CHM1465: Foundations of Molecular Simulation

PROBLEM SET 2

Notes:

- This set contains 3 problems.
- This second is due in two weeks, October 22, 2008.

1. Consider a three state process in which the probability vector $\mathbf{p}(t)$ satisfies the master equation

$$\mathbf{p}(t+1) = \mathsf{K} \cdot \mathbf{p}(t),$$

with a transition matrix given by

$$\mathsf{K} = \begin{pmatrix} \frac{3}{4} & \frac{1}{32} & \frac{1}{16} \\ \frac{1}{8} & \frac{13}{16} & \frac{1}{8} \\ \frac{1}{8} & \frac{5}{32} & \frac{13}{16} \end{pmatrix}. \tag{1}$$

   (a) What are the eigenvalues of the transition matrix K? Give the stationary vector $\bar{\mathbf{p}}$ (i.e. that which satisfies $\mathsf{K} \cdot \bar{\mathbf{p}} = \bar{\mathbf{p}}$). Make sure it is normalized such that the sum of its components is one.

   (b) Show that detailed balance is not obeyed by this process.

   Recall from linear algebra that any symmetric matrix S one can brought to diagonal form D by a similarity transformation P, in that

$$\mathsf{D} = \mathsf{P}^{-1} \cdot \mathsf{S} \cdot \mathsf{P} = \begin{pmatrix} \lambda_1 & & \emptyset \\ & \lambda_2 & \\ \emptyset & & \lambda_3 \end{pmatrix}, \tag{2}$$

   where λ_k are the eigenvalues and the columns of the matrix P are the (right) eigenvectors $\hat{\mathbf{e}}_k$ of S. Yet K is not symmetric and has degenerate eigenvalues. For such cases, linear algebra tells us that the matrix can be brought to Jordan normal block form:

$$\mathsf{J} = \mathsf{P}^{-1} \cdot \mathsf{K} \cdot \mathsf{P} = \left(\begin{array}{cccc|ccc|c} \lambda_1 & 1 & & \emptyset & & & & \\ & \lambda_1 & \ddots & & & & & \emptyset \\ & & \ddots & 1 & & & & \\ \emptyset & & & \lambda_1 & & & & \\ \hline & & & & \lambda_2 & 1 & & \emptyset \\ & & & & & \lambda_2 & \ddots & \\ & & & & & & \ddots & 1 \\ & & & & \emptyset & & & \lambda_2 \\ \hline & & & & & & & \ddots \\ & & \emptyset & & & & & \end{array}\right), \tag{3}$$

where the size g_k of each block is equal to the degeneracy of the corresponding eigenvalue λ_k, and P contains the generalized eigenvectors, which follow from the generalized eigenvalue equation $(\mathsf{K} - \lambda_k \mathsf{1})^{g_k} \cdot \hat{\mathbf{e}}_k^{(i)} = 0$ $(i = 1 \ldots g_k)$.

(c) What is the Jordan normal form of the matrix K in equation (1)?

(d) Determine the similarity matrix P that brings it to that form.

The Jordan normal form is possibly a complicating factor because the iterated matrix K^t is harder to find.

(e) Show that here

$$\mathsf{J}^t = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \lambda_2^t & t\lambda_2^{t-1} \\ 0 & 0 & \lambda_2^t \end{pmatrix}.$$

(f) Determine the matrix

$$\mathsf{K}_\infty = \lim_{t\to\infty} \mathsf{K}^t,$$

and show that it transforms any initial probability vector into the stationary probability vector.

2. Consider now a slightly different process with transition matrix

$$\mathsf{K} = \begin{pmatrix} \frac{3}{4} & \frac{1}{16} & \frac{1}{16} \\ \frac{1}{8} & \frac{13}{16} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} & \frac{13}{16} \end{pmatrix}. \tag{4}$$

(a) Determine the normalized stationary probability vector $\bar{\mathbf{p}} = (\bar{p}_1, \bar{p}_2, \bar{p}_3)$.

(b) Show that detailed balance is satisfied.

