

Calculation of the Free Energy from the Average of the Modified Effective Acceptance Ratio for the Two-Center-Lennard-Jones Liquid

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The method of calculating the excess Helmholtz free energy from the averaged effective acceptance ratio for the Lennard-Jones fluid and the inverse twelve fluid has been slightly modified and applied to the two-center-Lennard-Jones liquid. The excess Helmholtz free energy is calculated directly from the average of the modified effective acceptance ratio through a single Metropolis Monte Carlo simulation. Therefore this method does not need any reference system. The results of the present method were satisfactory compared with those of the perturbation theories and the overlap ratio method.

Introduction

The evaluation of the free energy or the entropy in computer simulation has been the important but difficult subject. There has been rapid progress in the field of computer simulation recently.¹ For the evaluation of the free energy or the entropy in computer simulation, a number of methods¹⁻³ have been proposed. The thermodynamic integration method⁴ has been used commonly in the absence of any satisfactory computer simulation method of calculating the free energy. In the thermodynamic integration method, computer simulations on many densities or temperatures should be performed to evaluate the excess free energy. Also this method would not be able to avoid difficulties arising from phase transitions. Accordingly this method is a cumbersome and wasteful means of obtaining the free energy at high densities.² The Widom's particle insertion method⁵ evaluates the chemical potential from the potential energy according to random insertion of a test particle. Consequently this method is closely related to the grand canonical Monte Carlo simulations.¹ The overlap ratio method,^{6,7} originated by Bennett,⁸ evaluates the free energy through the comparison of energy distributions. The umbrella sampling method^{9,10} was proposed as a way to obtain the free energy difference from a single Monte Carlo run in which the parts of configurational space relevant to a range of physical situations is sampled. The umbrella sampling method evaluates the average over non-physical sampling distribution to calculate the free energy difference. As a result, this method needs the relevant reference system. Also this method uses a trial and error choosing of the weighing function. The success of this method would be doubtful if two systems are not so similar.¹¹ Valleau *et al.* extended this method to the thermodynamic scaling Monte Carlo method.¹²⁻¹⁴ The umbrella sampling method or the thermodynamic scaling Monte Carlo method gives the relative free energy, and so these methods need the relevant reference system.

It will be difficult to evaluate the free energy or the entropy from the canonical ensemble average.² We proposed

recently a practical method^{15,16} to evaluate the excess Helmholtz free energy from the averaged effective acceptance ratio in the Monte Carlo simulation for model potential systems, where the excess free energy represents the configurational free energy of the model potential system over that of the ideal gas. In this method, the free energy has been evaluated as the canonical ensemble average. This method did not need any reference system. The results of this method for the Lennard-Jones fluid and the inverse twelve fluid were satisfactory compared with those of other methods. This method can be applied to high density fluids and also overcome the difficulties arising from phase transitions.¹⁷ The two-center-Lennard-Jones (2CLJ) fluid^{18,19} is composed of homonuclear diatomic molecules with two Lennard-Jones interaction sites. For the 2CLJ liquid, the effective acceptance ratio used in previous studies^{15,16} has been slightly modified. In the present work, the excess Helmholtz free energy for the 2CLJ liquid has been evaluated from the modified effective acceptance ratio. The results of the present method for the 2CLJ liquid were satisfactory compared with those of the perturbation theories and the overlap ratio method. Also the present method can be applied directly to molecular dynamics simulation.

Method

We proposed recently an efficient equation^{15,16} for the evaluation of the excess entropy given by

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

where $\langle \rangle$ denotes the canonical ensemble average and r is a configuration of a molecule sampled during the Metropolis Monte Carlo simulation²⁰ and r_R is a random configuration within the cell generated by the separate parallel Monte Carlo procedure. The cell for the evaluation of the effective acceptance ratio $f(r_R, r)$ was selected as a cube with fixed volume V/N centered on a configuration of a molecule sampled

during the Metropolis Monte Carlo procedure. The effective acceptance ratio introduced for the Lennard-Jones fluid and the inverse twelve fluid is slightly modified for the 2CLJ liquid as

$$f(r_R, r) = \exp[-(\phi_R - \phi)/kT], \text{ if } \phi_R > \phi$$

$$f(r_R, r) = 1 + 1.7\{\exp[-(\phi_R - \phi)/2kT] - 1\}, \text{ if } \phi_R > \phi \quad (2)$$

where ϕ is the potential energy of a molecule sampled during the Metropolis Monte Carlo simulation and ϕ_R is the potential energy of random configuration of a molecule within the cell generated by the separate parallel Monte Carlo procedure. In the cases of the Lennard-Jones fluid and the inverse twelve fluid, the value of 2.3 was used instead of 1.7 in Eq. (2) for the 2CLJ liquid. The physical meaning of these numbers will be discussed later.

