# Evaluation of the Excess Free Energy for Two-Center-Lennard-Jones Liquids Using the Bent Effective Acceptance Ratio

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A method of calculating the excess Helmholtz free energy from the average of the bent effective acceptance ratio for two-center-Lennard-Jones liquids has been presented. The bent effective acceptance ratio has been newly composed from the acceptance ratio for the potential energy difference between a configuration in the Metropolis Monte Carlo procedure and random virtual configuration generated by the separate parallel Monte Carlo procedure and the Boltzmann factor for half the potential energy difference. The excess Helmholtz free energy was calculated directly from the average of the bent effective acceptance ratio through a single Metropolis Monte Carlo run. Because the separate parallel Monte Carlo procedure was used, this method can be applied to molecular dynamics simulations. For two-center-Lennard-Jones liquids, the average of the bent effective acceptance ratio gave better results than use of the modified effective acceptance ratio in the previous work.

## Introduction

The calculation of the free energy or entropy in computer simulations has been an important subject in physical chemistry. For the evaluation of the free energy or entropy in computer simulations, a number of methods[1~3] have been proposed including the thermodynamic integration method,[4] the particle insertion method,[5] the overlap ratio method,[6,7] and the temperature-density scaling Monte Carlo method.[8] Nevertheless, a direct and general method for evaluating the free energy or entropy in computer simulations has not been established yet. The overlap ratio method evaluates the free energy through a comparison of energy distributions. The temperature-density scaling Monte Carlo method, which originated from the umbrella sampling method,[9] evaluates the free energy from a single Monte Carlo run. This method evaluates the free energy difference in the range covered over the non-Boltzmann sampling distribution, employing a trial and error selection of the weighting function. Though a general recipe[10,11] for the successful non-Boltzmann sampling simulation has been presented, the temperature-density scaling Monte Carlo method needs a relevant reference system. Generally speaking, it is difficult to evaluate the free energy or the entropy from the canonical ensemble average.[1]

We have presented recently a practical method for calculating the excess Helmholtz free energy from the canonical ensemble average of the modified effective acceptance ratio for two-center-Lennard-Jones (2CLJ) liquids.[12] The excess free energy represents the configurational free energy of the model potential system over that of the ideal gas. In the previous work,[12] the modified effective acceptance ratio was composed using the acceptance ratio for the potential energy difference which is the difference between the potential energy of a configuration in the Metropolis Monte Carlo procedure and that of random virtual configuration generated by the separate parallel Monte Carlo procedure and the Boltzmann factor for half the potential energy difference. This method needed no reference system. This method can be applied to high-density fluids and also overcome the difficulties arising from phase transitions.[13~15] The modified effective acceptance ratio in the previous work[12] is a monotonously increasing function and the value of the effective acceptance ratio equals that of the acceptance ratio for $\phi_R \geq \phi$, where $\phi$ is the potential energy of a molecule sampled during the Metropolis Monte Carlo simulation and $\phi_R$ is the potential energy of virtual random configuration generated through the separate parallel Monte Carlo procedure. However, the modified effective acceptance ratio is not an optimized function. Therefore, a new type of effective acceptance ratio may be composed.

A bent-type of the effective acceptance ratio function can be composed for high-density fluids because of sufficient sampling for the low potential energy region during virtual random sampling. In the present work, the bent effective acceptance ratio is composed for 2CLJ liquids using the acceptance ratio for the potential energy difference between a configuration in the Metropolis Monte Carlo procedure and virtual random configuration generated by the separate parallel Monte Carlo procedure and the Boltzmann factor for half the potential energy difference. The excess Helmholtz free energy is calculated directly from the average of the bent effective acceptance ratio through a single Metropolis Monte Carlo run. For 2CLJ liquids, the average of the bent effective acceptance ratio in the present work gave better results than use of the modified effective acceptance ratio in the previous work.[12] Also, the present method can be applied directly to molecular dynamics simulations because the separate parallel Monte Carlo procedure is used. The present method is very efficient because the excess free energy is evaluated through a single Monte Carlo run at fixed density and temperature.

