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Note

DISTANCE-SCALED FORCE BIASED MONTE CARLO SIMULATION FOR SOLUTIONS CONTAINING A STRONGLY INTERACTING SOLUTE

MIHALY MEZEI

Department of Chemistry and Center for Study in Gene Structure and Function,

Hunter College of the CUNY, New York, NY 10021, USA.

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INTRODUCTION

The force-biased extension of the Metropolis Monte Carlo method [1] improves convergence by sampling moves preferentially along the directions of force (and torque) [2]. For solvated systems it is particularly effective [3] when coupled with the prefererential sampling scheme [4] that attempts to move solvents near the solute more frequently. However, in recent force-biased simulations of aqueous ionic solutions [5] some of the water molecules in the vicinity of the solute remained essentially stationary. Only significant reduction in the stepsize produced some accepted moves.

The present note describes the development and testing of the Distance-Scaled Force Bias method that allows the full use of force-biased displacement of the water molecules far from the solute and still provides for an adequate sampling of the solvent molecules near the solute.

BACKGROUND AND THEORY

A component of a force-bias trial displacement, δ, in the range $[-\Delta, \Delta]$ is selected with probability

$$P_i(\delta) = \exp(\lambda\beta F_i\Delta)/\sinh(\lambda\beta F_i\Delta)/(\lambda\beta F_i/2) \qquad (1)$$

where $i = x$, y or z, $\beta = 1/kT$, and F_i is the force along the axis i and λ is a scalar parameter. λ=1/2 is considered optimal[6] in first order. For a rotation, replace the force by the torque. $P_i(\delta)$ increases monotonously and

$$P_i(\Delta)/P_(-\Delta) = \exp(\lambda\beta F_i\Delta). \qquad (2)$$

The half-width of the distribution is ln $2/(\lambda\beta F_i)$. As F_i tends to infinity, $P_i(\delta)$ becomes a Dirac-delta centered at $\mathrm{sign}(F_i) * \Delta$.

If the force acting on a molecule is too large the likelihood that an attempted move is significantly smaller than Δ is small. Thus, a solvent molecule in the vicinity of a strongly attractive solute would keep trying to make a move toward the source of the attraction, but if the trial move is always of sufficient magnitude to bring the molecule into the repulsive region of the solute, the move will be perpetually rejected.

A simple solution places a limit for all molecules on the magnitude of the force and torque components in Eq.(1). The optimal value of the limits can be determined empirically.

More sigificant improvements can be obtained if λ is made a smooth monotonically increasing function of the solute-solvent distance R, $\lambda(R)$, that has a small value at distances less than the molecular diameter and increases to 1/2. It should not get too close to zero, since that would lead to an indeterminate δ_i in Eq. (1). Using $\lambda(R)$ the trial move is obtained with the standard force-bias prescription:

$$\delta_i = \ln[\exp(-\lambda\beta F_i\Delta) + 2\xi\sinh(\lambda\beta F_i\Delta)]/(\lambda\beta F_i) \tag{3}$$

where ξ is a random number in the [0,1] interval. The the move is accepted with probability

$$P_{\mathrm{acc}} = \min\{1, (\exp[\beta(U_o - U_n)])[(P(-\delta, \lambda(R_n))/P(\delta, \lambda(R_o))]\} \tag{4}$$

where the subscripts o and n refer to the configurations before and after the move, U is the energy, and $P(\delta, \lambda(R))$ is the product of the probabilities of the components of δ including the torque. This ratio of probabilities is similar to that used for the regular force bias method; the new feature is the R-dependent λ. This technique is called the Distance-Scaled Force Bias method.

For anisotropic solutes the solute-solvent distance R here has been defined as the distance between a selected point on the solvent (for example, center of mass) and the nearest heavy atom (i.e. other than hydrogen) on the solute. For isotropic solutes this quantity coincides with the distance between the centres of masses of the solute and solvent while for anisotropic solutes it is more useful than the distance between centres of masses.

The scaling algorithm itself, however, is independent of the definition of R. Preferential sampling [4] can be based on this definition of R as well.

CALCULATIONS AND RESULTS.

The method has been tested on a system of 1800 TIP4P water molecules [7] surroundig a DNA octamer duplex and Na^+ ions. The AMBER force-field [8,9] was used for the DNA-water interactions and the OPLS model [10] was used for the Na^+-water interactions. $\lambda(R)$ was chosen to be constant λ_o in the range 0 to 3 Å and 1/2 in the range 7 Å to infinity with linear interpolation between λ_o and 1/2. The preferential sampling, used for all calculations, was also based on the distance R defined above.

Several test calculations of 2×10^5 attempted moves were performed with stepsize parameters 0.275 Å and 17.5^o. Table 1 gives the average stepsizes and the minimum, maximum and average acceptance rates are given for all the runs performed. Earlier simulations on liquid water gave 4.1*10^{-10} N and 3.2*10^{-20}J/rad. for the root mean square force and torque components, respectively [11].

Table 1 shows that both limiting sufficiently the force/torque components and using the scaled force-bias technique ($\lambda_o < 1/2$) helps to make all solvents move. In the best combination, the smallest acceptance rate is higher than the corresponding rate using the Metropolis method. The scaling is more effective than limiting the components but the combination of the two techniques is the most powerful. This is achieved at negligible computational expense and without any degradation of the overall performance when compared with the original force-bias technique.

Table 1. Convergence characteristics of the different runs.

	λ_o	F_{max}	T_{max}	$\langle P^{\rm acc}\rangle$	$P^{acc}_{\rm min}$	P^{acc}_{max}	$\langle r\rangle$	$\langle\phi\rangle$
Metropolis:				0.213	0.045	0.550	0.229	7.71
FB	1/2	8.2	6.5	0.347	0.000	0.747	0.269	8.65
FB	1/2	4.1	3.5	0.351	0.014	0.740	0.259	8.34
FB	0.05	8.2	6.5	0.362	0.050	0.712	0.262	8.50
FB	0.1	8.2	6.5	0.365	0.061	0.707	0.263	8.50
FB	0.15	8.2	6.5	0.363	0.034	0.741	0.263	8.51
FB	0.1	4.1	3.5	0.352	0.021	0.688	0.254	8.26
FB	0.1			0.365	0.027	0.702	0.265	8.55

Legend: a) λ_o: the value of λ at R¡3 Å (λ_o=1/2 means no scaling; b)$F_{\rm max}$ and $T_{\rm max}$ are the limits on the force and torque components, respectively in 10^8 J and 10^{20} J/rad, respectively; c)$\langle P^{\rm acc}\rangle$, $P^{\rm acc}_{\rm min}$ $P^{\rm acc}_{\rm max}$ are the average, minimum and maximum acceptance rates, respectively; d) $\langle r\rangle$ and $\langle f\rangle$ are the average total displacement and rotation angle, respectively, in Å and degrees, respectively.

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