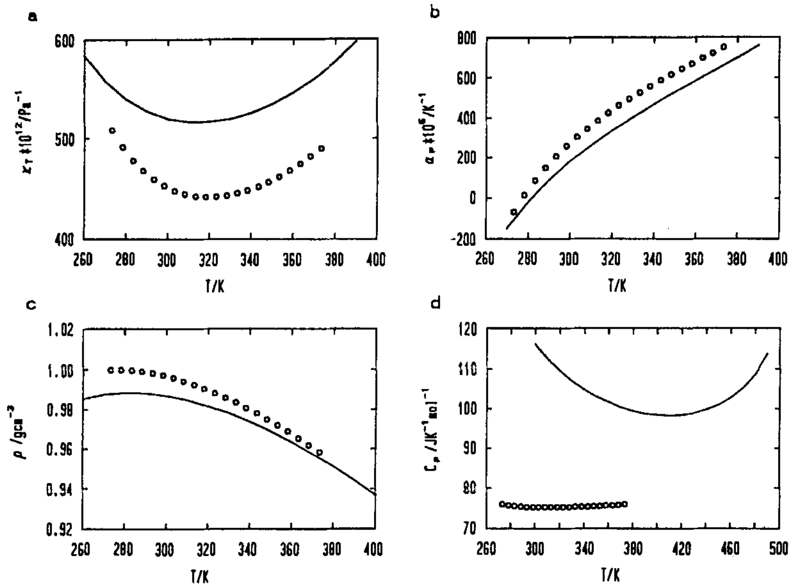


Figure 7 Plots of isothermal compressibility κ_T (a), coefficient of thermal expansion α_p (b), density ρ (c) and heat capacity at constant pressure C_p (d) at 0.1 MPa against temperature, respectively. Circles are experimental data [12].

minimum at 0.1 MPa (Figure 7a). From our partition function, this tendency is reproduced satisfactorily.

Figure 7b shows the temperature dependence of α_p at 0.1 MPa. For the case of liquid water, the first term of Equation (24) has negative value, while the second term has positive value. At low temperature, α_p has negative value because the former term becomes dominant. This interesting tendency is reflected in the temperature dependence of density of liquid water. Thus the density of liquid water becomes maximum at near the freezing point (see Figure 7c). Our partition function reproduces this important tendency. This is, of course, due to the effect of the "bond" term.

The calculated temperature dependence of C_p at 0.1 MPa is shown in Figure 7d and compared with the experimental data. The experimental data has a minimum at 308 K, while our results has a minimum at 500 K. This discrepancy suggests that it should be necessary to refine our simple partition function further.

8. CONCLUSIONS

Our simple partition function reproduces the thermodynamic properties of liquid water satisfactorily. In the present study, it was shown the contribution of the "bond" term is significant for C_v and also for other anomalous thermodynamic properties of liquid water.

Acknowledgements

The authors are grateful for receipt of computer programs for Monte Carlo simulations from Dr. Hideki Tanaka of Kyoto University. Numerical calculation were carried out partly at the computer center of the Institute for Molecular Science. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture.

APPENDIX

Computational Details

In the course of the Monte Carlo simulations using our new potential function, the most time consuming part is the calculations of overlap integrals. One can save the computer time largely by the use of a overlap integral table. The table contains the overlap integrals over contracted Gaussian type orbitals (GTO) between all constituent atoms at distances from 0 to 10 Å with a increment of 0.05 Å.

The coordinate system employed for preparing the overlap integral table is shown in Figure A1a (the diatomic coordinate system). In Monte Carlo simulations, overlap integrals in the molecular coordinate system (Figure A1b) are required. The integrals between atoms are easily calculated from the corresponding ones given in the diatomic coordinate system just by an interpolation and a transformation of the coordinate system.