(c) Show that the matrix

$$\tilde{\mathsf{K}} = \mathsf{Q}^{-1} \cdot \mathsf{K} \cdot \mathsf{Q}$$

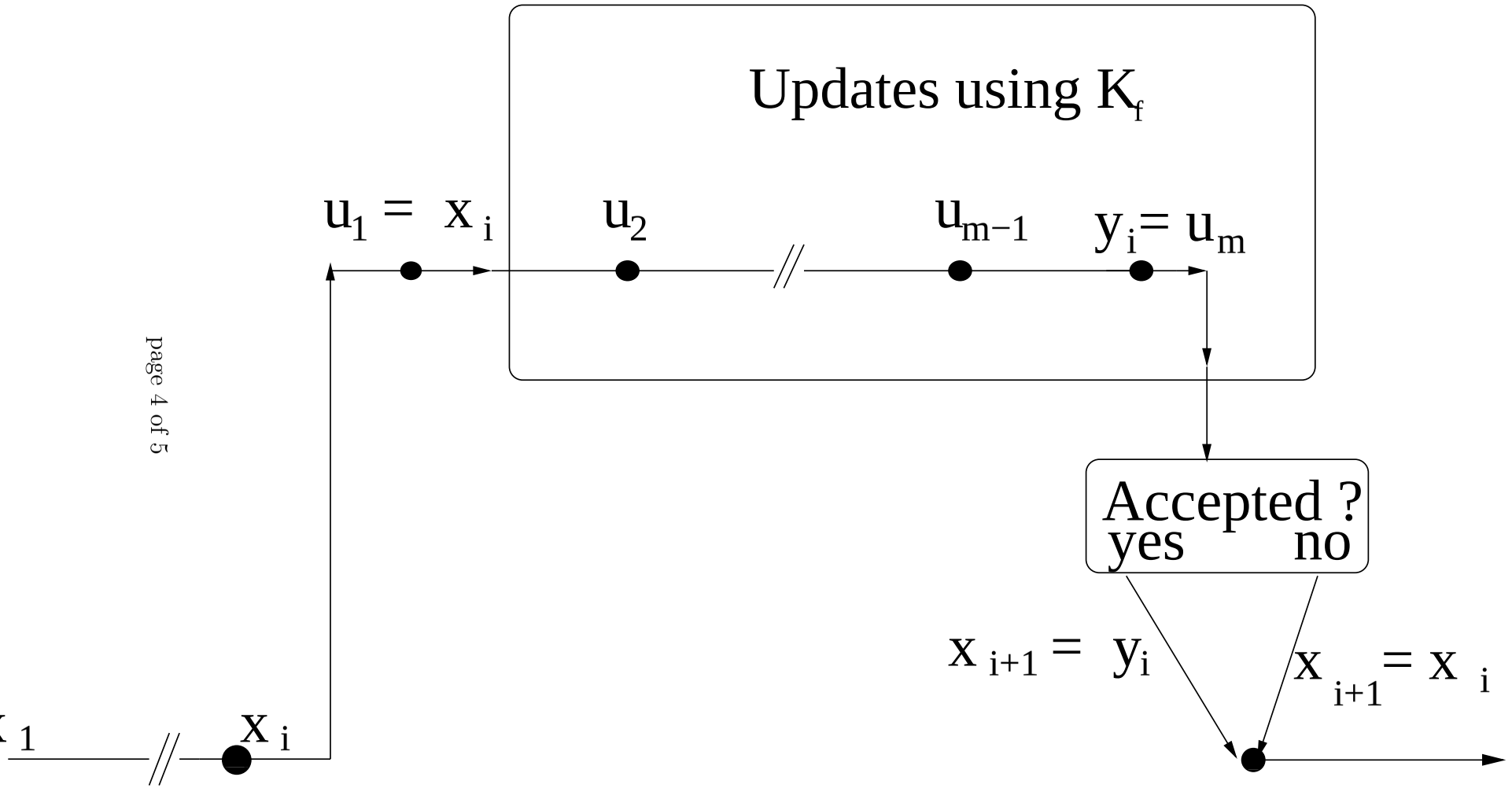
is symmetric, where the similarity transformation Q is defined as

$$\mathsf{Q} = \begin{pmatrix} \sqrt{\bar{p}_1} & 0 & \\ 0 & \sqrt{\bar{p}_2} & 0 \\ 0 & 0 & \sqrt{\bar{p}_3} \end{pmatrix}.$$

(d) What does this imply for the Jordan normal form of K?

(e) Show that for any n-state process which satisfies detailed balance with stationary probability vector $\bar{\mathbf{p}}$, the transformed matrix $\mathsf{Q}^{-1} \cdot \mathsf{K} \cdot \mathsf{Q}$ is symmetric when $\mathsf{Q} = \mathrm{diag}(\sqrt{\bar{p}_1}, \sqrt{\bar{p}_2}, \ldots)$.

3. Suppose one defines a random walk procedure to generate a Markov chains of states $\Gamma = \{x_1, \ldots, x_N\}$, where each configuration of the system x_i appears with canonical ensemble probability $\Pi(x_i) = e^{-\beta U(x_i)}/Z$. Consider the case in which it is very computationally demanding to compute the potential energy $U(x_i)$, and much easier to compute an approximate potential energy $U_f(x_i)$. For example, the true potential energy $U(x_i)$ could be computed by *ab-initio* electronic structure methods, and $U_f(x_i)$ could be the potential energy computed by a molecular-mechanical or low-level *ab-initio* method.


Updates using K_f
$u_1 = x_i$
u_2
u_{m-1}
$y_i = u_m$
Accepted ?
yes
no
$x_{i+1} = y_i$
$x_{i+1} = x_i$
x_i

(a) Suppose one develops a transition matrix $K_f(u_i \to u_j)$ that satisfies detailed balance in the canonical ensemble for the system with potential energy U_f,

$$p_f(u_i)K_f(u_i \to u_j) \;\; = \;\; p_f(u_j)K_f(u_j \to u_i),$$

where $p_f(u_i) = e^{-\beta U_f(u_i)}/Z_f$. At a given time step i of the Markov chain Γ, suppose the configuration is x_i. If one defines $u_1 = x_i$ and then generates an auxiliary sequence of states $\{u_1, \ldots, u_m\}$ according to a random walk with probabilities determined by K_f, and then selects the trial state for the $i+1$ step of the Markov chain to be $y_i = u_m$, what is the probability $T(x_i \to y_i)$ of generating the configuration y_i starting from x_i via the sequence $\{u_1, \ldots, u_m\}$? What is the reverse probability $T(y_i \to x_i)$ via the path $\{u_m, \ldots, u_1\}$?

(b) How should the acceptance probability $A(x_i \to y_i)$ of the trial configuration be defined to ensure that the chain of states Γ has limiting distribution Π? How does this probability depend on the number of steps m used in the auxiliary chain $\{u_1, \ldots, u_m\}$?

(c) What might the advantage be of such a procedure over a simple, symmetric trial proposal procedure where $T(x_i \to y_i) = T(y_i \to x_i)$? What conditions are important if the auxiliary chain method is to be efficient?