Bennett's acceptance ratio and energy reweighting

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Abstract

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I. BAR

The Metropolis function is defined as

$$M(x) = min\{1, exp(-x)\}, \tag{1}$$

which has the property

$$M(x)/M(-x) = exp(-x). \tag{2}$$

If we make a trial move that keeps the same configuration $(q_1, \cdots, q_N)$ but swithes the potential function from U_0 to U_1 or vice-versa. The acceptance probabilities for such a pair of trial move must satisfy the detailed balance

$$M(U_1 - U_0)exp(-U_0) = M(U_0 - U_1)exp(-U_1). \tag{3}$$

Integrating this identity over all of configuration space and multipying by the trivial factors Q_0/Q_0 and Q_1/Q_1, one obtains:

$$Q_0 \frac{\int M(U_1 - U_0)exp(-U_0)d\mathbf{q}}{Q_0} = Q_1 \frac{\int M(U_0 - U_1)exp(-U_1)d\mathbf{q}}{Q_1}, \tag{4}$$

or simply

$$\frac{Q_0}{Q_1} = \frac{< M(U_0 - U_1) >_1}{< M(U_1 - U_0) >_0}. \tag{5}$$

The physical meaning of this formula is that a Monte Carlo calculation that included potential-swithching trial moves would distribute configurations between U_1 and U_0 in the ratio of their configurational integrals.

A more general formula than Eq. 5 can be written as

$$\frac{Q_0}{Q_1} = \frac{Q_0}{Q_1} \frac{\int Wexp(-U_0 - U_1)d\mathbf{q}}{\int Wexp(-U_1 - U_0)d\mathbf{q}} = \frac{< Wexp(-U_0) >_1}{< Wexp(-U_1) >_0}, \tag{6}$$

where W is an arbitrary weighting function.

Optimization of the free energy estimate is most easily carried out in the limit of large sample sizes. Let the available data consist of n_0 statistically independent configurations from the U_0 ensemble and n_1 from the U_1 ensemble, and let the data be used in Eq. 6 to obtain a finite-sample estimate of the reduced free energy difference $\Delta A = A_1 - A_0 = ln(Q_0/Q_1)$. Using the error propagation equation,

$$Var\left[y(x_1,x_2)\right] = \left(\frac{\partial y}{\partial x_1}\right)^2 Var(x_1) + \left(\frac{\partial y}{\partial x_2}\right)^2 Var(x_2). \tag{7}$$

Thus we have the variance of ΔA

$$\begin{aligned} Var(\Delta A) &= \left(\frac{\partial \Delta A}{\partial Q_0}\right)^2 Var(Q_0) + \left(\frac{\partial \Delta A}{\partial Q_1}\right)^2 Var(Q_1) &(8)\\ &= (\frac{1}{Q_0})^2 Var(Q_0) + (-\frac{1}{Q_1})^2 Var(Q_1) &(9)\\ &= (\frac{1}{Q_0})^2 Var(Q_0) + (\frac{1}{Q_1})^2 Var(Q_1). &(10) \end{aligned}$$

With the definition of variance $Var(X) = \langle X^2\rangle - \langle X\rangle^2$, we have

$$\begin{aligned} VarQ_0 &= Var\left(\langle Wexp(-U_0)\rangle_1\right) &(11)\\ &= Var\left(\frac{1}{n_1}\sum_{i=1}^{n_1} W_i exp\left(-U_0(i)\right)\right) &(12)\\ &= \sum_{i=1}^{n_1}\left(\frac{1}{n_1}\right)^2 Var\left(W_i exp\left(-U_0(i)\right)\right) &(13)\\ &= \frac{1}{n_1} Var\left(W_i exp\left(-U_0(i)\right)\right) &(14)\\ &= \frac{1}{n_1}\left\{\left\langle (Wexp(-U_0))^2\right\rangle_1 - \left(\langle Wexp(-U_0)\rangle_1\right)^2\right\} &(15)\\ &= \frac{1}{n_1}\left\{\left\langle W^2 exp(-2U_0)\right\rangle_1 - \left[\langle Wexp(-U_0)\rangle_1\right]^2\right\} &(16) \end{aligned}$$

With sufficiently large sample sizes, the error of this estimate will be nearly Gaussian, and its expected square is exactly the variance of ΔA

$$\begin{aligned} &E(\Delta A_{est} - \Delta A)\\ &\approx \frac{< W^2 exp(-2U_1) >_0}{n_0[< Wexp(-U_1) >_0]^2} + \frac{< W^2 exp(-2U_0) >_1}{n_1[< Wexp(-U_0) >_1]^2} - \frac{1}{n_0} - \frac{1}{n_1}\\ &= \frac{\int \left[(Q_0/n_0)exp(-U_1) + (Q_1/n_1)exp(-U_0)\right] W^2 exp(-U_0-U_1)d\mathbf{q}}{[\int Wexp(-U_0-U_1)d\mathbf{q}]^2} - \frac{1}{n_0} - \frac{1}{n_1}. \end{aligned} \tag{17}$$