### The Bent Effective Acceptance Ratio

We proposed recently a practical and efficient equation[12~15] 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 < > denotes the canonical ensemble average, $r$ is a configuration of a molecule sampled during the Metropolis Monte Carlo simulation[16] and $r_R$ is virtual random configuration within the cell generated by the separate parallel Monte Carlo procedure. This equation was derived approximately[14] from the concept of the free volume in the cell methods.[17] 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 the center of mass of a molecule sampled during the Metropolis Monte Carlo procedure. The modified effective acceptance ratio introduced for 2CLJ liquids in the previous work[12] was expressed as

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

where $\phi$ is the potential energy of a molecule sampled during the Metropolis Monte Carlo simulation and $\phi_R$ is the potential energy of virtual random configuration of a molecule within the cell generated by the separate parallel Monte Carlo procedure. Here the acceptance ratio in the cell can be written by

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

The acceptance ratio $a(r_R, r)$ will be obtained if the constant 1.7 is replaced with 0 in Eq. (2) for the modified effective acceptance ratio. To reduce the fluctuations according to the average of the Boltzmann factor, especially for $\phi_R < \phi$, an effective function $h(r_R, r)$ is introduced as

$$h(r_R, r) = \exp[-(\phi_R - \phi)/kT], \quad \text{if} \quad \phi_R \geq \phi,$$
$$h(r_R, r) = \exp[-(\phi_R - \phi)/2kT], \quad \text{if} \quad \phi_R < \phi. \quad (4)$$

The factor of ½ introduced in this effective function is closely related to the factor of ½ used for the lattice energy in the cell methods.[17] Then the modified effective acceptance ratio in the previous work[12] $f(r_R, r)$ can be expressed as $1.7h(r_R, r)$–$0.7a(r_R, r)$. The shape of the modified acceptance ratio is similar to that of the Boltzmann factor as shown in Figure 1.

On the other hand, a new type of effective acceptance ratio instead of the modified effective acceptance ratio can be used as an effective acceptance ratio for high-density fluids such as 2CLJ liquids. Therefore, a bent effective acceptance ratio is introduced in the present study as

$$f(r_R, r) = 2.27\exp[-(\phi_R - \phi)/kT], \quad \text{if} \quad \phi_R \geq \phi,$$
$$f(r_R, r) = 3.27-\exp[-(\phi_R - \phi)/2kT], \quad \text{if} \quad \phi_R < \phi. \quad (5)$$

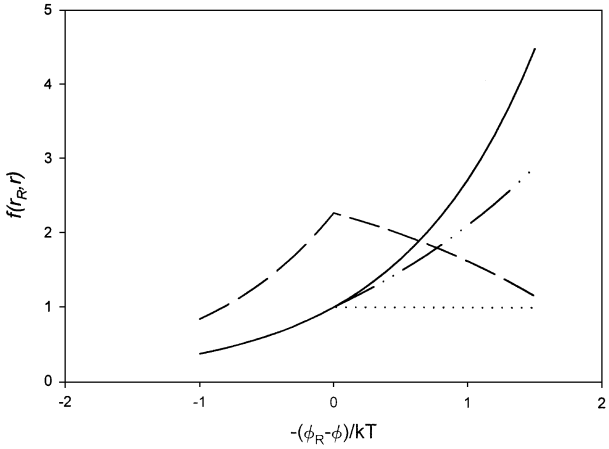


**Figure 1**. The solid line denotes the Boltzmann factor, the dotted line the acceptance ratio, the dashed line the bent effective acceptance ratio, and the dash-dotted line the modified effective acceptance ratio.

The bent effective acceptance ratio in the present study $f(r_R, r)$ can be expressed as $3.27a(r_R, r)$–$h(r_R, r)$ and is shown in Figure 1. The shape of the bent effective acceptance ratio is different from that of the modified effective acceptance ratio. The value of the bent effective acceptance ratio increases for $\phi_R \geq \phi$ and decreases for $\phi_R < \phi$.

### Method of Calculation

The 2CLJ fluid[18,19] consists of homonuclear diatomic molecules with two Lennard-Jones interaction sites. This potential function was used as a model potential for such molecules as nitrogen, bromine, and carbon dioxide. The 2CLJ potential $U_{2CLJ}$ is composed of four Lennard-Jones potentials $U_{LJ}(r_{ij})$ between two Lennard-Jones interaction sites given by

$$U_{2CLJ} = \sum_{i,j=1}^{2} U_{LJ}(r_{ij}),$$
$$U_{LJ}(r_{ij}) = 4\varepsilon\left\{\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right\}, \quad (6)$$

where $\varepsilon$ is the potential energy well depth, $\sigma$ is the length parameter with $u_{LJ}(\sigma) = 0$, and $i$ and $j$ denote two interaction sites on different molecules. The distance between two interaction sites on one molecule is denoted by the elongation $l$. The reduced quantities $T^*$, $\rho^*$ and $l^*$ denote $kT/\varepsilon$, $\rho\sigma^3$ and $l/\sigma$, respectively.