The homonuclear 2CLJ potential U_{2CLJ} has the form

$$U_{2CLJ} = \sum_{i,j=1}^2 U_{LJ}(r_{ij})$$

$$U_{LJ}(r_{ij}) = 4\varepsilon \left\{ \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right\} \quad (3)$$

where ε is the potential energy well depth and σ is the length parameter with and i and j denote two interaction sites on different molecules. The distance between two interaction sites on one molecule is denoted by elongation l . The reduced quantities T^* , ρ^* and l^* denote kT/ε , $\rho\sigma^3$ and l/σ , respectively.

In each configuration sampled during the Metropolis Monte Carlo simulation, the center of mass of a sampled molecule is moved temporarily to random position within the cell and rotated freely about the moved center of mass. Then the modified effective acceptance ratio at the temporary random configuration is evaluated and averaged over the canonical ensemble. Thereafter the temporary configuration in the cell is removed and the usual Metropolis Monte Carlo procedure is performed. The excess Helmholtz free energy is obtained by

$$A^{ex} = U - TS^{ex} \quad (4)$$

where U is the potential energy of the 2CLJ system averaged over the canonical ensemble.

For the 2CLJ liquid, 108 molecules were used in the simulation and about 5×10^5 configurations were averaged after equilibration. Only one atom was moved at a time. The mean acceptance ratio of the Metropolis Monte Carlo procedure was adjusted to about 0.5. The long-range energy correction and the periodic boundary condition were used and the cutoff distance for the 2CLJ potential was half the box length.

Results and Discussion

Calculations have been performed for the 2CLJ liquids with elongations $l^* = 0.3292$, 0.63 and 0.793, respectively. The values of excess Helmholtz free energy for the 2CLJ liq-

uid with $l^* = 0.3292$ are listed in Table 1. For the 2CLJ liquid with $l^* = 0.3292$, simulations have been performed at various temperatures and densities. The results of the present method have been satisfactory compared with those of the perturbation theories^{18,19} and the overlap ratio method.^{6,7} The excess Helmholtz free energy in the present work is identical, in definition, with the configurational free energy in the perturbation theories.^{18,19} For the 2CLJ liquids with $l^* = 0.3292$ at various temperatures and densities, the present method shows consistent tendency. The results for the 2CLJ liquids with $l^* = 0.63$ and 0.793 were not good at high densities, but the results at some densities were satisfactory compared with those of the perturbation theory.¹⁸ The values of excess Helmholtz free energy for the 2CLJ liquids with $l^* = 0.63$ and 0.793 at some densities are listed in Tables 2-3, respectively.

The present method used only one fixed parameter for the modified effective acceptance ratio even though the value of 1.7 used in Eq. (2) was different from the value of 2.3 used

Table 1. Excess Helmholtz free energy A^{ex}/NkT of the 2CLJ liquid with $l^* = 0.3292$

T^*	ρ^*	The present method	Previous results
3.0	0.70	-1.75	-1.71 ^a , -1.73 ^b
	0.68	-1.78	-1.81 ^a , -1.75 ^c
	0.66	-1.83	-1.89 ^a , -1.83 ^c
	0.64	-1.84	-1.95 ^a , -1.90 ^c
	0.62	-1.89	-1.99 ^a , -1.95 ^c
	0.60	-1.91	-2.02 ^a , -2.01 ^b
2.0	0.70	-4.75	-4.67 ^a , -4.68 ^b
	0.68	-4.76	-4.71 ^a , -4.72 ^c
	0.66	-4.71	-4.72 ^a , -4.72 ^c
	0.64	-4.67	-4.67 ^a , -4.69 ^c
	0.62	-4.64	-4.66 ^a , -4.66 ^c
	0.60	-4.52	-4.60 ^a , -4.58 ^b
1.55	0.70	-7.55	-7.39 ^a , -7.37 ^b
	0.68	-7.50	-7.36 ^a , -7.37 ^c
	0.66	-7.41	-7.29 ^a , -7.30 ^c
	0.64	-7.24	-7.19 ^a , -7.18 ^c
	0.62	-7.04	-7.07 ^a , -7.08 ^c
	0.60	-6.93	-6.92 ^a , -6.97 ^b

