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Monte Carlo Simulation of Liquid Ammonia and an Evaluation of the Thermodynamic Properties. The Comparative Study of NH_3, H_2O, and HF

Kazuhiko HONDA, Kazuo KITAURA,† and Kichisuke NISHIMOTO*,††
Knowledge-Based Information Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441
† College of Integrated Arts and Sciences, University of Osaka Prefecture, Gakuen-cho, Sakai 593
†† Department of Chemistry, Osaka City University, Sumiyoshi-ku, Osaka 558

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Monte Carlo (MC) simulation was done for liquid ammonia using the potential function expressed by the intermolecular overlap integrals and fractional point charges on the atoms. Thermodynamic properties were estimated using a partition function whose parameters are obtained by referring the results of the MC simulation. The calculated thermodynamic properties were examined by the physically meaningful interaction terms. A comparative study with NH_3, H_2O, and HF was done and a new index proposed to characterize the liquid with hydrogen bondings.

Hydrogen bonds have a great effect on the macroscopic properties of molecular assemblies.$^{1)}$ The quantitative contribution of the hydrogen bonding to the thermodynamic properties, however, is not very clear. Ammonia, water, and hydrogen fluoride are isoelectronic to each other and form hydrogen-bonded liquids by themselves. Better understanding of the effects of hydrogen bonding on the thermodynamic properties, therefore, will be possible from the comparative study of these liquids. Thermodynamic properties are estimated straightforwardly if the partition function of a given liquid is available.

In previous papers, we discussed the thermodynamic properties of water$^{2)}$ and liquid hydrogen fluoride$^{3)}$ using a partition function the parameters of which are obtained by MC simulation. This approach can reduce ambiguousness of the choice of the physical parameters and be applied to any liquids. In this study, liquid ammonia is examined by the same approach and the three hydrogen-bonding liquids mentioned above are compared.

MC Simulation

Intermolecular potential function between NH_3 molecules is expressed by intermolecular overlap integrals associated with the LMO's (localized molecular orbitals) and Coulomb potential between fractional point charges. To keep the consistency of the previous work, we use the STO-3G energy surface, though this surface has the drawback of shorter intermolecular separations. The parameters and the optimized structure of dimers are shown in our previous paper.$^{4)}$

MC simulations were done with the N, T, V Metropolis sampling algorithm$^{5)}$ for 125 molecules in the base cell using periodic boundary conditions. For the statistical averaging, 10—20 K steps were adopted after 10 K steps were discarded, where a step is regarded as a random trial for all molecules in the base cell; 125 attempted moves corresponds to a step.

Results and Discussion

Radial Distribution Function, Internal Energy. In Fig. 1, the N–N radial distribution function is shown and compared with an X-ray experiment.$^{6)}$ The first peak in the vicinity of 3.0 Å is located at a rather shorter distance than that of the experimental ones. This is due to the shorter distance of optimized structure with an ab initio STO-3G calculation for dimer. This tendency is common for STO-3G calculations. Our radial distribution function has a broad shoulder as well as the experiment. Thus the structural character of liquid ammonia can be reproduced by our simulation using a new type of potential function (bond–bond type potential). For the comparison, the radial distribution function obtained by Jorgensen$^{7)}$ et al. is shown in Fig. 1. They used the atom-atom type potential function, which is also generated by referring to the ab initio STO-3G surfaces, however, the first peak of their distribution function has no shoulder. It may be noted that this shoulder cannot be obtained by any simulations in the

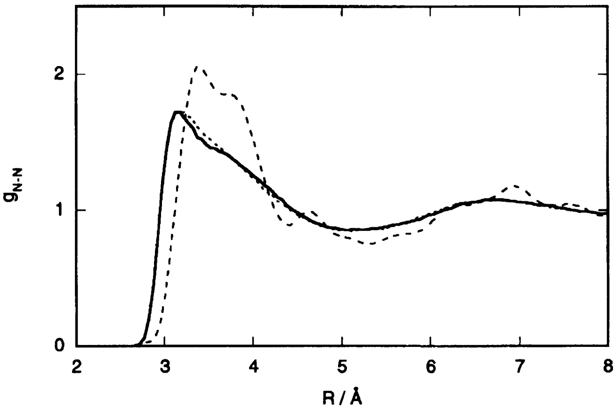

Fig. 1. N–N radial distribution functions; this work (solid line), using Jorgensen's potential function (dotted line) and X-ray experiment (dashed line). The simulations are performed at 273 K 0.63 g cm^{-3} and the experimental result was measured at 277 K.

