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LETTER TO THE EDITOR

Monte Carlo approach to the evaluation of the configurational free energy of chains

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Abstract. The application of a Monte Carlo approach for computing the configurational free energy of chains is described. Whereas the effectiveness of the previous Monte Carlo methods is limited to the systems in which the energies of the *states* (configurations) are not far from zero, the present approach can yield accurate estimates of the free energy of the systems with large configurational energy. The method utilises the relationship:

$$\frac{-\Delta G_{AB}}{kT} = \ln \langle M(U_B - U_A) \rangle_A \quad \text{for} \quad U_B > U_A$$

where ΔG_{AB} is the free energy difference between a pair of systems *A* and *B* and $\langle M(U_B - U_A) \rangle_A$ is the canonical ensemble average of the Metropolis function over *A*, U_A and U_B being the energies of a *state* (configuration) corresponding to *A* and *B* respectively. $\langle M(U_B - U_A) \rangle_A$ is estimated from the configuration samples generated by a method described previously. Calculations of the free energy as a function of bond flexibility are performed for a chain of twenty bonds confined to a tetrahedral lattice.

During the past two decades or so Monte Carlo methods have shown remarkable success in the computation of the ensemble means relating to such properties as configurational energy, configurational heat capacity and pressure (Wood 1968, Lal 1971). However, since a Monte Carlo sample contains only a small fraction of the total configurations assumed by a system, the applicability of the method in the evaluation of the configurational partition function (*Q*) has been severely limited. Recently Valleau and co-workers and Bennett carried out studies on models for monatomic fluids with the main objective of enhancing the scope of the Monte Carlo approach in the evaluation of the partition function (e.g. Torrie and Valleau 1974, 1977, Bennett 1976). Their investigations indicate that it is feasible to estimate the ratio of the partition functions of a pair of systems; the computation is greatly facilitated if there exists sufficient overlap in the canonical ensembles corresponding to the two systems.

The viability of a Monte Carlo scheme for calculating the partition function ratio depends essentially on the existence of a relationship between such a ratio and the ensemble means that are amenable to accurate estimation. Following Bennett consider a pair of systems, *A* and *B*, with configurational energies U_A and U_B , respectively, corresponding to a point *q* in the configuration phase space. Now let there be a function $f(x)$ such that

$$f(x)/f(-x) = e^{-x}. \tag{1}$$

Putting $x = U_B - U_A - C$ (where C is a constant) in (1), one obtains after slight re-arrangement,

$$f(U_B - U_A - C)e^{-U_A} = e^C f(U_A - U_B + C)e^{-U_B}. \quad (2)$$

Integrating both sides of (2) with respect to q and subsequently multiplying the left-hand side by Q_A/Q_A and the right-hand side by Q_B/Q_B ,

$$\frac{Q_A \int f(U_B - U_A - C) e^{-U_A} dq}{Q_A} = \frac{Q_B \int f(U_A - U_B + C) e^{-U_B} dq}{Q_B} e^C$$

or

$$\frac{Q_A}{Q_B} = \frac{\langle f(U_A - U_B + C) \rangle_B}{\langle f(U_B - U_A - C) \rangle_A} e^C \quad (3)$$

where $\langle \rangle_A$ and $\langle \rangle_B$ symbolise the canonical ensemble means over A and B . The configurational free energy difference between A and B , ΔG_{AB} ($= G_B - G_A$), is given by

$$\Delta G_{AB} = kT \ln(Q_A/Q_B) = kT \left[\ln \left(\frac{\langle f(U_A - U_B + C) \rangle_B}{\langle f(U_B - U_A - C) \rangle_A} \right) + C \right]. \quad (4)$$

Two known functions which comply with equation (1) are the Metropolis function, $M(x) = [\min(1, e^{-x})]$ and the Fermi function, $F(x) = (1 + e^x)^{-1}$ (Bennett 1976). Thus

$$\frac{Q_A}{Q_B} = \frac{\langle M(U_A - U_B + C) \rangle_B}{\langle M(U_B - U_A - C) \rangle_A} e^C \quad (5)$$

$$= \frac{\langle F(U_A - U_B + C) \rangle_B}{\langle F(U_B - U_A - C) \rangle_A} e^C. \quad (6)$$

Bennett (1976) showed that the optimum estimation of the ratio Q_A/Q_B is provided by equation (6) with $\langle F(U_A - U_B + C) \rangle_B = \langle F(U_B - U_A - C) \rangle_A$. However, if the soft parts of the potentials governing the configurational energies U_A and U_B are identical, then (5) and (6) would produce equivalent estimates.

