An Efficient Method for the Direct Evaluation of the Excess Entropy for Two-Center-Lennard-Jones Liquids Using the Average of Scaled Acceptance Ratios

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(Received December 25, 2001; CL-011292)

We present a direct evaluation of the excess entropy for two-center-Lennard-Jones liquids from the canonical ensemble average of scaled acceptance ratios during a single Monte Carlo or molecular dynamics simulation. The scaled acceptance ratios are averaged over virtual random configurations generated by separate parallel Monte Carlo procedures. No reference system is needed except the ideal gas and so the absolute excess entropy is obtained. The method is extremely efficient.

The evaluation of the free energy and the entropy for chemical and biological systems has been a topic of fundamental importance. However, it is very difficult to calculate them directly from computer simulations. Owing to recent rapid progress in the field of computer simulation, a number of methods have been proposed for their evaluation.[1–3] Thermodynamic integration[1–3] often used in the absence of any appropriate method requires a large number of simulations to evaluate the free energy at a particular condition. The particle insertion (PI) method,[4] successfully applicable for simple systems, is hard to apply for high-density phases due to the extremely low acceptance ratio of the test particle. The method has been modified to the cavity insertion method[5] and applied to biological transport processes.[6] The temperature-and-density-scaling Monte Carlo method[7] evaluates the relative excess free energies and so it requires enormous calculations for a wide range of temperatures and densities with a relevant reference system. The overlap ratio method,[8] originated from the acceptance ratio method of Bennett,[9] evaluates the free energy difference from the comparison of energy distributions. For successful applications of these methods,[8,9] the difference between the model system and the reference one must be small. A fluctuating cell model,[10] using the Metropolis algorithm[11] to generate the canonical ensemble, has been proposed recently. However, its application has been limited only to two-dimensional hard dumbbells in the high-density phases. Thus a general method for the direct evaluation of the free energy or the entropy has not been known up to date.

An efficient method,[12] originated from the cell model,[13] has been proposed for the direct evaluation of the excess entropy of model potential systems. In the method, the excess entropy of a system having N molecules was approximately expressed utilizing the effective acceptance ratio $f(r_R, r)$ as

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

where r, r_R, and ϕ are a configuration of a molecule sampled during the Metropolis Monte Carlo[11] or the constant NVT molecular dynamics[3] simulation, a virtual random configuration generated by a separate parallel Monte Carlo procedure within the cell Δ, and the potential energy of the molecule at the configuration r, respectively. The excess entropy is easily changed into the absolute entropy by adding the entropy of the ideal gas to the excess entropy. In equation 1, $< f(r_R, r) >_\Delta$ denotes the canonical ensemble average of $f(r_R, r)$ at r_R generated within the cell. The effective acceptance ratio has been expressed as[12]

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

where ϕ_R is the potential energy at r_R of the sampled molecule. The cell has been selected as a cube with a fixed volume V/N, centered at the molecule sampled during computer simulation.

Even though it is almost impossible to evaluate the free energy throughout averaging the Boltzmann factors,[1] the average of $f(r_R, r)$ reduces the fluctuation arising from the evaluation of the excess entropy considerably.[12] Nevertheless, the significant fluctuation still remains in the method. Therefore it would be hard to apply the method generally to complex systems. Thus the acceptance ratio $a(r_R, r)$ may be averaged instead of $f(r_R, r)$ to reduce large fluctuations further. Here $a(r_R, r)$ 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 average of $a(r_R, r)$ gives much more stable value compared with that of $f(r_R, r)$. If $a(r_R, r)$ instead of $f(r_R, r)$ is averaged in equation 1, the excess entropy becomes inevitably underestimated. Hard-sphere and hard-dumbbell fluids can have merely 0 or 1 as an acceptance ratio. Their excess entropies[14] were evidently underestimated when the averages of $a(r_R, r)$ were used. This implies that the excess entropy is systematically underestimated regardless of specific model potentials when $a(r_R, r)$ is averaged. If $a(r_R, r)$ is to be used, the systematic underestimation has to be corrected. In this Letter we have introduced a scaling factor for the correction. We have applied the method to the two-center-Lennard-Jones (2CLJ) system.[8,15,16] The 2CLJ system bridges a gap between simple systems such as the Lennard-Jones system and complex systems. The homonuclear 2CLJ potential U_{2CLJ} composed of four Lennard-Jones potentials $U_{LJ}(r_{ij})$ has the form

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

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

where ε is the potential energy well depth, σ 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^*, ρ^* and l^* denote kT/ε, $\rho\sigma^3$ and l/σ, respectively. We have performed calculations for the 2CLJ liquids with $l^* = 0.3292$ as a model of liquid nitrogen.