previous work[8] except for the case using an artificial potential function for a solid state model.[9] This might be due to the following reason. In the simulations, they used the atom–atom type potential, such as Lennard-Jones or Buckingham type potentials, which represent essentially spherical potential. Thus it is difficult to express the oriented forces, such as hydrogen bonds and the charge transfer force.

In this simulation, calculated internal energy at 240 K and 0.68 $\mathrm{g\,cm^{-3}}$ was to be $-7.4\ \mathrm{kJ\,mol^{-1}}$, while that of the experiment[10] is to be $-15.6\ \mathrm{kJ\,mol^{-1}}$. The same order of disagreement is also observed by Jorgensen's potential for liquid ammonia. For the sophisticated simulation, higher quality potential surfaces calculated using the larger basis set including electron correlation is required.

The Model Potential of Hydrogen Bonding Systems Derived from MC Simulation and a Partition Function. With respect to the theoretical models of water, there are two trends. One emphasizes forming and breaking the hydrogen bonds[1] and the other is treated as oscillators,[11] that is, an analogy of solids. Two models stand at the extremes. Unification of two models, then, is done as follows. We assume a molecule wanders around a multi-minimum potential surface; the molecule does not stay in a potential minimum but encounters many local minima. The local minima are collected and counted up before the general treatment of statistical mechanics. Our model is schematically shown in Fig. 2. The minimum of the basin is measured from the background potential energy, E^{P}, and has a discrete energy corresponding to the number of hydrogen bonds, n. E_{H} is an energy per one hydrogen bond and is a gap between the levels. The number of basins having the same number of hydrogen bonds is taken into account, which are called the density of state in statistical mechanics. In the basin, the motion is treated as oscillators. The measurement of the parameters in this model is overcome by referring to MC simulations, extracting the parameters by MC procedures.

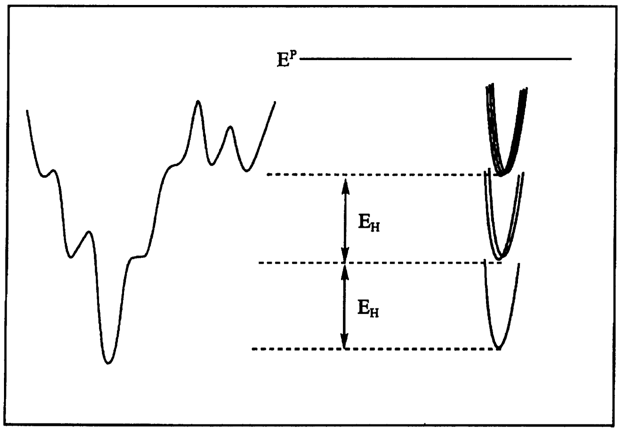

Fig. 2. The model of hydrogen bond liquids. The multi-minimum energy in the left hand side is collected by some basins which have the discrete energies in the right hand side.

Hamiltonian of a given system is expressed as follows,

$$\mathscr{H} = E_{\mathrm{H}}\cdot n + E^{\mathrm{P}} + E^{\mathrm{O}}. \tag{1}$$

In the equation, the energy terms of the right side refer to "bond", "potential", and "oscillator", respectively.

