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Entropy of water calculated from harmonic approximation: Estimation of the accuracy of method

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INTRODUCTION

The entropy calculations of systems containing a condensed phase, such as liquid water, are a very important but difficult task. Recently, Henchman¹ has proposed an elegant and simple method for estimation of the entropy of water using harmonic approximation. As it was shown by Schlitter,² however, the “harmonic oscillator” approximation always produces an upper limit of absolute entropy of the system. In other words, it overestimates entropy. Therefore, it is interesting to estimate the accuracy of this approximation. For this purpose, we perform a series of molecular dynamics simulations using both TIP4P and SPC models of water at various temperatures covering the range of 5–90 °C. We also resort to the available literature data for estimation of the absolute entropy of water; the results of this comparison are reported here.

METHOD

Simulations were carried out at nine temperatures: 5, 10, 15, 25, 35, 45, 60, 75, and 90 °C, and at a constant volume corresponding to solvent density of 1.000 g/cm³; periodic boundary conditions were used. The system contained 516 TIP4P or 512 SPC water molecules within a cubic box. The AMBER8 (Ref. 3) and GROMOS96 (Ref. 4) programs were used for the simulation. The temperature was kept constant by weakly coupling to a temperature bath with a relaxation time equal to 0.1 ps. Each system was initially equilibrated for at least 1 ns at a given temperature, then the atomic positions were written to file for further analysis; the trajectory was at least 300 ps length and it was saved after each 1 fs.

RESULTS AND DISCUSSION

The original Henchman’s procedure requires modification of the molecular dynamics code for obtaining average values of forces and torques acting on the water molecule. In this work, accelerations (for force and torque determination) were calculated from the coordinate trajectory file. We used the time step for a single iteration equal to 1 fs, but we found that even 2 fs time step led to the same results. We perform our calculations in a slightly different but more rigorous manner than it was proposed by Henchman. The single water molecule was placed into a “natural” coordinate system, which originated at the center of mass of the molecule, and the coordinate axes were the same as the main axes of the inertia tensor. The axes were ordered so that $I_x < I_y < I_z$ (note

that our OX and OY directions correspond to the OY and OX directions, respectively, in Ref. 1). Both force F and torque T vectors were calculated within this “internal” coordinate system, and the absolute values of their components were averaged over the whole simulation run. We usually use the run of 300 ps length, but we found that several tens of picoseconds are sufficient for obtaining accurate results.

At the beginning, we wish to reproduce the original results given in Ref. 1. For this purpose, we perform NPT ($P=1.0$ atm) simulation for both models at 298 K, and results are given in Table I; the original Henchman’s results are also included in this table for comparison. As can be seen, the translational parts of entropy excellently agree with the ones from Ref. 1. Some small differences are observed for rotational parts. There are two reasons for these discrepancies. First, we originate the coordinate system at the center of mass of the water molecule, while Henchman originates it at the oxygen atom. Second, we use the calculated values of the main moments of inertia for each model, which differ from the ones used by Henchman.

Now, we wish to analyze the results obtained from our NVT simulations. We take two quantities into account: the specific heat c_v and the entropy S of the system.

The heat capacity of water was calculated from the temperature dependence of the total energy of the system. Average energies (obtained from 1 ns length run) are reported in Table II. Note that the total energy slightly deviates (as a

TABLE I. Comparison of the entropy results obtained in this work with the literature data (Ref. 1). All the values are in J/mol K units. Temperature $T=298$ K, pressure $p=1$ atm.

| | TIP4P | | SPC | |
|-------------------------------|-----------|--------|-----------|--------|
| | This work | Ref. 1 | This work | Ref. 1 |
| Translational contributions | | | | |
| x | 15.19 | 15.2 | 15.39 | 15.4 |
| y | 14.63 | 14.6 | 14.42 | 14.4 |
| z | 16.56 | 16.6 | 17.39 | 17.4 |
| Summarized | 46.38 | 46.4 | 47.20 | 47.2 |
| Rotational contributions | | | | |
| x | 5.42 | 5.4 | 5.48 | 5.6 |
| y | 6.49 | 6.6 | 7.59 | 7.1 |
| z | 6.87 | 6.9 | 7.14 | 6.8 |
| Summarized | 18.78 | 18.9 | 20.21 | 19.5 |
| $R \ln(3/2)$ | 3.37 | 3.37 | 3.37 | 3.37 |
| Total calculated entropy, S | 68.53 | 68.7 | 70.78 | 70.1 |

