National University of Singapore
Semester Examination for the Degree of B.Sc.

(Semester I, 2006/07)

CZ3272 – Monte Carlo and Molecular Dynamics

6 Dec 2006 – Time Allowed: 2 hours

Instructions to Candidates:

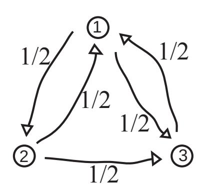
1. This is a closed book examination.
2. This examination paper contains FIVE (5) questions and comprises THREE (3) printed pages.
3. weightage of the questions is indicated by marks.
4. Answer ALL the questions.

1. Briefly answer the following questions:
    a. If the probability of picking a site is 1/5, and flipping it is 1/2, what is the probability of doing both (pick and then flip)? What is the condition needed for your answer?
    b. Let P be a probability distribution (a row vector), and W a transition matrix, give the equation to say that P is stationary (invariant) with respect to W.
    c. Why in Metropolis algorithm, the probability of making a move, T(x –> x'), must be a symmetric matrix? What is the transition matrix of the generalized method known as Metropolis-Hastings?
    d. In Monte Carlo valuation of a quantity, the error goes as $1/N^{p}$, where N is the number of samples. Give the value of the power p.
    e. Give the central difference formula for approximation of a second derivative.

[20 marks]

a. *1/5 × ½ = 1/10; the two events are independent.*
b. *P = PW.*
c. *In order to satisfy detailed balance; W(X->Y) = T(X->Y) min(1, P(Y)T(Y->X)/(P(X) T(X->Y))).*
d. *p=1/2.*
e. $f''(x) \approx (f(x+h) - 2 f(x) + f(x-h))/h^2$.

2. Consider the following diagram representing a Markov chain with three states, 1, 2, and 3. The transition probabilities to other states are labeled.



    a. Give the transition matrix W.
    b. Find the equilibrium (invariant) probability distribution P by solving an eigenvalue problem.
    c. Is the detailed balance satisfied for the Markov chain?
    d. Is the Markov a reversible Markov chain? Give the transition matrix W^R corresponding to the time-reversed Markov chain of W.

[20 marks]

a. $W = \begin{bmatrix} 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \\ 1/2 & 0 & 1/2 \end{bmatrix}$

b. *Solving P = P W, let row vector P=(x,y,z), we get* *x = (y+z)/2, y = x/2, z = (x+y+z)/2. With normalization condition x+y+z =1, we get z = ½, x = 1/3, y = 1/6. P = (1/3, 1/6, 1/2).*

c. *No, because, P(2) W(2->3) = (1/6)×(1/2) = 1/12, P(3) W(3->2) =0 , is not equal.*
d. *It is not reversible Markov chain, because detailed balance is not satisfied. P(i) W(i->j) = P(j)W^R(j->i) so*

$$W^R = \begin{bmatrix} 0 & 1/4 & 3/4 \\ 1 & 0 & 0 \\ 1/3 & 1/6 & 1/2 \end{bmatrix}.$$

3. One of the advantages of Metropolis algorithm is its generality for any given probability distribution. Consider the following distribution with one discrete variable σ = +1, or −1, and one continuous variable $0 < x < 1$:

   $P(\sigma, x) = c \exp(\sigma x)$.

   a. The probability must be normalized to 1. Use this condition to determine the constant c in the above. Do we need the value c in a Metropolis algorithm?
   b. Propose a possible move for the variable σ, holding x fixed, write down the selection or proposing probability $T(\sigma \to \sigma')$.
   c. Write down the conditional probability $T(x \to x')$, if we move x within an interval of 0.1 uniformly distribution and centered around original value.
   d. Write a set of pseudo code to generate the join distribution of σ and x according to $P(\sigma, x)$. Compute the averages <σ> and <x> in your code.