^aResults of the perturbation theory from Reference 18. ^bResults of the overlap ratio method from References 6,7. ^cResults of the perturbation theory from Reference 19 for the 2CLJ liquid with $l^* = 0.33$.

Table 2. Excess Helmholtz free energy A/NkT of the 2CLJ liquid with $l^* = 0.63$

T^*	ρ^*	The present method	Previous results ^a
2.5	0.48	-0.91	-0.93
	0.46	-0.98	-1.01
2.0	0.48	-2.07	-2.02
	0.46	-2.11	-2.07
1.5	0.48	-4.06	-3.93
	0.46	-4.02	-3.89

^aResults of the perturbation theory from Reference 18.

Table 3. Excess Helmholtz free energy A/NkT of the 2CLJ liquid with $l^* = 0.793$

T^*	ρ^*	The present method	Previous results ^a
2.0	0.40	-1.31	-1.29
	0.38	-1.35	-1.33
1.75	0.40	-2.02	-1.92
	0.38	-2.02	-1.94

^aResults of the perturbation theory from Reference 18.

for the Lennard-Jones fluid and the inverse twelve fluid.¹⁶ The effective acceptance ratio was introduced to reduce the fluctuations originated from the average of the Boltzmann factor. Accordingly, the value of 2.3 in the effective acceptance ratio used for the spherically symmetric model potential systems can be changed appropriately in the unsymmetrical 2CLJ system. The present method using the modified effective acceptance ratio gives consistent results for the 2CLJ liquids with $l^* = 0.3292$. Also, the present method does not need any reference system. As a result, the present method gives the free energy and other thermodynamic properties in a single Metropolis Monte Carlo run. Because the separate Monte Carlo procedure is adopted for the evaluation of the excess entropy, the present method is very easy to implement. The present method can be applied directly to molecular dynamics simulation because the present method evaluates the average of the effective acceptance ratio over the Boltzmann distribution. As pointed out by Mezei and Beveridge,³ such methods as the present method may not be applied efficiently to systems consisting of large molecules. Nevertheless, the present method using very simple effective acceptance ratio can be a practical and efficient method to evaluate the free energy because general method of evaluating directly the free energy in computer simulations has not been known yet. Accordingly, the present method may be extended to more complex molecular fluids. If we want fast evaluation of the free energy for simple fluids, we would be able to use the present method. Considering the present method has been applied satisfactorily to the inverse twelve fluid with only repulsive potential,¹⁶ it is thought that the present method does not depend sensitively on model potential function. The quasi-ergodicity related to slow potential energy barrier crossing behavior of the Metropolis Monte Carlo method may be overcome using the jump-walking method²¹⁻²³ or the restricted random search method.²⁴

The umbrella sampling method^{9,10} or the thermodynamic scaling Monte Carlo method¹²⁻¹⁴ gives free energy differences or relative free energies in the range covered over non-Boltzmann sampling distribution. Of course, these methods gives at the same time the usual mechanical quantities such as energy and correlation functions. On the contrary, the present method gives the free energy over Boltzmann sampling distribution. The efficiency of the method using the effective acceptance ratio was represented in our previous work.¹⁵ For the square-well fluid at $T^* = 1.29$ and $\rho^* = 0.68$, the thermodynamic scaling Monte Carlo method¹⁴ gives the result of $A^{ex}/NkT = -1.33$ through average of about 2×10^9

configurations, using the square-well fluid at $T^* = 1.29$ and $\rho^* = 0.1$ as the reference system. However, the method using the effective acceptance ratio gives the result of $A^{ex}/NkT = -1.34$ through a single Monte Carlo run of 1×10^6 configurations for the square-well fluid at $T^* = 1.29$ and $\rho^* = 0.68$ with no reference system.²⁵ As a result, the present method is very efficient method for calculating the free energy.