In each configuration sampled during the Metropolis Monte Carlo simulation, the center of mass of a sampled molecule is moved temporarily to virtual random position within the cell and rotated freely about the virtual center of mass. Then the bent effective acceptance ratio at the virtual random configuration is evaluated and averaged over the canonical ensemble. Thereafter, the virtual configuration in the cell is removed and the usual Metropolis Monte Carlo procedure is performed. When molecular dynamics simula-

tions are performed, the bent effective acceptance ratio can be averaged through the same separate parallel Monte Carlo procedure. The excess Helmholtz free energy $A^{ex}$ is obtained by

$$A^{ex} = U - TS^{ex}, \quad (7)$$

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

For 2CLJ liquids, 108 molecules were used in the simulations and about $1 \times 10^6$ 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. Calculations were performed for 2CLJ liquids with the elongation $l^* = 0.3292$, which is the model of liquid nitrogen.

## Results and Discussion

The values of the excess Helmholtz free energy for 2CLJ liquids with $l^* = 0.3292$ are listed in Table 1. The results of the present method from the average of the bent effective acceptance ratio were compared with those of the perturbation theories[18,19] and the overlap ratio method.[6,7] Also, the results of the present work were compared with the previous results[12] from the average of the modified effective acceptance ratio. The excess Helmholtz free energy in the present work is the same property as the configurational free energy in the perturbation theories.[18,19] The results in the present work are estimated to be accurate within 0.01 for $T^* = 2.0$ and $T^* = 3.0$ and within 0.02 for $T^* = 1.55$. For 2CLJ liquids with $l^* = 0.3292$ at various temperatures and densities, the present method shows very good results and consistent tendency. Surprisingly, the results of the present method using the bent effective acceptance ratio are better than those from the modified effective acceptance ratio.

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

| $T^*$ | $\rho^*$ | BEAR[a] | MEAR[b] | Other results |
|---|---|---|---|---|
| 3.0 | 0.70 | -1.69 | -1.75 | -1.71,[c] -1.73[d] |
| | 0.68 | -1.79 | -1.78 | -1.81,[c] -1.75[e] |
| | 0.66 | -1.84 | -1.83 | -1.89,[c] -1.83[e] |
| | 0.64 | -1.89 | -1.84 | -1.95,[c] -1.90[e] |
| | 0.62 | -1.93 | -1.89 | -1.99,[c] -1.95[e] |
| | 0.60 | -1.97 | -1.91 | -2.02,[c] -2.01[d] |
| 2.0 | 0.70 | -4.69 | -4.75 | -4.67,[c] -4.68[d] |
| | 0.68 | -4.71 | -4.76 | -4.71,[c] -4.72[e] |
| | 0.66 | -4.69 | -4.71 | -4.72,[c] -4.72[e] |
| | 0.64 | -4.64 | -4.67 | -4.67,[c] -4.69[e] |
| | 0.62 | -4.61 | -4.64 | -4.66,[c] -4.66[e] |
| | 0.60 | -4.56 | -4.52 | -4.60,[c] -4.58[d] |
| 1.55 | 0.70 | -7.42 | -7.55 | -7.39,[c] -7.37[d] |
| | 0.68 | -7.37 | -7.50 | -7.36,[c] -7.37[e] |
| | 0.66 | -7.31 | -7.41 | -7.29,[c] -7.30[e] |
| | 0.64 | -7.22 | -7.24 | -7.19,[c] -7.18[e] |
| | 0.62 | -7.05 | -7.04 | -7.07,[c] -7.08[e] |
| | 0.60 | -6.89 | -6.93 | -6.92,[c] -6.97[d] |

[a]Results of the present work using the bent effective acceptance ratio. [b]Results of the previous work using the modified effective acceptance ratio. [c]Results of the perturbation theory from Reference 18. [d]Results of the overlap ratio method from References 6, 7. [e]Results of the perturbation theory from Reference 19 for 2CLJ liquids with the elongation $l^* = 0.33$.

In the present work, 108 molecules were used in the simulations and consequently the face-centered cubic structure was adopted as the initial configurations. When 125 molecules with the simple cubic structure and 216 molecules with the face-centered cubic structure were used in the simulations, almost the same results were obtained. Because 2CLJ liquids in the present work are relatively simple systems, the simulations using 108 molecules are thought to be satisfactory sufficiently.

In fact, the bent effective acceptance ratio is a special function. At a glance, the modified effective acceptance ratio appears to be more meaningful than the bent effective acceptance ratio because the former is more similar to the Boltzmann factor compared with the latter as shown in Figure 1. Nevertheless, the bent effective acceptance ratio gave better results than the modified effective acceptance ratio. Of course, such results will be possible for high-density fluids such as 2CLJ liquids. Figure 1 shows that the crossing of the bent effective acceptance ratio and the modified effective ratio occurs near $-(\phi_R-\phi)/kT = 0.77$. For use of the bent effective acceptance ratio, sufficient sampling having less virtual sampling energy $\phi_R$ than the crossing point is needed. Sampling probabilities averaged with the interval of 0.2 for $-(\phi_R-\phi)/kT$ during the separate parallel Monte Carlo procedure for the evaluation of the excess entropy are represented in Figure 2. Figure 2 shows that sampling having less virtual sampling energy $\phi_R$ than the crossing point exists sufficiently for 2CLJ liquids. Moreover, sampling having much less virtual sampling energy than the crossing point exhibited a