TABLE II. Total energy E and the entropy of system calculated by using harmonic approximation S_H for TIP4P and SPC water models at various temperatures T .

| T (K) | TIP4P | | SPC | |
|---------|--------------|-----------------|--------------|-----------------|
| | E (kJ/mol) | S_H (J/mol K) | E (kJ/mol) | S_H (J/mol K) |
| 278 | -35.74 | 64.28 | -35.94 | 66.39 |
| 283 | -35.30 | 65.37 | -35.55 | 67.40 |
| 288 | -34.86 | 66.39 | -35.14 | 68.35 |
| 298 | -34.01 | 68.42 | -34.37 | 70.28 |
| 308 | -33.19 | 70.45 | -33.63 | 72.18 |
| 318 | -32.38 | 72.33 | -32.90 | 74.00 |
| 333 | -31.23 | 75.09 | -31.84 | 76.64 |
| 348 | -30.12 | 77.67 | -30.81 | 79.16 |
| 363 | -29.05 | 80.19 | -29.79 | 81.54 |

function of temperature) from the straight line. The mean value of specific heat c_v calculated from these results equals (78.95 ± 1.00) J/mol K for TIP4P model and (72.34 ± 0.72) J/mol K for SPC one. These values can be compared to literature data. Jorgensen and Jenson⁵ have calculated various thermodynamic quantities for both TIP4P and SPC water models: isobaric heat capacity c_p , thermal expansion coefficient α , and isothermal compressibility factor κ . From the thermodynamic relation,

$$c_p - c_v = \frac{\alpha^2 VT}{\kappa} \quad (1)$$

and by using the values given in Ref. 5, we found $c_v = (83.7 \pm 3.7)$ J/mol K for the TIP4P model, and $c_v = (74.6 \pm 4.8)$ J/mol K for the SPC model. Thus, our results agree with the literature data.

The results of our entropy calculations at various temperatures are given in Table II; the literature data of the absolute entropy of TIP4P water were taken from the paper of Saija *et al.*⁶ The results for TIP4P model (plotted as a function of $\ln T$) are graphically presented in Fig. 1; the dashed line on this figure represents variation of the absolute entropy of water S_{abs} estimated by taking into account the temperature dependence of c_v value. The heat capacity was calculated from the temperature dependence of the total energy, where energy was approximated by the third degree polynomial of temperature. Looking at this figure, we see that Henschman's method better describes the entropy of TIP4P water at higher temperatures: the difference $\Delta S = S_H - S_{\text{abs}}$ equals 5.6 J/mol K at 278 K, but only 0.4 J/mol K at 363 K; also for SPC water similar behavior is supposed. Consequently, harmonic approximation underestimates the

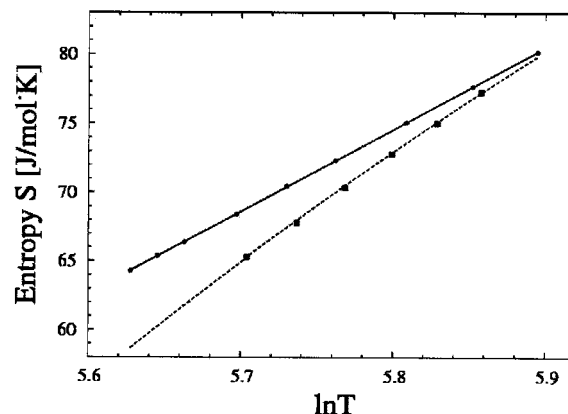


FIG. 1. Calculated entropy of TIP4P water as a function of $\ln T$. Black dots represent S_H results, calculated using harmonic approximation. Filled squares represent the literature values (taken from Ref. 6) of the absolute entropy of TIP4P water obtained under constant pressure conditions ($P=1$ atm).

heat capacity: we found 59.55 J/mol K for TIP4P and 56.90 J/mol K for SPC. We explain these results as follows. The water molecule moves within the potential well with a relatively “flat” bottom and steeply inclined walls. The main contributions to the mean force (or torque) originate from this wall region. Therefore, Henschman's method approximates the wall potential rather than the bottom one. Since this wall region is dominant at higher temperatures, then harmonic approximation will work better if temperature rises.

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