Direct Entropy Calculation of Liquid Water Using Acceptance Ratios

Seung Do Hong* and Du-Jeon Jang
School of Chemistry, Seoul National University, Seoul 151-742, Korea

(Received June 10, 2002; CL-020487)

The excess entropy has been calculated directly employing acceptance ratios during a single Monte Carlo or molecular dynamics simulation. Very stable excess entropies have been obtained for both water and hard-dumbbell fluids. The upper and lower limits of the cell volumes are suggested as well.

The calculation of the free energy and the entropy for chemical and biological systems has been a topic of central importance. Thanks to recent rapid progress in the field of computer simulations, a number of methods[1–4] have been proposed for the calculation. However, it is very difficult yet to calculate the free energy and the entropy directly from computer simulations.

The excess entropy of an N-particle system could be approximately expressed using the average of effective acceptance ratios $f(r_R, r)$ as[5]

$$\frac{S^{ex}}{Nk} \approx \ln \frac{\int_{\Delta} f(r_R, r) \exp(-\phi/kT) dq}{\int_{\Delta} \exp(-\phi/kT) dq} = \ln \langle f(r_R, r) \rangle_{\Delta}, \quad (1)$$

where r is a configuration of a molecule sampled during the Metropolis Monte Carlo[6] or the constant NVT molecular dynamics[3] simulation and r_R is a virtual random configuration generated by a separate parallel Monte Carlo procedure within the cell Δ. On the other hand, ϕ is the potential energy of the molecule at the configuration r. In equation 1, $\langle f(r_R, r) \rangle_{\Delta}$ denotes the canonical ensemble average of $f(r_R, r)$ over r_R. An effective acceptance ratio was expressed as

$$f(r_R, r) = \begin{cases} \exp[-(\phi_R - \phi)/kT] & \text{if } \phi_R \geq \phi, \\ 1 + 2.3\{\exp[-(\phi_R - \phi)/2kT] - 1\} & \text{if } \phi_R < \phi, \end{cases} \quad (2)$$

where ϕ_R is the potential energy at r_R of the sampled molecule. The cell was selected as a cube having a fixed volume V/N, centered at the configuration r. While it is actually impossible to average the Boltzmann factors owing to great fluctuations, we can reduce the fluctuations considerably by averaging $f(r_R, r)$.[5] However, the residual fluctuations still remain in the method. In particular, the averages of $f(r_R, r)$ in computer simulations for liquid water having strong electrostatic interactions show significant fluctuations. Therefore it would be hard to apply the method generally to complex systems such as water.

The average of acceptance ratios should give much more stable results than the effective acceptance ratio. An acceptance ratio $a(r_R, r)$ is expressed as

$$a(r_R, r) = \begin{cases} \exp[-(\phi_R - \phi)/kT] & \text{if } \phi_R \geq \phi, \\ 1 & \text{if } \phi_R < \phi. \end{cases} \quad (3)$$

The acceptance ratio and the Boltzmann factor are shown in Figure 1. However, the excess entropy is inevitably underestimated if $a(r_R, r)$, instead of $f(r_R, r)$, is averaged in equation 1.

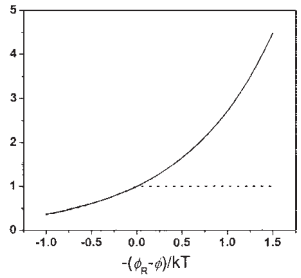

Figure 1. The Boltzmann factor (solid) and the acceptance ratio (dotted) as functions of the potential energy difference $(\phi_R - \phi)$ obtained throughout virtual random sampling.

We can consider two possible recipes to correct the underestimation. One is that we preserve the cell volume as V/N and introduce a scaling factor. The other is that we regard the cell volume as a parameter, change it to a smaller value, and then calculate the excess entropy utilizing only $a(r_R, r)$. We have applied the former recipe to the two-center-Lennard-Jones liquids and the details of the method are described elsewhere.[7] In this Letter we focus on the latter one because it may be applied to complex systems. This method utilizing the average of $a(r_R, r)$ along with the cell volume smaller than V/N will be named as acceptance ratio averaging (ARA). We have applied ARA to liquid water and hard-dumbbell fluids.