We wish to apply the approach embodied in equation (3) to a system of an isolated chain. We should remark that the previous Monte Carlo methods for estimating the configurational free energy of chains can be applied to evaluate ΔG_{AB} only if $U_A = 0$ for all the *states* (Mazur and McCracken 1968, McCracken *et al* 1973). This implies that the effectiveness of such methods is limited to the systems in which the energies of the *states* (configurations) are not far from zero—large difference in the configurational energies of the systems A and B will reduce the overlap in the two ensembles to such an extent that the size of the configuration samples required for estimating the appropriate ensemble means with reasonable accuracy can be prohibitively large. The present approach allows the determination of ΔG_{AB} for non-zero U_A , and as we shall see in the following, this leads to satisfactory estimation of the free energy of the systems with large configurational energy.

We consider a linear tetrahedral chain of N bonds (or $N+1$ segments). The interactions between the non-bonded segments are assumed to be given by the function:

$$u_{ij} = \begin{cases} 0, & d_{ij} \geq l \\ \infty, & d_{ij} < l \end{cases} \quad (7)$$

where u_{ij} is the interaction energy between a pair of segments i, j with distance between them equal to d_{ij} and l is the bond length. Equation (7) stipulates the usual excluded volume condition that no two or more segments can simultaneously occupy the same position in space. A bond in the chain can assume three conformational (rotational) states: *trans*, *gauche*⁺ and *gauche*⁻. The bond conformational energy is accounted for in terms of the parameter $\Delta\epsilon_{t \rightarrow g}$ which expresses the difference between the energies of the *gauche* and the *trans* states (Clark and Lal 1977); it is assumed that $\Delta\epsilon_{t \rightarrow g} \geq 0$. The bond flexibility can be conveniently represented by the parameter $\omega = \exp(-\Delta\epsilon_{t \rightarrow g}/kT)$ which will lie in the range $0(\Delta\epsilon_{t \rightarrow g} = \infty)$ to $1(\Delta\epsilon_{t \rightarrow g} = 0)$. A system is completely defined in terms of the number of bonds in the chain and the parameter $\Delta\epsilon_{t \rightarrow g}$ (or ω).

In the present investigation we attempt to evaluate the configurational free energy of a chain of twenty bonds as a function of ω . For this purpose we consider a series of systems with the values of the bond conformational energy parameter $\Delta\epsilon_{t \rightarrow g}$ so closely spaced that there would exist a high degree of overlap in the configurational ensembles of the successive systems. The series considered here is comprised of the systems defined by $\Delta\epsilon_{t \rightarrow g}/kT = 0, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75$ and 2.00 . Our essential task is to determine the ratio $\langle f(U_A - U_B + C) \rangle_B / \langle f(U_B - U_A - C) \rangle_A$ for all the pairs of the consecutive systems in the series. In the light of the comment following equation (6) it is readily seen that for the model under consideration it is unnecessary to use Bennett's optimised solution, and equation (5) with $C = 0$ should suffice. For $U_B > U_A$, $\langle M(U_A - U_B) \rangle_B = 1$; therefore,

$$Q_A/Q_B = (\langle M(U_B - U_A) \rangle_A)^{-1}. \quad (8)$$

In order to estimate the means of the Metropolis function over appropriate canonical ensembles, configuration samples were generated by a Monte Carlo method which has been described in a previous paper (Clark and Lal 1977). The method constitutes the adaptation of the Metropolis sampling scheme to chain molecular systems. This scheme allows one to generate samples in which the configurations occur with frequencies proportional to their Boltzmann factors. The simple mean of a quantity over such a sample will therefore represent the estimate of the canonical ensemble average of that quantity. Sample sizes of 200 000 to 400 000 configurations yielded converged values of the means with standard deviations well below 0.5%. A typical convergence behaviour of the computed means is shown in figure 1 where they are plotted against the sample size. We observe that in the part of the sample shown in the figure the maximum deviation of the points from the estimated value (mean over all the points), shown by the horizontal line, is less than 0.7% and the standard deviation of the estimate is 0.29%. Estimates of $\langle M(U_B - U_A) \rangle_A$, computed for the

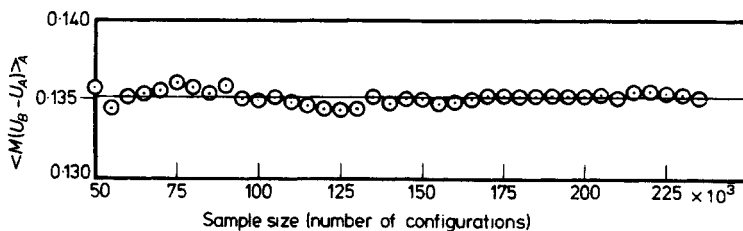


Figure 1. $\langle M(U_B - U_A) \rangle_A$ against sample size for the pair of the systems $\Delta\epsilon_{t \rightarrow g}/kT = 0.75, 1.00$.

various pairs of the systems and the ΔG_{AB} values calculated therefrom are listed in table 1. The standard deviations of the estimates have been identified with the limits of uncertainty quoted in the brackets.