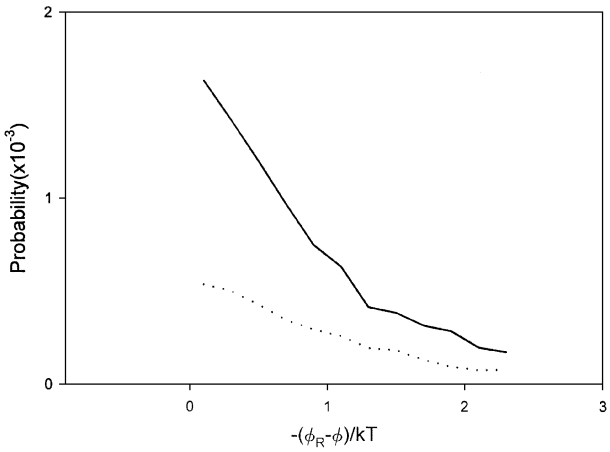


**Figure 2**. Sampling probability averaged with the interval of 0.2 for $(\phi_R-\phi)/kT$ during the separate parallel Monte Carlo procedure. The solid line and dotted line represent the results for $\rho^* = 0.7$ and $\rho^* = 0.6$ at $T^* = 2.0$, respectively.

steep decrease. As a result, the difficulty related to the fluctuations according to the average of the bent effective acceptance ratio is avoided in the case of the 2CLJ liquid.

The methods of calculating the excess free energy from the average of the effective acceptance ratio gave very good results at high densities for the Lennard-Jones fluid and the inverse twelve fluid.[14,15] For 2CLJ liquids, a new type of effective acceptance ratio is designed in the present study. The modified effective acceptance ratio in the previous work emphasizes the effective function $h(r_R, r)$ more than the acceptance ratio $a(r_R, r)$, whereas the bent effective acceptance ratio in the present work emphasizes the acceptance ratio more than the effective function. It is thought that such emphasis on the role of the acceptance ratio reduces prominently the fluctuations according to the average of the bent effective acceptance ratio. As a result, a bent-type of the effective acceptance ratio might be a good choice for high-density fluids such as 2CLJ liquids.

The present method uses no adjustable parameter except for the composition of the bent effective acceptance ratio. Also, the present method uses the cell as a cube with fixed volume V/N, which is the volume per unit molecule. The bent effective acceptance ratio was introduced to reduce the fluctuations originating from the average of the Boltzmann factor as the modified effective acceptance ratio in the previous work. Because the separate parallel Monte Carlo procedure is used to the evaluate the excess entropy, the present method is very easy to implement and can be applied directly to molecular dynamics simulations. Also, the present method does not need a reference system. As a result, the present method can give the excess entropy and other thermodynamic properties in a single Metropolis Monte Carlo or molecular dynamics run. The present method uses the canonical ensemble average, giving the excess free energy over the Boltzmann sampling distribution.

The non-ergodicity or quasi-ergodicity, related to the slow potential energy barrier crossing encountered during computer simulations of more complex systems, can be overcome using the jump-walking method[20] or the taboo search method.[21,22] If the acceptance ratio at long distances are averaged, the excess chemical potential will be obtained.[23,24] This method of using the acceptance ratio at long distances and the present method are thought to be complementary. The acceptance ratio at long distances and the bent effective acceptance ratio can be averaged at the same time in the same frame. The efficiency of the method using the effective acceptance ratio is reported in our previous work.[12-15] Calculations of excess free energy using the present method will save considerable computing time. The present method using the bent effective acceptance ratio must be a practical and very efficient method of evaluating the excess entropy or free energy because the general method of evaluating directly the free energy in computer simulations has not been established yet. It is expected that the present method can be extended to more complex molecular fluids and solutions. Studies on more complex molecular fluids and solutions using the present method will be performed in near future.

## Conclusion

A method for calculating the excess Helmholtz free energy from the average of the bent effective acceptance ratio for 2CLJ liquids has been presented. The bent effective acceptance ratio has been newly composed for the application to 2CLJ liquids. The excess Helmholtz free energy is calculated directly from the average of the bent effective acceptance ratio through a single Metropolis Monte Carlo run. Because the separate parallel Monte Carlo procedure is used, this method is very easy to implement and can be applied to molecular dynamics simulations. For 2CLJ liquids, the average of the bent effective acceptance ratio gave better results than use of the modified effective acceptance ratio in the previous work.

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