Overlap integrals between s type basis functions depend only on the interatomic distance but does not depend on the coordinate system. So, the integral is easily calculated by an interpolation using the integrals stored in the overlap integral table. We used the three points Lagrange interpolation method,

$$\begin{aligned} S^d_{ss}(r) &= S^d_{ss}(r_0)\frac{(r - r_1)(r - r_2)}{(r_0 - r_1)(r_0 - r_2)} \\ &+ S^d_{ss}(r_1)\frac{(r - r_0)(r - r_2)}{(r_1 - r_0)(r_1 - r_2)} \end{aligned}$$

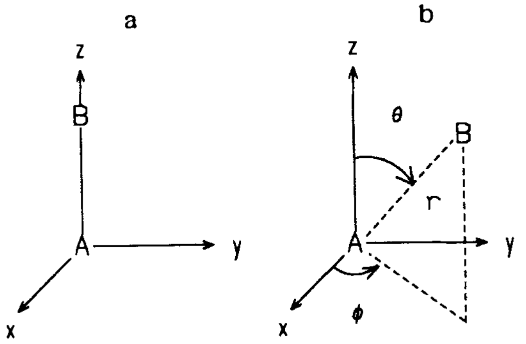


Figure A1 (a) The diatomic coordinate system. Molecules A and B are both placed on the *Z* axis. (b) The molecular coordinate system.

$$+S^d_{ss}(r_2)\frac{(r - r_0)(r - r_1)}{(r_2 - r_0)(r_2 - r_1)} \tag{A.1}$$

$$S^m_{ss}(r) = S^d_{ss}(r)$$

where $S^m_{ss}(r)$ means the overlap integral at the interatomic distance r in the molecular coordinate system. $S^d_{ss}(r_i)$ refers the overlap integral at the interatomic separation r_i in the diatomic coordinate system, which is calculated and stored in the table beforehand. Among the interatomic distances r, r_0, r_1 and r_2, there is a relationship of $r_0 < r_1 \leqslant r < r_2$.

The following unitary transformations are necessary for calculating an overlap integral between p type orbitals, in addition to the interpolation procedure.

$$S^m_{pp}(r) = T^t_{pp}S^d_{pp}(r)\,T_{pp} \tag{A.2}$$

where S^m_{pp}, S^d_{pp} and T_{pp} are 3×3 matrices. $S^d_{pp}(\mathrm{r})$ is the overlap integral at the interatomic separation r in the diatomic coordinate system obtained in the same manner as S^d_{ss}. The transformation matrix, T_{pp}, is written as follows;

$$T_{pp} = \begin{pmatrix} \cos\theta\cos\phi & -\sin\phi & \sin\theta\cos\phi \\ \cos\theta\sin\phi & \cos\phi & \sin\theta\sin\phi \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \tag{A.3}$$

Similarly, $S^m_{sp}(r)$ is calculated as follows;

$$S^m_{sp}(r) = S^d_{sp}(r)\,T_{pp} \tag{A.4}$$

where S^d_{sp} and S^m_{sp} are 3×1 matrices.

By the interpolation procedure mentioned above, the computer time can be reduced greatly compared with that of the analytical calculations. According to our experience, this procedure makes the integral calculations about ten times faster than that of the analytical treatments. And the computation of our potential functions is about 3 to 5 times slower than that of simple atom–atom type potentials [16].

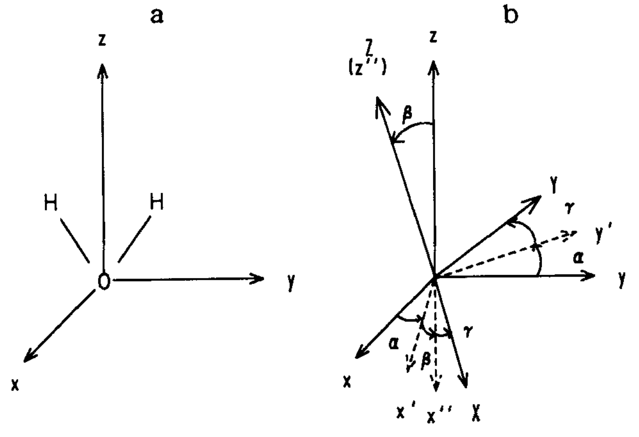


Figure A2 A water molecule in the standard configuration (a) and the rotated configuration (b).