The partition function is derived from Eq. 1.

$$\begin{aligned} Z(M,T,V) &= \int_0^{n_{\max}} g(n)\cdot\exp\{-(E_{\mathrm{H}}\cdot n)/(k_{\mathrm{B}}T)\}\mathrm{d}n \\ &\times \exp\{-E^{\mathrm{P}}/(k_{\mathrm{B}}T)\} \\ &\times Z^{\mathrm{O}} \end{aligned} \tag{2}$$

where M is the number of molecules and taken to equal the number in a base cell of the simulation. For the huge number of N, the relationship between $Z(N,V,T)$ and $Z(M,T,V)$ is shown by

$$Z(N,T,V) \propto Z(M,T,V)^{N/M} \tag{3}$$

This equation is consistent with evaluating the thermodynamic properties in the simulation.

The "bond" term must be integrated over n, where $g(n)$ is the density of state for the number of hydrogen bonds. Only for water, the direct estimation of the $g(n)$ was done to enumerate the possible combinations of hydrogen bonds. Individual models, then, are required for liquids. This causes arbitrariness and difficulty of comparative study. Using the simulation, it is possible to estimate the averaged number of hydrogen bonds, $\langle n\rangle$, and its distribution, $dis(n)$. Moreover these properties are derived by the partition function as

$$\langle n\rangle = \frac{\int_0^{n_{\max}} n\cdot g(n)\cdot\exp\{-E_{\mathrm{H}}\cdot n/(k_{\mathrm{B}}T)\}\mathrm{d}n}{\int_0^{n_{\max}} g(n)\cdot\exp\{-E_{\mathrm{H}}\cdot n/(k_{\mathrm{B}}T)\}\mathrm{d}n} \tag{4}$$

and

$$dis(n) = g(n)\cdot\exp\{-E_{\mathrm{H}}\cdot n/(k_{\mathrm{B}}T)\}. \tag{5}$$

Comparing the distribution of Eq. 5 with that of MC simulation, we found the distribution can be reproduced simply by the quadratic form about n as

$$g(n) = \exp(an^2 + bn) = \exp\left[a\left(n + \frac{b}{2a}\right)^2 - \frac{b^2}{4a}\right], \tag{6}$$

where a and b are the parameters that are decided to reproduce $\langle n\rangle$ and $dis(n)$ in the simulation.

E_{H} and E^{P} are also parameters and can be estimated by the simulations. The quadratic functions of ρ, ρ is the density of liquid, are adopted for both E_{H} and E^{P} as

$$E_{\mathrm{H}} = a_{\mathrm{H}}(\rho - \rho_{\mathrm{H}})^2 + b_{\mathrm{H}} \tag{7}$$

and

$$E^{\mathrm{P}} = a_{\mathrm{O}}(\rho - \rho_{\mathrm{O}})^2 + b_{\mathrm{O}}. \tag{8}$$

In "oscillator" term, frequencies of libration modes and Grüneisen's γ, according to γ the term contributes to pressure, are not estimated directly from the simple MC simulation. In the previous paper on liquid hydrogen fluoride, the experimental values of frequencies were used. In this paper, the purpose is the comparative study of hydrogen-bonding liquids. Arbitrariness of the parameters should be reduced. Classic approximations of the oscillators, then, are used.

Finally, the internal energy, which is a fundamental thermodynamic property, can be derived as

$$\langle E\rangle = \left(E_\mathrm{H}\langle n\rangle + \langle E^\mathrm{P}\rangle + \langle E^\mathrm{O}\rangle\right)/M, \tag{9}$$

where $\langle E^\mathrm{P}\rangle$ and $\langle E^\mathrm{O}\rangle$ are the averaged energies from "potential" and "oscillator" terms, respectively.

Evaluation of Parameters. The parameters required for the construction of the partition function are E_H, E^P, $g(n_\mathrm{H})$, and γ. The simulations were done for various densities, 0.75, 0.8, 0.9, and 1.0 g cm^{-3} at 273 K. The higher temperature and higher density comparing with the normal liquid state are used for evaluating the parameters because of minimizing the statistical error for temperature and avoiding an encounter with the instability phase for density. By the procedure listed below, we can evaluate them.

