10.34. Numerical Methods Applied to Chemical Engineering
HW 8. Brownian Dynamics and Monte Carlo simulation
Due Wednesday 11/30/2005. 9am

Submit a Word document *username_HW8.doc* and the files for each program.

<u>Problem 1.</u> Brownian motion in an external field

Consider the Brownian motion in the *x*-direction of a spherical particle of radius R_p and density ρ_p moving in a Newtonian fluid of viscosity μ_f. Stokes' law gives a drag constant of $\zeta = 6\pi\mu_f R_p$. The particle experiences an external potential energy field $U(x)$ such that the force imparted to the particle by the field is $-(dU/dx)$. Let us say that the fluid itself is moving in the *x*-direction with a velocity V_f. With a random force $F_R(t)$ due to collisions with individual fluid molecules, Newton's second law of motion for the particle is

$$m\frac{dv_x}{dt} = -\zeta(v_x - V_f) - \frac{dU}{dx} + F_R(t) \qquad \text{(EQ 1)}$$

As shown in class, the mass of a particle, $m = \frac{4}{3}\pi\rho_p R_p^3$, becomes negligibly small compared to the drag constant $\zeta = 6\pi\mu_f R_p$ when R_p is very small. This results in extremely short velocity correlation times $\tau_v = m/\zeta$. If we are concerned only with the observed motion of the particle on times scales long compared to τ_v, we can neglect the inertial effects completely by taking the limit $m \to 0$ while holding ζ constant. In this limit, the motion of the particle follows

$$0 = -\zeta(v_x - V_f) - \frac{dU}{dx} + F_R(t) \qquad \text{(EQ 2)}$$

Upon rearrangement, and multiplying by dt, using $dx = v_x dt$, this yields

$$dx = \left[V_f - \zeta^{-1}\frac{dU}{dx}\right]dt + \zeta^{-1}F_R(t)dt \qquad \text{(EQ 3)}$$

As we have shown in class, in the case where $V_f = 0$, $U(x) = 0$, we get the correct statistical properties of the random displacement by simulating the SDE (Stochastic Differential Equation)

$$dx = (2D)^{1/2}dW_t \qquad \text{(EQ 4)}$$

For a finite time step Δt, we have the simulation algorithm

$$x(t + \Delta t) - x(t) = (2D)^{1/2}\Delta W_t \qquad \text{(EQ 5)}$$

ΔW_t is a random number generated at each time step with

$$\Delta W_t = (\sqrt{\Delta t})\theta \qquad P(\theta) = \frac{1}{\sqrt{2\pi}} e^{-\theta^2/2} \tag{EQ 6}$$

ΔW_t is drawn from a normal distribution with a mean of zero and a variance of $\sigma^2 = \Delta t$.

Therefore, to agree with this limiting case, we write the SDE for the particle motion in a moving fluid and an external field as

$$dx = \left[V_f - \zeta^{-1} \left. \frac{dU}{dx} \right|_{x(t)} \right] dt + (2D)^{1/2} dW_t \tag{EQ 7}$$

which yields the simulation algorithm

$$x(t + \Delta t) - x(t) = \left[V_f - \zeta^{-1} \left. \frac{dU}{dx} \right|_{x(t)} \right] (\Delta t) + (2D)^{1/2} \Delta W_t \tag{EQ 8}$$

As shown in class, the drag constant and the diffusivity are related by Einstein's relation

$$D = \frac{k_b T}{\zeta} \tag{EQ 9}$$

Part 1.A.

Considering the SDE above, we see that if we had no random force, we would have a deterministic velocity of the particle equal to $v_p = V_f - \zeta^{-1} \left. \frac{dU}{dx} \right|_{x(t)}$. So, the deterministic (non-random) part of the SDE appears to describe convective motion, and the random part (as we have seen) describes diffusive motion. This appears to suggest that the probability distribution $p(t, x)$ follows a convection/diffusion equation

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}[v_p p(t, x)] + D \frac{\partial^2 p}{\partial x^2} \tag{EQ 10}$$

In fact, it is shown in the text that for a system described by the SDE

$$dx = a(t, x)dt + b(t, x)dW_t \tag{EQ 11}$$

the probability distribution is governed by a corresponding ***Fokker-Planck equation***

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x}[a(t, x)p(t, x)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\{[b(t, x)]^2 p(t, x)\} \tag{EQ 12}$$

Here, you are asked to perform a number of Brownian dynamics simulations to demonstrate that the probability distribution does indeed follow this convection/diffusion equa-

tion in the case of a constant fluid velocity V_f and in the absence of an external field, $U(x) = 0$.