Table 1. Computed values of $\langle M(U_B - U_A) \rangle_A$ and ΔG_{AB} for the various pairs of systems.

Pair of systems $\Delta\epsilon_{t \rightarrow g}/kT$	Sample size (configurations)	$\langle M(U_B - U_A) \rangle_A$	$\Delta G_{AB} (= G_B - G_A)/kT$
<i>A B</i>			
0.00, 0.50	235 000	$0.524(\pm 0.002) \times 10^{-2}$	$5.251(\pm 0.004)$
0.50, 0.75	200 000	$0.1044(\pm 0.0004)$	$2.259(\pm 0.004)$
0.75, 1.00	235 000	$0.1351(\pm 0.0004)$	$2.002(\pm 0.003)$
1.00, 1.25	300 000	$0.1771(\pm 0.0004)$	$1.731(\pm 0.002)$
1.25, 1.50	365 000	$0.228(\pm 0.001)$	$1.477(\pm 0.004)$
1.50, 1.75	315 000	$0.284(\pm 0.001)$	$1.259(\pm 0.004)$
1.75, 2.00	360 000	$0.350(\pm 0.001)$	$1.050(\pm 0.005)$

The absolute configurational free energy of a system q is given in terms of ΔG as

$$G(q) = G_0 + \sum_{i=0}^{q-1} \Delta G_{i,i+1} \quad (9)$$

where G_0 is the configurational free energy of the excluded volume chain at $\Delta\epsilon_{t \rightarrow g}/kT = 0$, and $\Delta G_{i,i+1}$ is the free energy difference between the pair of systems i and $i+1$. The value of G_0 for the present chain can be immediately calculated from the exact enumeration data of Wall and Hioe (1970). G_0 thus obtained is equal to $-19.354 kT$. Using equation (9), G/NkT was calculated for each system. The results are presented in table 2 as well as in figure 2 where G/NkT is plotted as a function of the bond flexibility ω . For the sake of comparison the results for the chain allowing self-intersection are also included. We note that at low values of ω the difference between the free energies of the excluded volume chain and that allowing self-intersection is too small to be detectable within present limits of accuracy which are well within 1% for the lowest values of ω considered.

Table 2. Computed values of the absolute configurational free energy per bond for various values of ω .

$\Delta\epsilon_{t \rightarrow g}/kT$	ω	$-G/NkT$ (chain allowing self-intersection)	$-G/NkT$ (excluded-volume chain)
0.00	1.000	0.989	0.968
0.50	0.606	0.715	0.705 ± 0.000
0.75	0.472	0.599	0.592 ± 0.000
1.00	0.369	0.496	0.492 ± 0.000
1.25	0.286	0.408	0.405 ± 0.001
1.50	0.223	0.332	0.332 ± 0.001
1.75	0.174	0.268	0.268 ± 0.001
2.00	0.135	0.216	0.216 ± 0.002

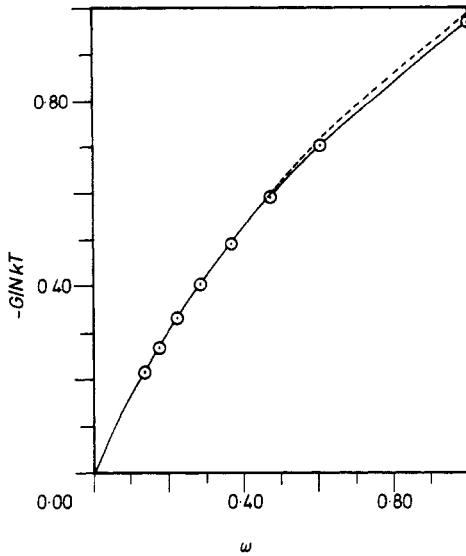


Figure 2. Configurational free energy per bond as a function of ω . $-\circ-$, excluded-volume chain; $----$, chain allowing self-intersection.

The application of the present approach can be readily extended to longer chains, and it offers an effective method for calculating free energies of the models corresponding to chain molecules in different solvent conditions and in the adsorbed state. We shall turn to these models in subsequent investigations.

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