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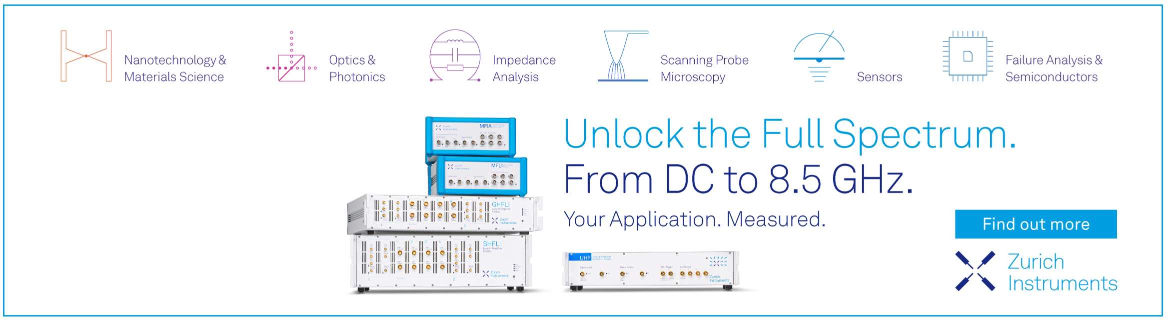

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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2004 issue.

ERRATA

Erratum: "Single-ensemble nonequilibrium path-sampling estimates of free energy differences" [J. Chem. Phys. 120, 10876 (2004)]

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In the single-ensemble path sampling (SEPS) method, described in Ref. 1, trial trajectories are generated by perturbing a reference trajectory. The trial trajectory is then accepted or rejected according to a Metropolis criterion. Unfortunately, there was an error in the criterion described and used in Ref. 1. Below we give the correct criterion. The corrected SEPS results presented here are found to be more efficient than those in Ref. 1, roughly by a factor of five. As discussed below, the final free energy value is unchanged. Further, all numbered equations in Ref. 1, and notably the general formalism, were correct as printed.

The acceptance criterion can be derived using the principle of detailed balance which states that[2–5]

$$P_{\mathrm{acc}}^{\mathbf{Z}_n \to \mathbf{Z}'_n} P_{\mathrm{gen}}^{\mathbf{Z}_n \to \mathbf{Z}'_n} Q(\mathbf{Z}_n) = P_{\mathrm{acc}}^{\mathbf{Z}'_n \to \mathbf{Z}_n} P_{\mathrm{gen}}^{\mathbf{Z}'_n \to \mathbf{Z}_n} Q(\mathbf{Z}'_n), \tag{1}$$

where $\mathbf{Z}'_n$ and $\mathbf{Z}_n$ are respectively, the trial and reference trajectories, $Q(\mathbf{Z}'_n)$ and $Q(\mathbf{Z}_n)$ are the statistical weights of the trial and reference trajectories respectively, $P_{\mathrm{acc}}^{\mathbf{Z}_n \to \mathbf{Z}'_n}$ and $P_{\mathrm{acc}}^{\mathbf{Z}'_n \to \mathbf{Z}_n}$ are, respectively, the probabilities of accepting a trial trajectory from the reference trajectory and vice versa, and $P_{\mathrm{gen}}^{\mathbf{Z}_n \to \mathbf{Z}'_n}$ and $P_{\mathrm{gen}}^{\mathbf{Z}'_n \to \mathbf{Z}_n}$ are, respectively, the probabilities of generating a trial trajectory from the reference trajectory and vice versa. Using Eq. (1) combined with importance sampling leads to the following acceptance criterion

$$P_{\mathrm{acc}}^{\mathbf{Z}_n \to \mathbf{Z}'_n} = \min\left[1, \frac{Q(\mathbf{Z}'_n) P_{\mathrm{gen}}^{\mathbf{Z}'_n \to \mathbf{Z}_n} e^{-(\beta/2)W'}}{Q(\mathbf{Z}_n) P_{\mathrm{gen}}^{\mathbf{Z}_n \to \mathbf{Z}'_n} e^{-(\beta/2)W}}\right], \tag{2}$$

where W' and W are the work values associated with the trial and reference trajectories respectively.