Moreover one can take advantage of the fact that overlap integrals become small at large interatomic separation. For instance the overlap integral between O and H becomes negligible at the separation larger than 5 Å.

Using the overlap integrals over basis functions calculated by the procedures mentioned above, one computes the overlap integrals over localized molecular orbitals (LMO). The LMO coefficients are usually given at a standard orientation of molecule in the molecular coordinate system. So, the LMO coefficients should be transformed (rotated) from the standard orientation to the required orientation in Monte Carlo simulation.

Let us assume the LMO coefficients are given in the coordinate system shown in figure A2a (the standard orientation). The molecular orientation appeared in the Monte Carlo calculation is shown in Figure A2b. The rotation angles between them are the Eular angles, α, β and γ. The transformations of the LMO coefficients between them are given as follows;

$$C_s^m = C_s^s \tag{A5}$$

$$C_p^m = U_p C_p^s \tag{A6}$$

$$U_p = \begin{pmatrix} \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & -\cos\alpha\sin\gamma - \sin\alpha\cos\beta\cos\gamma & \sin\alpha\sin\beta \\ \sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma & -\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma & -\cos\alpha\sin\beta \\ \sin\beta\sin\gamma & \sin\beta\cos\gamma & \cos\beta \end{pmatrix} \tag{A7}$$

where C_s^s and C_p^s are the LMO's coefficients at the standard orientation for the s and the p orbitals, respectively. C_s^m and C_p^m are the coefficients at a given orientation. C_s^s and C_s^m are 1 × 1 and C_p^s and C_p^m are 3 × 1 matrices.

The overlap integrals over LMO are calculated as follows;

$$S_{ij} = \sum_r \sum_s C_{ir}^m C_{js}^m S_{rs}^m \tag{A8}$$

where S_{ij} is the overlap integrals between LMOs i and j and S_{rs} is the overlap integrals between basis functions r and s, respectively

The potential function used in this work is made so as to reproduce the *ab initio*

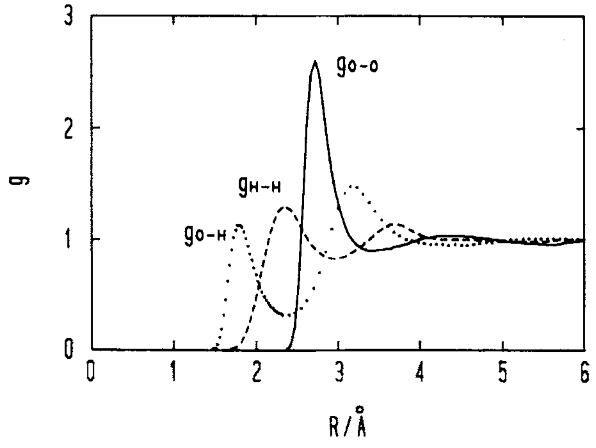


Figure A3 Radial distribution functions at 400 K, 1.0 gcm^{-3}.

STO-3G interaction energies. Figure A3 shows the calculated radial distribution functions for O–O, O–H, H–H at 400 K and density of 1.0 $\mathrm{g\,cm^{-3}}$. The first peaks correspond to the separation where a water dimer has the most stable linear form [1]. All peak positions are biased to shorter distances than the experimental values. It is caused by the *ab initio* STO-3G energies. The similar tendency was reported by Jorgensen [17] who has performed MC simulations using the 12-6-3-1 potential function whose parameters were also obtained from *ab initio* STO-3G calculations.

References

[1] K. Honda and K. Kitaura, "A new form for intermolecular potential energy functions", *Chem. Phys. Lett.* **140,** 53 (1987).

[2] G. Némethy and H.A. Scheraga, "Structure of water and hydrophobic bonding in proteins. I. A model for the thermodynamic properties of liquid water", *J. Chem. Phys.* **36,** 3382 (1962).