In cases of the Lennard-Jones fluid and the inverse twelve fluid, the present method gave excellent results for high density fluids.¹⁶ A method similar to the present method had been applied to hard sphere and hard dumbbell fluids previously.²⁶ From the average of the acceptance ratio or the effective acceptance ratio within the cell centered on the sampled molecule, the excess free energy can be calculated efficiently for hard²⁶ or soft^{15,16} potential systems. Even though Eq. (1) is an approximate equation, the effective acceptance ratio must be a useful function. The present method needs further study.

Conclusion

The method of calculating the excess Helmholtz free energy from the averaged effective acceptance ratio has been applied to the two-center-Lennard-Jones liquid. The effective acceptance ratio used for the Lennard-Jones fluid and the inverse twelve fluid was slightly modified for the application to the two-center-Lennard-Jones liquid. The excess Helmholtz free energy for the two-center-Lennard-Jones liquid could be evaluated efficiently from the average of the modified effective acceptance ratio through a single Metropolis Monte Carlo run.

References

- Panagiotopoulos, A. Z. *Fluid Phase Equilibria* **1996**, *116*, 257.
- Valleau, J. P.; Torrie, G. M. In *Modern theoretical chemistry, Statistical mechanics A, Equilibrium techniques*; Berne, B. J., Ed.; Plenum Press: New York, U. S. A., 1977; Vol. 5, p 169.
- Mezei, M.; Beveridge, D. L. *Ann. NY Acad. Sci.* **1986**, *482*, 1.
- Kirkwood, J. G. In *Theory of Liquids*; Alder, B. J., Ed.; Gordon and Breech: New York, U. S. A., 1968.
- Widom, B. *J. Chem. Phys.* **1963**, *39*, 2808.
- Quirke, N.; Jacucci, G. *Mol. Phys.* **1982**, *45*, 823.
- Jacucci G.; Quirke, N. *Mol. Phys.* **1980**, *40*, 1005.
- Bennett, C. H. *J. Comput. Phys.* **1976**, *22*, 245.
- Torrie, G. M.; Valleau, J. P. *Chem. Phys. Lett.* **1974**, *28*, 578.
- Torrie, G. M.; Valleau, J. P. *J. Comput. Phys.* **1977**, *23*, 187.
- Han, K.-K. *Phys. Lett. A* **1992**, *165*, 28.
- Valleau, J. P. *J. Comput. Phys.* **1991**, *96*, 193.
- Valleau, J. P. *J. Chem. Phys.* **1993**, *99*, 4718.
- Brilliantov, N. V.; Valleau, J. P. *J. Chem. Phys.* **1998**, *108*, 1115.
- Hong, S. D.; Yoon, B. J.; Jhon, M. S. *Chem. Phys. Lett.*

- 1992**, 188, 299.
16. Hong, S. D.; Jhon, M. S. *Chem. Phys. Lett.* **1997**, 273, 79.
 17. Yoon, B. J.; Hong, S. D.; Jhon, M. S.; Scheraga, H. A. *Chem. Phys. Lett.* **1991**, 181, 73.
 18. Fischer, J. J. *Chem. Phys.* **1980**, 72, 5371.
 19. Kohler, F.; Quirke, N.; Perram, J. W. *J. Chem. Phys.* **1979**, 71, 4128.
 20. Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, 21, 1087.
 21. Frantz, D. D.; Freeman, D. L.; Doll, J. D. *J. Chem. Phys.* **1990**, 93, 2769.
 22. Frantz, D. D.; Freeman, D. L.; Doll, J. D. *J. Chem. Phys.* **1992**, 97, 5713.
 23. Tsai, C. J.; Jordan, K. D. *J. Chem. Phys.* **1993**, 99, 6957.
 24. Hong, S. D.; Jhon, M. S. *Chem. Phys. Lett.* **1997**, 267, 422.
 25. Hong, S. D. (to be published).
 26. Hong, S. D.; Yoon, B. J.; Jhon, M. S. *Mol. Phys.* **1992**, 75, 355.
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