The expression for Q is given by Eq. (8) in Ref. 1 for the case of the Brownian dynamics trajectories used here. The probability of generating the trial trajectory from the reference trajectory $P_{\mathrm{gen}}^{\mathbf{Z}_n \to \mathbf{Z}'_n}$ depends upon simulation details, and many choices are possible. For our simulations, completely new, but ordinary, Brownian trajectories were constructed to pass through the displaced point described in Ref. 1. In this case, the Metropolis criterion reduces to (cf. Refs. 4–6)

$$P_{\mathrm{acc}}^{\mathbf{Z}_n \to \mathbf{Z}'_n} = \min\left[1, \frac{e^{-\beta H_0(\vec{x}'_0)} e^{-(\beta/2)W'}}{e^{-\beta H_0(\vec{x}_0)} e^{-(\beta/2)W}}\right]. \tag{3}$$

Figure 1 shows the results of our simulations using the corrected Metropolis criterion of Eq. (3). This plot replaces Fig. 2 in Ref. 1. The results for thermodynamic integration and Jarzynski simulations are unchanged from Ref. 1. Also, the method for generating the current SEPS results is identical to that in Ref. 1 with the exception that the new (correct) Metropolis criterion given by Eq. (3) is used.

Remarkably, the corrected SEPS data are more efficient than the previous SEPS results. This is due to the fact that

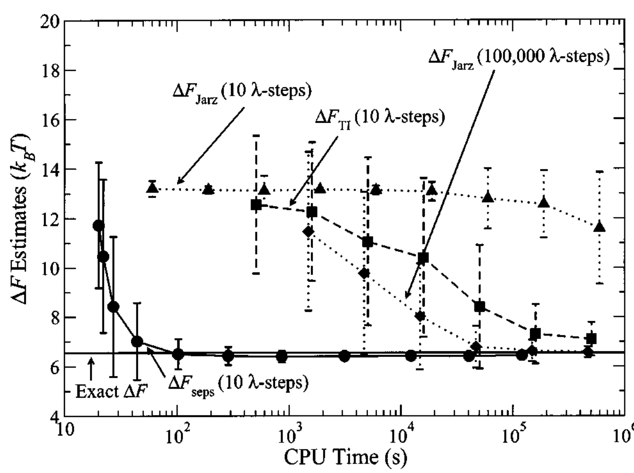

FIG. 1. Revised Fig. 2 from Ref. 1: Comparison between free energy estimates from the Jarzynski method, conventional thermodynamic integration (TI), and our single-ensemble path sampling (SEPS) method. The circles show the results of the SEPS method using ten λ-steps. The results of the Jarzynski method for a very short trajectory (ten λ-steps, squares) and the most efficient trajectory length (100 000 λ-steps, triangles) are also shown. TI estimates based on ten λ increments are shown as diamonds. The exact answer of $\Delta F = 6.55 k_B T$ is shown as a solid horizontal line. Each data point represents the mean estimate, with standard deviations given by the error bars, based on 100 independent estimates of ΔF for each method.

the criterion given by Eq. (3) is ‘‘less stringent’’ than that in Ref. 1, thus allowing more trial trajectories (work values) to be accepted. The acceptance ratio is now about 5%, approximately five times larger than in Ref. 1. The efficiency increases by roughly the same factor.

It is of interest to understand why the SEPS results in Ref. 1 converge to the correct free energy difference, even though detailed balance was not implemented properly. This is apparently because, in the limit of generating an infinite number of trajectories, the average generating probabilities are expected to be symmetric—that is, $\langle P_{\mathrm{gen}}^{\mathbf{Z}_n \to \mathbf{Z}_n'} \rangle \approx \langle P_{\mathrm{gen}}^{\mathbf{Z}_n' \to \mathbf{Z}_n} \rangle$. Substituting this average into Eq. (2) gives the criterion used in Ref. 1. Thus, the final results for ΔF from the acceptance criterion used in Ref. 1 are equivalent to those presented here.

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[1] F. M. Ytreberg and D. M. Zuckerman, J. Chem. Phys. **120**, 10876 (2004).
[2] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, San Diego, 1996).
[3] P. G. Bolhuis, D. Chandler, C. Dellago, and P. L. Geissler, Annu. Rev. Phys. Chem. **53**, 291 (2002).
[4] C. Dellago, P. G. Bolhuis, and D. Chandler, J. Chem. Phys. **110**, 6617 (1999).
[5] C. Dellago, P. G. Bolhuis, F. S. Csajka, and D. Chandler, J. Chem. Phys. **108**, 1964 (1998).
[6] S. X. Sun, J. Chem. Phys. **118**, 5769 (2003).