The scaling factor for the above-mentioned correction can be obtained easily throughout simple test calculations at several conditions. It has been adjusted to $3.3 - 2.25\rho^*$ as a linear function of the density. Thus the scaled acceptance ratio $s(r_R, r)$ is expressed as

$$s(r_R, r) = (3.3 - 2.25\rho^*)a(r_R, r). \tag{5}$$

It is noteworthy that the change of the scaling factor with the variation of the density is small. The method utilizing the average of $s(r_R, r)$ will be named as the scaled acceptance ratio (SAR) method. The scaled acceptance ratio becomes 1.95 $a(r_R, r)$ at $\rho^* = 0.6$ and it is compared with $f(r_R, r)$, $a(r_R, r)$, and the Boltzmann factor as functions of $-(\phi_R - \phi)/kT$ in Figure 1.

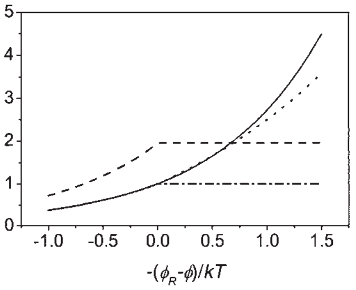

Figure 1. The scaled acceptance ratio at $\rho^* = 0.6$ (dashed), the effective acceptance ratio (dotted), the acceptance ratio (dash-dotted), and the Boltzmann factor (solid) with the variation of $-(\phi_R - \phi)kT$.

In each configuration sampled during the Metropolis Monte Carlo simulation, a sampled molecule is moved temporarily to r_R and rotated freely. Then $s(r_R, r)$ is evaluated at r_R and averaged. Thereafter the virtual configuration is removed and the usual Metropolis Monte Carlo procedure is performed. The SAR method can be applied directly to molecular dynamics simulation because the separate Monte Carlo procedure is executed in parallel for the average of $s(r_R, r)$. At each time step of molecular dynamics, $s(r_R, r)$ is averaged throughout the separate Monte Carlo procedure. The excess Helmholtz free energy A^{ex} is obtained by

$$A^{ex} = U - TS^{ex}, \tag{6}$$

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

For the 2CLJ liquids, 108 molecules were used in the simulation and about 1×10^6 configurations were averaged after equilibration. Only one atom was moved at a time. The long-range energy correction and the periodic boundary condition were used and the cutoff distance was half the box length.

The excess Helmholtz free energies for the 2CLJ liquids with $l^* = 0.3292$ are listed in Table 1. Our results utilizing the average of $s(r_R, r)$ are in good agreement with those of the overlap ratio method[8] and the perturbation theories.[15,16] The relative errors of the SAR method in the evaluation of the excess entropy are estimated to be within 0.5%.

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

T^*	ρ^*	SAR[a]	Previous results
3.0	0.70	−1.66	−1.73,[b] −1.71[c]
	0.68	−1.72	−1.75,[d] −1.81[c]
	0.66	−1.83	−1.83,[d] −1.89[c]
	0.64	−1.88	−1.90,[d] −1.95[c]
	0.62	−1.98	−1.95,[d] −1.99[c]
	0.60	−2.01	−2.01,[b] −2.02[c]
2.0	0.70	−4.70	−4.68,[b] −4.67[c]
	0.68	−4.73	−4.72,[d] −4.71[c]
	0.66	−4.72	−4.72,[d] −4.72[c]
	0.64	−4.68	−4.69,[d] −4.67[c]
	0.62	−4.65	−4.66,[d] −4.66[c]
	0.60	−4.62	−4.58,[b] −4.60[c]
1.55	0.70	−7.43	−7.37,[b] −7.39[c]
	0.68	−7.39	−7.37,[d] −7.36[c]
	0.66	−7.33	−7.30,[d] −7.29[c]
	0.64	−7.24	−7.18,[d] −7.19[c]
	0.62	−7.12	−7.08,[d] −7.07[c]
	0.60	−6.97	−6.97,[b] −6.92[c]

[a] Calculated from the average of $s(r_R, r)$. [b] Ref 8. [c] Ref 15. [d] Ref 16.

The SAR method is very easy to implement and does not need any reference system except the ideal gas. Consequently, the method gives the absolute excess free energy instead of the relative excess free energy and also can overcome the difficulties arising from phase transitions of high-density fluids or solids.[17] Our method is extremely efficient, as reported elsewhere.[12,14] The SAR method may be successfully extended and applied to water,[18] solutions, and biological systems as if the PI method[4] has been modified[5] and applied to biological transport processes.[6]

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

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