1. The configuration energies are averaged by the configuration having the same number of hydrogen bonds, n. For counting of n's, the energy threshold of the molecular pair is used.
2. The linear fitting against n is done for the averaged configuration energy obtained from procedure 1. E_H is given by the slope of the line.
3. E_H's are obtained for various densities and decide the density dependence of E_H.
4. The parameters of density of state, $g(n)$, are obtained by referring to the distribution of n in the simulations.
5. By the procedure mentioned above, all parameters for internal energy (see Eq. 9) except $\langle E^\mathrm{P}\rangle$ are obtained. $\langle E^\mathrm{P}\rangle$ is, then, decided to reproduce the internal energies for simulations for various densities.
6. The γ is regarded as only an adjustable parameter that is decided by referring to the experimental value of density.

To calculate the hydrogen bond term, the upper limit of the integral in Eq. 2 is required. In a solid,[12)] an ammonia molecule has six nearest neighborhoods. The maximum number of hydrogen bonds per a molecule is six and $6M/2$ for the M molecular system. The duplicated counting for bonding neighbor is avoided by dividing by two. All the parameters required to reproduce the thermodynamic properties are given in Table 1.

Thermodynamic Properties. The temperature dependence of various thermodynamic properties at 0.1 MPa, such as internal energy ($\langle E\rangle$), density (ρ), isothermal compressibility (κ_T), and coefficient of thermal expansion (α_P), is shown in Fig. 3. The agreement with the experiment is rather poor for $\langle E\rangle$. This might be due to the drawback of STO-3G interaction energy mentioned previously. The slope of the internal energy, in other words, the heat capacity at constant volume, agrees with the experiment. Concerning the temperature dependence of the energy, the difference seems to be constant.

Table 1. Parameters of the Partition Function for Hydrogen Bonding Liquids, NH_3, H_2O, and HF

	NH_3	H_2O	HF
a_H/kJ mol^{-1} (g cm $^{-3}$)$^{-2}$	5.78	−6.83	0.296
ρ_H/g cm^{-3}	0.2620	1.522	−2.651
b_H/kJ mol^{-1}	−5.54	−7.85	−14.2
a_O/10^{3}kJ mol^{-1} (g cm^{-3})$^{-2}$	7.76	4.98	0.235
ρ_O/g cm^{-3}	0.8234	1.302	2.326
b_O/10^{3}kJ mol^{-1}	−2.11	−4.28	−2.50
a	−0.01361	−0.007796	−0.02707
b	0.3629	−1.681	1.925
n_max	$3M$[a)]	$2M$[a)]	M[a)]
γ	0.80	1.1	0.25

1) M is the number of molecules in basic cell of the simulation and to be 125 in this study.

For the calculation of density, we introduce the adjustable parameter γ to reproduce the experimental density. By taking the derivatives of volume with respect to pressure and temperature, we obtain κ_T and α_P.

Comparative Study of Hydrogen-Bonding Liquids. In Table 1, the parameters of the partition function for liquid ammonia, water, and hydrogen fluoride are shown. In this section, we concentrate our discussion on the properties of the heat capacities at constant volume and the isotherms, because these properties reflect the effects of hydrogen bonding well. (There are differences between this work and our previous one in the calculated thermodynamic properties for hydrogen fluoride. This is because of the classic approximation of oscillators is used for the comparative study of these three liquids. However, the difference between approximations does not affect the substantial discussion in this work.)

The temperature dependence of C_V's at 0.1 MPa is shown in Fig. 4. C_V^B, the contribution from the "bond" term, shows only the temperature dependence because now the classical approximation is used for the "oscillator" term. As mentioned in our previous paper, C_V decreases with increases of temperature for water. On the other hand, for hydrogen fluoride an opposite tendency is found. In hydrogen fluoride, the number of hydrogen bonds is close to the upper bound and the energy to the lower bound according to decreasing temperature. This makes C_V lower. For water, a region where water has the saturated number of hydrogen bonds cannot be