[20 marks]

a. The normalization is $\sum_{\sigma=+1,-1} \int_0^1 dx\, c \exp(\sigma x) = c(e - 1/e) = 1$. *So c = 1/(e-$e^{-1}$). We do not need c in a Metropolis algorithm.*

b. E.g., flip σ -> -σ, with probability 1, T(σ->-σ) =1, T(σ->σ) = 0.

c. T(x ->x') = 10 if |x-x'| < 0.05, and 0 otherwise. (This is a probability density).

d. Initialize σ and x (e.g, σ=1, x = 0) ave_sig = 0, ave_x = 0..
Do σ move, compute r = min(1, exp(-2σx))
Set σ = - σ, if (ξ < r) where ξ is a uniformly distributed random number from 0 to 1.
Do x mov , x' = x + 0.05(2ξ_2-1), if x' outside the interval [0,1], reject the move, otherwise, compute r = min(1, exp(σ(x'-x)), set x = x' if (ξ_3<r).
Take average of σ and x, ave_sig += σ, ave_x += x.

Finally, divide ave_sig and ave_x by the total number of samples.

4. In molecular dynamics, we prefer to use dimensionless numbers in simulation. Consider the problem of harmonic oscillation of a molecule described by

$$m\frac{d^2x}{dt^2} = -kx ,$$

where m is mass, k is spring constant, x is displacement (distance), for carbon bond type modules, we take

m = 12 a.m.u, 1 a.m.u. = 1.66×10^{-27} kg

k = 10 eV/(Å)^2 1 eV = 1.6×10^{-19} J, 1Å = 10^{-10} m

(a) If we choose the units for mass to be a.m.u., units for distance to be Å, and units for k to be eV/Å^2, what would be units for time t (expressed as seconds)?

(b) Write down the Verlet algorithm for the equation above, replacing all symbols like the mass by pure numbers.

[15 marks]

a. *From the equation we see the units for time must be t0 = sqrt(m0/k0) =sqrt(1 a.m.u/(eV/(A0)^2) =* $\sqrt{\dfrac{1.66\times10^{-27}kg}{1.6\times10^{-19}J/(10^{-10}m)^2}} \approx 10^{-14} sec$.

b. *x(t+h) = 2x(t) – x(t-h) – 0.8333 h^2 x(t). h is a small step size (e.g., h = 0.01).*

5. Consider a molecular dynamic simulation of coupled oscillators. The Hamiltonian is given by,

$$H(p_x, p_y, x, y) = \frac{1}{2}p_x^2 + \frac{1}{2}p_y^2 + \frac{1}{2}(x-y)^2$$

where the first two terms are kinetic energy, and the last term is potential energy.

a. Derive the Hamilton's equations of motion from the above Hamiltonian function.
b. Rewrite the Hamilton's equations in the form of second order equations involving only x and y, i.e., the Newton's equation of motion.
c. Show that the Hamilton H is a constant of motion, i.e., dH/dt = 0.
d. Give the Verlet algorithm for the Newton's equation of motion applied to this problem.
e. With the Verlet algorithm, H is no longer an exact constant but only approximately so. Give a finite-difference approximation to H and also indicated the order of error (i.e. O(h^n) with a proper exponent n).

[25 marks]

a. *since*

$\dot{p} = -\dfrac{\partial H}{\partial q}$, $\dot{q} = \dfrac{\partial H}{\partial p}$, *we get* $dp_x/dt = -x+y$, $dp_y/dt = x-y$, $dx/dt = p_x$, $dy/dt = p_y$.

b. *Substitute p_x and p_y into the first two Hamilton's equations we get the Newton's equations*

$$d^2x/dt^2 = -x + y, \quad d^2y/dt^2 = x - y.$$

c.

$$\frac{dH}{dt} = \frac{\partial H}{\partial p_x}\dot{p}_x + \frac{\partial H}{\partial p_y}\dot{p}_y + \frac{\partial H}{\partial x}\dot{x} + \frac{\partial H}{\partial y}\dot{y} =$$

$$\dot{x}\dot{p}_x + \dot{y}\dot{p}_y - \dot{p}_x\dot{x} + \dot{p}_y\dot{y} = 0$$

d.

$$x(t+h) = 2x(t) - x(t-h) + h^2(-x(t) + y(t)),$$
$$y(t+h) = 2y(t) - y(t-h) + h^2(x(t) - y(t)).$$

e.

$$H = \frac{1}{8h^2}\left[\left(x(t+h) - x(t-h)\right)^2 - \left(y(t+h) - y(t-h)\right)^2\right] + \frac{1}{2}\left(x(t) - y(t)\right)^2 + O(h^2).$$

-- the end --