Liquid water has been a topic of fundamental importance until recently.[8] On the contrary, the hard dumbbell is a very simple system having no attractive force. The relevant cell volume could be easily obtained from simple test calculations. Simulations for the TIP4P[9] and ST2[10] models of water have been performed at 25 °C and 1 g/cm^3. We have chosen 8 Å^3 (0.2674 V/N) as the cell volume for liquid water, which is considered to give the lower limit of the cell volumes. 216 molecules were simulated and 3×10^6 configurations were averaged after equilibration. The periodic boundary conditions were used and the cut-off distances of TIP4P and ST2 models were 8.5 Å[9] and 8.46 Å,[10] respectively. The hard-dumbbell system[11] consists of two fused hard spheres with the elongation l/σ, in which l is the center-to-center separation of two hard spheres having the diameter σ. The reduced density ρd^3 is defined as $\rho\sigma^3[1 + 1.5(l/\sigma) - 0.5(l/\sigma)^3]$. The relevant cell volume of the hard-dumbbell system has been estimated to be 0.5615 V/N,[11] which is presumed to be the upper limit of the cell volumes. Because a bug was found in the used program,[11] we have newly performed calculations for hard-dumbbell fluids. 216 molecules were simulated and about 1×10^6 configurations were averaged after equilibration using the periodic boundary conditions.

In each configuration sampled during the Metropolis Monte Carlo simulation, a sampled molecule is moved to a virtual random configuration r_R and rotated freely throughout a separate

parallel Monte Carlo procedure. Then $a(r_R, r)$ is evaluated at r_R and averaged. Thereafter the virtual configuration is removed and the normal Metropolis Monte Carlo procedure is performed. At each time step of the constant *NVT* molecular dynamics simulation, $a(r_R, r)$ is evaluated and averaged throughout the separate parallel Monte Carlo procedure as well. The excess Helmholtz free energy is obtained by $A^{ex} = U - TS^{ex}$ where U is the averaged potential energy.

The internal energies and excess entropies of water models calculated using ARA are summarized in Table 1 with reported values.[9,10,12] Their excess free energies are also shown in Table 2 to compare with reported values.[12–15] ARA gives much more stable results, converged within ± 0.02, compared with other calculation methods. The results of hard-dumbbell fluids with $l/\sigma = 1.0$ are reported in Table 3. Our results are in good agreement with those from the particle insertion[11,16] (PI) and thermodynamic integration (TI) using Tildesley-Streett[17] and Boublik-Nezbeda[18] equations of state. Very stable results converged within ± 0.01 have been obtained for hard-dumbbell fluids. The results calculated using 125 and 256 molecules for hard-dumbbell fluids have been almost the same as those using 216 molecules. ARA gives satisfactory results for hard-sphere fluids as well as for hard-dumbbell fluids with various elongations.[11]

Table 1. Internal energies and excess entropies calculated for water models at 25 °C and 1 g/cm^3

	U/kcal/mol		TS^{ex}/kcal/mol	
	ARA[a]	Reported	ARA[a]	Reported
TIP4P	−10.06	−10.10[b]	−4.45	
ST2	−10.08	−10.11[c]	−4.38	
Experiment[d]		−9.974		−4.242

[a]Calculated from the average of $a(r_R, r)$. [b]Calculated.[9] [c]Fitted from calculated results.[10] [d]Ref 12.

Table 2. Excess Helmholtz free energies calculated for water models at 25 °C and 1 g/cm^3

	A^{ex}/kcal/mol	
	ARA	Reported
TIP4P	-5.60 ± 0.02	-5.60 ± 0.09[a], -5.5 ± 0.3[b]
ST2	-5.71 ± 0.02	−5.40[c]
Experimental[d]		−5.732

[a]Calculated using the Monte Carlo recursion method.[13] [b]Calculated using the single solvent perturbation method.[14] [c]Calculated from thermodynamic integration.[15] [d]Ref 12.

Table 3. Excess Helmholtz free energies of hard-dumbbell fluids with the elongation $l/\sigma = 1.0$

ρd^3	A^{ex}/NkT			
	ARA	PI[a]	TS[b]	BN[c]
0.3	1.16	1.12	1.13	1.11
0.4	1.68	1.66	1.66	1.64
0.5	2.34	2.21	2.32	2.27
0.6	3.12	3.14	3.12	3.03
0.7	4.08	—[d]	4.13	3.93

[a]Calculated using the particle insertion method.[11,16] [b]Calculated from thermodynamic integration using Tildesley-Streett equation of state.[17] [c]Calculated from thermodynamic integration using Boublik-Nezbeda equation of state.[18] [d]The excess free energies in high-density regions could not be well evaluated throughout 1×10^6 configurations, owing to extremely low acceptance ratios of sampled molecules.