To minimize it with respect to W, we have

$$W = const \times \left(\frac{Q_0}{n_0}exp(-U_1) + \frac{Q_1}{n_1}exp(-U_0)\right)^{-1}. \tag{18}$$

Substituting this into Eq. 6 yields

$$\frac{Q_0}{Q_1} = \frac{< f(U_0 - U_1 + C) >_1}{< f(U_1 - U_0 - C) >_0} exp(+C), \tag{19}$$

where

$$C = ln\frac{Q_0 n_1}{Q_1 n_0}, \tag{20}$$

and f denotes the Fermi function

$$f(x) = \frac{1}{1 + exp(+x)} \tag{21}$$

II. BAR WITH ENERGY REWEIGHTING

Suppose we want to calculate the free energy difference between state $H_{MM,1}$ and state $H_{QM,0}$, but we do not want to run simulations under $H_{QM,0}$. We introduce an auxiliary state $H_{MM,0}$, of which the dominate phase space has strong overlap with that of $H_{QM,0}$. Starting with Eq. 6, we have

$$\frac{Q_{QM,0}}{Q_{MM,1}} = \frac{\langle W \exp(-U_{QM,0}) \rangle_{MM,1}}{\langle W \exp(-U_{MM,1}) \rangle_{QM,0}} \tag{22}$$

$$= \frac{\langle W \exp(-U_{QM,0}) \rangle_{MM,1} \langle \exp(-U_{QM,0} + U_{MM,0}) \rangle_{MM,0}}{\langle W \exp(-U_{MM,1}) \exp(-U_{QM,0} + U_{MM,0}) \rangle_{MM,0}} \tag{23}$$

From $\Delta A = A_{MM,1} - A_{QM,0} = ln(Q_{QM,0}/Q_{MM,1})$, we have

$$Var(\Delta A_{est} - \Delta A) = \frac{\langle W^2 \exp(2U_{MM,0} - 2U_{MM,1} - 2U_{QM,0})\rangle_{MM,0}}{n_{MM,0}\left[\langle W \exp(U_{MM,0} - U_{MM,1} - U_{QM,0})\rangle_{MM,0}\right]^2} \tag{24}$$

$$+ \frac{\langle W^2 \exp(-2U_{QM,0})\rangle_{MM,1}}{n_{MM,1}\left[\langle W \exp(-U_{QM,0})\rangle_{MM,1}\right]^2} \tag{25}$$

$$+ \frac{\langle \exp(-2U_{QM,0} + 2U_{MM,0})\rangle_{MM,0}}{n_{MM,0}\left[\langle \exp(-U_{QM,0} + U_{MM,0})\rangle_{MM,0}\right]^2} \tag{26}$$

$$- \frac{1}{n_{MM,1}} - \frac{2}{n_{MM,0}} \tag{27}$$

$$= \frac{Q_{MM,0}\int W^2 \exp(U_{MM,0} - 2U_{MM,1} - 2U_{QM,0}) d\mathbf{q}}{n_{MM,0}\left[\int W \exp(-U_{MM,1} - U_{QM,0}) d\mathbf{q}\right]^2} \tag{28}$$

$$+ \frac{Q_{MM,1}\int W^2 \exp(-2U_{QM,0} - U_{MM,1}) d\mathbf{q}}{n_{MM,1}\left[\int W \exp(-U_{QM,0} - U_{MM,1}) d\mathbf{q}\right]^2} \tag{29}$$

$$+ \frac{Q_{MM,0}\int \exp(-2U_{QM,0} + U_{MM,0}) d\mathbf{q}}{n_{MM,0}\left[\int \exp(-U_{QM,0}) d\mathbf{q}\right]^2} \tag{30}$$

$$- \frac{1}{n_{MM,1}} - \frac{2}{n_{MM,0}} \tag{31}$$

Minimizing $Var(\Delta A_{est} - \Delta A)$ with respect to W, we have

$$W \propto \left[\frac{Q_{MM,0}}{n_{MM,0}} \exp(U_{MM,0} - U_{QM,0} - U_{MM,1}) + \frac{Q_{MM,1}}{n_{MM,1}} \exp(-U_{QM,0})\right]^{-1}. \tag{32}$$