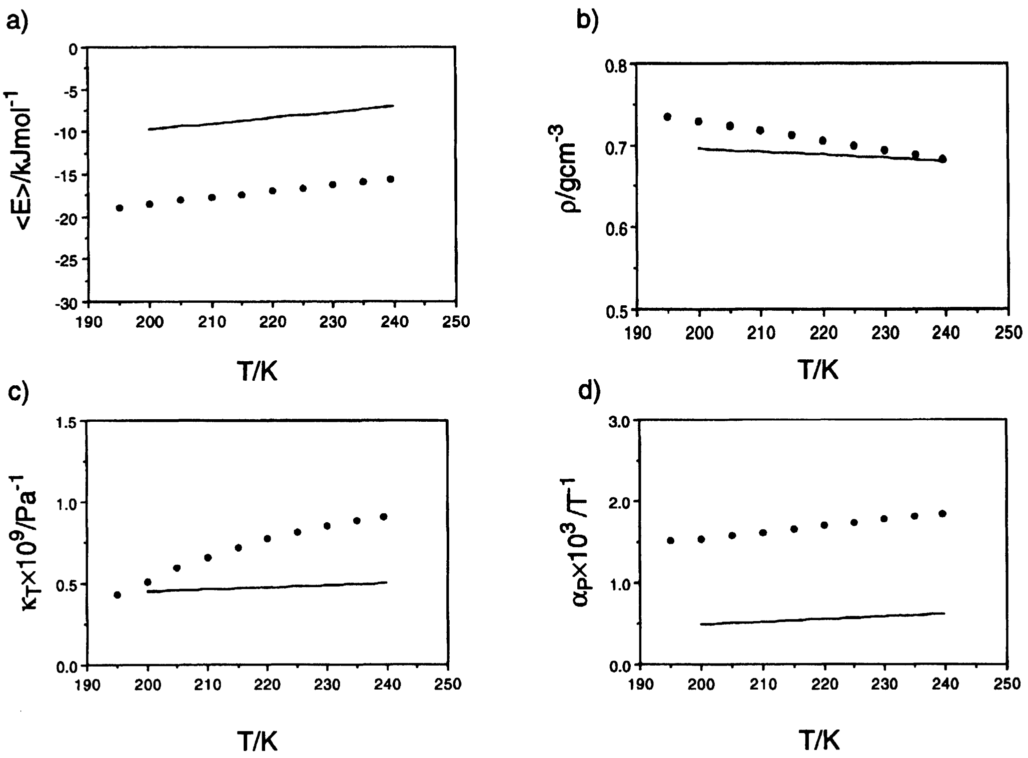

Fig. 3. Temperature dependence of thermodynamic properties at 0.1 MPa; a) internal energies $\langle E\rangle$, b) density ρ, c) isothermal compressibility κ_T, d) coefficient of thermal expansion, α_P. The solid line is derived from the partition function and the circles are from the experimental data.[10)]

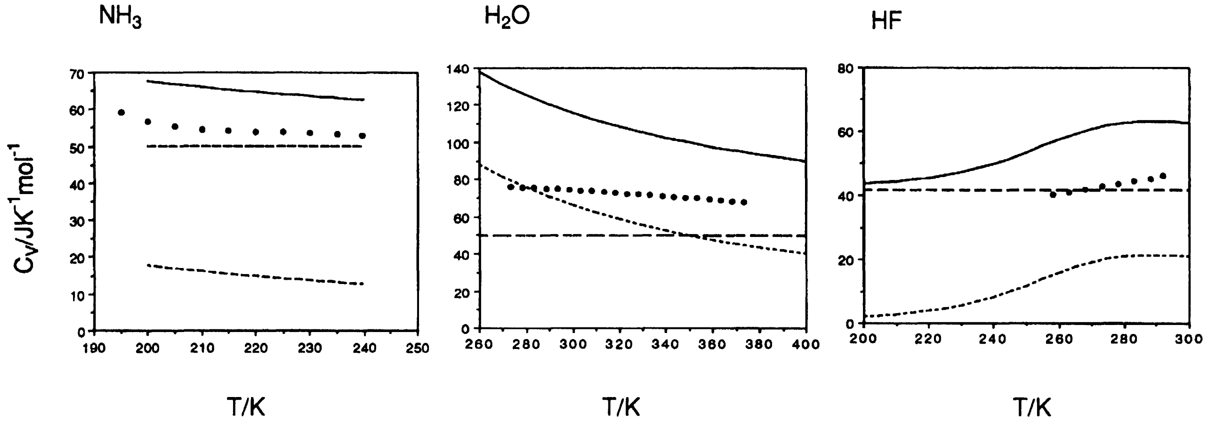

Fig. 4. Temperature dependence of heat capacity at constant volume, C_V, at 0.1 MPa; from partition function (Solid line), from the "bond" term (dotted line), from the "oscillator" term (dashed line). Circles are from the experimental data for NH_3,[10)] for H_2O,[13)] and for HF.[14)]