PI is hard to apply for high-density regions of hard-dumbbell fluids due to the extremely low acceptance ratio of the test particle. The acceptance ratio of a hard-dumbbell molecule at $\rho d^3 = 0.9$ from ARA is about 1×10^{-3}, whereas the acceptance ratio of the test particle in PI is estimated to be only 3×10^{-14}.[17]

The cell volumes of the above-mentioned two systems give us very important criteria for the direct calculation of the excess entropy. For example, the Lennard-Jones system can be regarded to be intermediate between liquid water and hard-dumbbell systems. For the Lennard-Jones fluid at $\rho\sigma^3 = 0.75$ and $kT/\varepsilon = 1.071$, the excess free energy ($A^{ex}/NkT = -2.25$) obtained from ARA employing the cell volume of 0.42 V/N is actually the same as the result from TI.[19]

The relative error of ARA in the evaluation of the excess entropy is estimated to be within 1% and 0.2% for liquid water and hard-dumbbell fluids, respectively. Our method does not need any reference system and so overcomes the difficulties arising from phase transitions of high-density fluids or solids.[20] ARA is an extremely efficient method because the excess entropy is directly calculated from a single computer simulation at fixed density and temperature.

We have calculated the excess entropies of liquid water and hard-dumbbell fluids directly by averaging the acceptance ratios during a single computer simulation. We have obtained very stable results for both liquid water and hard-dumbbell fluids. The upper and lower limits of the cell volumes have been suggested as well. This method is expected to be applicable to more complex systems extensively.

We acknowledge the Brain Korea 21 Program and the Center for Molecular Catalysis.

References

1 J. P. Valleau and G. M. Torrie, in "Modern theoretical chemistry," ed. by B. J. Berne, Plenum Press, New York (1977), Vol. 5, p 169.
2 M. P. Allen and D. J. Tildesley, "Computer Simulation of Liquids," Clarendon, Oxford (1987).
3 A. Z. Panagiotopoulos, *Fluid Phase Equilib.*, **116**, 257 (1996).
4 S. C. Gay, J. C. Rainwater, and P. D. Beale, *J. Chem. Phys.*, **112**, 9841 (2000).
5 a) S. D. Hong and M. S. Jhon, *Chem. Phys. Lett.*, **273**, 79 (1997). b) S. D. Hong, B. J. Yoon, and M. S. Jhon, *Chem. Phys. Lett.*, **188**, 299 (1992).
6 N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).
7 S. D. Hong and D.-J. Jang, *Chem. Lett.*, **2002**, 442.
8 a) F. H. Stillinger, *Science*, **209**, 451 (1980). b) P. L. Geissler, C. Dellago, D. Chandler, J. Hutter, and M. Parrinello, *Science*, **291**, 2121 (2001).
9 W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.*, **79**, 926 (1983).
10 a) W. L. Jorgensen and J. D. Madura, *Mol. Phys.*, **56**, 1381 (1985). b) F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, **60**, 1545 (1974).
11 S. D. Hong, B. J. Yoon, and M. S. Jhon, *Mol. Phys.*, **75**, 355 (1992).
12 A. Ben-Naim and Y. Marcus, *J. Chem. Phys.*, **81**, 2016 (1984).
13 Z. Li and H. A. Scheraga, *Chem. Phys. Lett.*, **154**, 516 (1989).
14 W. L. Jorgensen, J. F. Blake, and J. K. Buckner, *Chem. Phys.*, **129**, 193 (1989).
15 M. Mezei, *Mol. Phys.*, **47**, 1307 (1982).
16 B. Widom, *J. Chem. Phys.*, **39**, 2808 (1963).
17 D. J. Tildesley and W. B. Streett, *Mol. Phys.*, **41**, 85 (1980).
18 T. Boublik and I. Nezbeda, *Chem. Phys. Lett.*, **46**, 315 (1977).
19 D. Levesque and L. Verlet, *Phys. Rev.*, **184**, 151 (1969).
20 B. J. Yoon, S. D. Hong, M. S. Jhon, and H. A. Scheraga, *Chem. Phys. Lett.*, **181**, 73 (1991).