If the biasing potential $V_0^b = U_{MM,0} - U_{QM,0} = 0$, Eq. 32 goes back to Eq. 18. Taking Eq. 32 into Eq. 23, we find

$$\Delta A = \ln \frac{\left\langle \frac{\exp(U_{MM,1})}{\frac{Q_{MM,0}}{n_{MM,0}}\exp(U_{MM,0}) + \frac{Q_{MM,1}}{n_{MM,1}}\exp(U_{MM,1})} \right\rangle_{MM,1} \langle \exp(U_{MM,0} - U_{QM,0})\rangle_{MM,0}}{\left\langle \frac{\exp(U_{MM,0})}{\frac{Q_{MM,0}}{n_{MM,0}}\exp(U_{MM,0}) + \frac{Q_{MM,1}}{n_{MM,1}}\exp(U_{MM,1})} \right\rangle_{MM,0}} \tag{33}$$

$$= \ln \frac{\langle f(U_{MM,0} - U_{MM,1} + C)\rangle_{MM,1} \langle \exp(U_{MM,0} - U_{QM,0})\rangle_{MM,0}}{\langle f(U_{MM,1} - U_{MM,0} - C)\rangle_{MM,0}} \cdot \exp(C) \tag{34}$$

$$= \ln \frac{\langle f(U_{MM,0} - U_{MM,1} + C)\rangle_{MM,1}}{\langle f(U_{MM,1} - U_{MM,0} - C)\rangle_{MM,0}} \cdot \exp(C) + \ln \langle \exp(U_{MM,0} - U_{QM,0})\rangle_{MM,0}, \tag{35}$$

which is BAR between $H_{MM,0}$ and $H_{MM,1}$ plus FEP between $H_{QM,0}$ and $H_{MM,0}$. And

$$
\begin{aligned}
Var(\Delta A_{est} - \Delta A) = & \frac{Q_{MM,0} \int \left[\frac{Q_{MM,0}}{n_{MM,0}} exp\left(U_{MM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-2} exp\left(U_{MM,0}\right) d\mathbf{q}}{n_{MM,0} \left(\int \left[\frac{Q_{MM,0}}{n_{MM,0}} exp\left(U_{MM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-1} d\mathbf{q}\right)^2} \\
& + \frac{Q_{MM,1} \int \left[\frac{Q_{MM,0}}{n_{MM,0}} exp\left(U_{MM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-2} exp\left(U_{MM,1}\right) d\mathbf{q}}{n_{MM,1} \left(\int \left[\frac{Q_{MM,0}}{n_{MM,0}} exp\left(U_{MM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-1} d\mathbf{q}\right)^2} \\
& + \frac{Q_{MM,0} \int exp\left(-2U_{QM,0} + U_{MM,0}\right) d\mathbf{q}}{n_{MM,0} \left(\int exp\left(-U_{QM,0}\right) d\mathbf{q}\right)^2} \\
& - \frac{1}{n_{MM,1}} - \frac{2}{n_{MM,0}}.
\end{aligned}
$$

For comparison, W and the variance of Non-Boltzmann BAR are

$$
W = \left[\frac{Q_{QM,0}}{n_{MM,0}} exp\left(-U_{MM,1}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(-U_{QM,0}\right)\right]^{-1}
$$

and

$$
\begin{aligned}
Var(\Delta A_{est} - \Delta A) = & \frac{Q_{MM,0} \int \left[\frac{Q_{QM,0}}{n_{MM,0}} exp(U_{QM,0}) + \frac{Q_{MM,1}}{n_{MM,1}} \exp(U_{MM,1})\right]^{-2} exp\left(U_{MM,0}\right) d\mathbf{q}}{n_{MM,0} \left(\int \left[\frac{Q_{QM,0}}{n_{MM,0}} exp\left(U_{QM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-1} d\mathbf{q}\right)^2} \\
& + \frac{Q_{MM,1} \int \left[\frac{Q_{QM,0}}{n_{MM,0}} exp\left(U_{QM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-2} exp\left(U_{MM,1}\right) d\mathbf{q}}{n_{MM,1} \left(\int \left[\frac{Q_{QM,0}}{n_{MM,0}} exp\left(U_{QM,0}\right) + \frac{Q_{MM,1}}{n_{MM,1}} exp\left(U_{MM,1}\right)\right]^{-1} d\mathbf{q}\right)^2} \\
& + \frac{Q_{MM,0} \int exp\left(-2U_{QM,0} + U_{MM,0}\right) d\mathbf{q}}{n_{MM,0} \left(\int exp\left(-U_{QM,0}\right) d\mathbf{q}\right)^2} \\
& - \frac{1}{n_{MM,1}} - \frac{2}{n_{MM,0}}.
\end{aligned}
$$