observed in MC simulation because of the region is not stable for the liquid state. In this case, C_V^B, can be written from the partition function as

$$\frac{N}{m} C_V^{\mathrm{B}} = -\frac{N}{m} \frac{E_{\mathrm{H}}{}^2}{2ak_{\mathrm{B}} T^2} \,. \tag{10}$$

C_V is decreased by increases of temperature. For ammonia, this tendency is the same as for water. The magnitude of contribution from "bond" is one-fourth as small as that for water.

It is well known that water has a negative α_P near the freezing point. We showed the condition for α_P having negative values in the partition function, that is, C_V^B increases with decreasing temperature. This condition applies to ammonia. Both values from the experiment and the partition function, however, are not to be negative. The reason is due to the small E_H of ammonia. Thus the hydrogen bond term cannot overcome the expanding character of volume by the "oscillator" term.

The isotherms derived from the partition function consists of three terms, "bond", "potential", and "oscillator" (Fig. 5). The "bond" and "oscillator" terms act

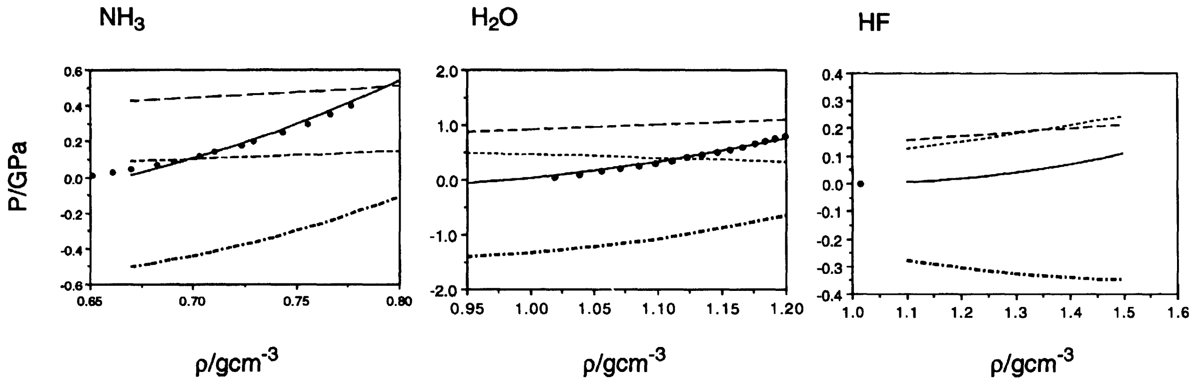

Fig. 5. Pressure dependence against the density (NH_3: 270 K, H_2O: 298 K, HF: 273 K) by the partition function (solid line) with the contribution from the "bond" term (dotted line), from the "oscillator" term (dashed line) and from the "potential" term (dash-dotted line). Circles are from the experimental data for NH_3,[10] for H_2O,[13] and for HF.[15]

Table 2. E_H and E_H/E^P for Three Simple Liquids, NH_3, H_2O, and HF

	NH_3[a]	H_2O[b]	HF[c]
$E_H/\mathrm{kJ\,mol^{-1}}$	−4.16	−9.71	−10.3
E_H/E^P	0.0020	0.0025	0.0049

a) 0.75 $\mathrm{g\,cm^{-3}}$. b) 1.0 $\mathrm{g\,cm^{-3}}$. c) 1.0 $\mathrm{g\,cm^{-3}}$.