[3] O. Weres and S.A. Rice, "A new model of liquid water", *J. Am. Chem. Soc.* **94,** 8983 (1972).

[4] a) H.E. Stanley, "A polychromatic correlated-site percolation problem with possible relevance to the unusual behaviour of supercooled H_2O and D_2O", *J. Phys. A: Math. Gen.* **12,** L329 (1979); b) H. E. Stanley and J. Teixeira, "Interpretation of the unusual behavior of H_2O and D_2O at low temperatures: Tests of a percolation model", *J. Chem. Phys.* **73,** 3404 (1980); c) R.L. Blumberg, H.E. Stanley, A. Geiger, and P. Mausbach, "Connectivity of hydrogen bonds in liquid water", *J. Chem. Phys.* **80,** 5230 (1984).

[5] S.A. Rice and M.G. Sceats, "A random network model for water", *J. Phys. Chem.* **85,** 1108 (1981).

[6] a) K. Okazaki, S. Nosé, Y. Kataoka, and T. Yamamoto, "Study of liquid water by computer simulations. I. Static properties of a 2D model", *J. Chem. Phys.* **75,** 5864 (1981); b) Y. Kataoka, H. Hamada, S. Nosé, and T. Yamamoto, "Studies of liquid water by computer simulations. II. Static properties of a 3D model", *J. Chem. Phys.* **77,** 5699 (1982); c) Y. Kataoka, "Studies of liquid water by computer simulations. V. Equation of state of fluid water with Carravetta-Clementi potential", *J. Chem. Phys.* **87,** 589 (1987).

[7] D. Levesque, J.J. Weis, and J.P. Hansen, "Recent developments in the simulation of classical fluids", in *Applications of the Monte Carlo Method in Statistical Physics*, K. Binder, ed, Springer-Verlag, Berlin, 1987, ch. 2.

[8] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, "Equation of state calculations by fast computing machines", *J. Chem. Phys.* **21,** 1087 (1953).

[9] a) A. Pohorille, L.R. Pratt, R.A. LaViolette, M.A. Wilson, and R.D. MacElroy, "Comparison of the structure of harmonic aqueous glasses and liquid water", *J. Chem. Phys.* **87,** 6070 (1987); b) I. Ohmine, H. Tanaka, and P.G. Wolynes, "Large local energy fluctuations in water. II. Cooperative motions and fluctuations", *J. Chem. Phys.* **89,** 5852 (1988).

[10] H. Tanaka and I. Ohmine, "Potential energy surfaces for water dynamics: Reaction coordinates, transition states, and normal mode analyses", *J. Chem. Phys.* **91,** 6318 (1989).

[11] a) R. Kubo, *Statistical Mechanics*, North-Holland, Amsterdam, 1988, pp. 136; b) J.W. Shaner, "Gruneisen gamma and acoustic velocity for soft sphere fluids", *J. Chem. Phys.* **89,** 1616 (1988); c) J. Belak, R.D. Etters, and R. LeSar, "Thermodynamic properties and equation of state of dense fluid nitrogen", *J. Chem. Phys.* **89,** 1625 (1988).

[12] G.S. Kell, "Thermodynamic and transport properties of fluid water", in *Water, A Comprehensive Treatise*, F. Franks, ed, Plenum, New York, 1972, vol. 1. ch. 10.

[13] F.H. Stillinger and T.A. Weber, "Inherent structure in water", *J. Phys. Chem.* **87,** 2833 (1983).

[14] Y. Marcus, *Introduction to Liquid State Chemistry*, John Wiley & Sons, New York, 1977, ch. 1.

[15] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford, London, 1969, ch. 4.

[16] W.L. Jorgensen, "Transferable Intermolecular Potential Functions for Water, Alcohols, and Ethers. Application to Liquid Water", *J. Am. Chem. Soc.* **103,** 335 (1981).

[17] W.L. Jorgensen, "Minimal Basis Set Description of the Structure and Properties of Liquid Water", *J. Am. Chem. Soc.* **101,** 2016 (1979).