as the positive pressure and the "potential" as the negative. For water, the shape of the "potential" term resembles that of the isotherm. This means the other two terms play only the role of shifting the curve upward. On the other hand, for liquid hydrogen fluoride, the contribution of the "bond" term is considerably larger and the curve of the isotherm does not reflect that of the "potential" term. The dependence of each term for liquid ammonia is similar to that of water. Concerning the isotherms, there are, therefore, characteristics common between ammonia and water, but hydrogen fluoride is an exception. The magnitude of E_H for water is close to that for hydrogen fluoride, while that for ammonia is about half, comparing with the two systems. The character of isotherms cannot be explained by the "bond" term only. We, then, introduce the index of the ratio, E_H/E^P. The E_H is obtained by the simulation procedure to extract the quantity from the anisotropic intermolecular interaction. Therefore the contribution from the isotropic interaction is stuffed into E^P. From Table 2, the indexes become larger in order from N to F. It is worth to notice that the index for hydrogen fluoride is twice as large as those for ammonia and for water.

Concluding Remarks

From the viewpoint of thermodynamic properties, ammonia has a resemblance to water although the larger E_H of water strongly affects the observable properties. E_H/E^P is a helpful index that shows the relative amount of the contribution from the "bond" term. According to the index, hydrogen fluoride has a highly expanded volume by the "bond" term.

We stress our discussion on the balance between the "bond" term and other terms. Our next target is a mixture including a hydrogen bonding liquid as a solvent. The change of the "bond" term will be the topic of our discussion.

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References

1) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962); O. Weres and S. A. Rice, *J. Am. Chem. Soc.*, **94**, 8983 (1972).

2) K. Honda, K. Kitaura, and K. Nishimoto, *Mol. Simul.*, **6**, 275 (1991).

3) K. Honda, K. Kitaura, and K. Nishimoto, *Bull. Chem. Soc. Jpn.*, **65**, 3122 (1992).

4) K. Honda and K. Kitaura, *Chem. Phys. Lett.*, **140**, 53 (1987).

5) N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).

6) A. H. Narten, *J. Chem. Phys.*, **66**, 3117 (1977).

7) W. L. Jorgensen and M. Ibrahim, *J. Am. Chem. Soc.*, **102**, 3309 (1980).

8) A. Hinchliffe, D. G. Bounds, M. L. Klein, I. R. McDonald, and R. Righini, *J. Chem. Phys.*, **74**, 1211 (1981); R. H. Kincaid and H. A. Scherage, *J. Phys. Chem.*, **86**, 833 (1982); A. L. Kielpinski, K. Mansour, and S. Murad, *Int. J. Thermophys.*, **7**, 421 (1986); K. P. Sagarik, R. Ahlrichs, and S. Brode, *Mol. Phys.*, **57**, 1247 (1986); J. M. Caillol, D. Levesque, J. J. Weis, J. S. Perkyns, and G. N. Patey, *Mol. Phys.*, **62**, 1225 (1987); M. Ferrario, M. Haughney, I. R. McDonald, and M. L. Klein, *J. Chem. Phys.*, **93**, 5156 (1990); J. Gao, X. Xia, and T. F. Geroge, *J. Phys. Chem.*, **97**, 9241 (1993).

9) M. L. Klein, I. R. McDonald, and R. Righini, *J.*

Chem. Phys., **71**, 3673 (1979).

10) L. Haar and J. S. Gallagher, *J. Chem. Phys. Ref. Data*, **7**, 635 (1978).

11) J. A. Pople, *Proc. R. Soc. London, Ser. A*, **205**, 163 (1951).

12) J. W. Reed and P. M. Reed, *J. Chem. Phys.*, **35**, 1730 (1961).

13) G. S. Kell, "Thermodynamic and Transport Properties of Fluid Water," in "Water, A Comprehensive Treatise," ed by F. Franks, Plenum, New York (1972), Vol. 1, Chap. 10.

14) R. T. Lagemann and C. H. Knowles, *J. Chem. Phys.*, **32**, 561 (1960).

15) I. Sheft, A. J. Perkins, and H. H. Hymsn, *J. Inorg. Nucl. Chem.*, **35**, 3677 (1973).