If we release a particle at $x = 0$ at time $t = 0$, the initial condition is $p(0, x) = \delta(x)$.

1.A.1. First, show that the solution of the convection/diffusion equation is

$$p(t, x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/(2\sigma^2)} \qquad \begin{aligned} \mu &= V_f t \\ \sigma^2 &= 2Dt \end{aligned} \tag{EQ 13}$$

1.A.2. Next, perform a large number of Brownian dynamics simulations of individual particles for the case $D = 1$, $V_f = 1$. Using the MATLAB histogram routines, generate approximate probability distributions $p(t, x)$ at $t = 0.5, 1, 2, 3$ from the random trajectories $x(t)$ that you generate in the simulations. Plot these vs. the analytical $p(t, x)$ to demonstrate that indeed the Brownian dynamics simulations result in the correct $p(t, x)$. Store your program as *username_HW8_1A.m*.

Part 1.B.

Now, set $V_f = 0$ and let us introduce a spatially-periodic potential

$$U(x) = E_a[\sin(x\pi)]^2 \tag{EQ 14}$$

of periodicity $U(x \pm m) = U(x)$, $m = 0, 1, 2, 3 \ldots$. This potential consists of a sequence of energy barriers of height E_a each separated by a distance of one.

Perform a Brownian dynamics simulation using periodic boundary conditions on the domain $0 \le x \le 1$ in which at any time the particle exits the domain, it is shifted by ± 1 to bring it back inside the domain. Since the potential energy is also periodic, this shifting has no deleterious effect on the simulation, and it enables us to compare the measured probability distribution $P(x)$ over the course of the simulation with the Boltzmann distribution

$$P(x) = \frac{e^{-U(x)/k_bT}}{\int_0^1 e^{-U(x)/k_bT} dx} \tag{EQ 15}$$

In your Brownian dynamics simulation, you should not start sampling the distribution of *x* until you have run the simulation for a while to "equilibrate" the system. Simulate the motion of a particle at $k_bT = 1$, $E_a = 1$, $D = 1$ and demonstrate that the Brownian dynamics simulation samples properly from the equilibrium distribution. That is, the probability distribution measured from the trajectory $x(t)$ agrees with the Boltzmann distribution. Store your program as *username_HW8_1B.m*.

Part 1.C.

Consider again the same external potential, but now do not use the periodic boundary conditions. Instead, generate trajectories $x(t)$ that are <u>not</u> shifted in space to remain in $[0, 1]$. In the limit $E_a \ll k_bT$, the energy barriers are negligibly small and the particles essentially undergo "regular" diffusion. But, when E_a becomes comparatively large relative to k_bT, we expect the barriers to be difficult to overcome such that the particle trajectories become "trapped" between barriers for a long time until they are finally able to "jump" to the next energy well. If we then continue the simulation over very long periods of time such that each trajectory has experienced many jumps, and we measure at various times the mean squared displacement, $\langle x^2(t) \rangle$, we can estimate the effective diffusivity, D_{eff}, in the presence of the barriers from the relation $\langle x^2(t) \rangle = 2D_{\text{eff}}t$ as $t \to \infty$.

Perform this calculation to measure D_{eff} when $D = 1$ for $E_a = 0.1, 0.5, 1, 2, 3, 4, 5$ when $k_bT = 1$ and plot $\ln D_{\text{eff}}$ vs. E_a. A reasonable prediction of how the effective diffusivity should be affected by the barrier height is

$$D_{\text{eff}} = De^{-E_a/k_bT} \qquad \text{(EQ 16)}$$

Compare the results of your calculation to this functional form to see if it is an accurate description of the effect of energy barriers on long-time diffusive motion. Store your program as *username_HW8_1C.m.*

<u>Problem 2.</u> Metropolis Monte Carlo Simulation

Consider again the 1-D system with the periodic potential energy

$$U(x) = E_a[\sin(x\pi)]^2 \qquad \text{(EQ 17)}$$

Write a program to sample the NVT equilibrium distribution of *x* using Metropolis Monte Carlo for the case $E_a = 1$, $k_bT = 1$, and show that the results agree with the Boltzmann distribution

$$P(x) = \frac{e^{-U(x)/k_bT}}{\int_0^1 e^{-U(x)/k_bT}dx} \qquad \text{(EQ 18)}$$

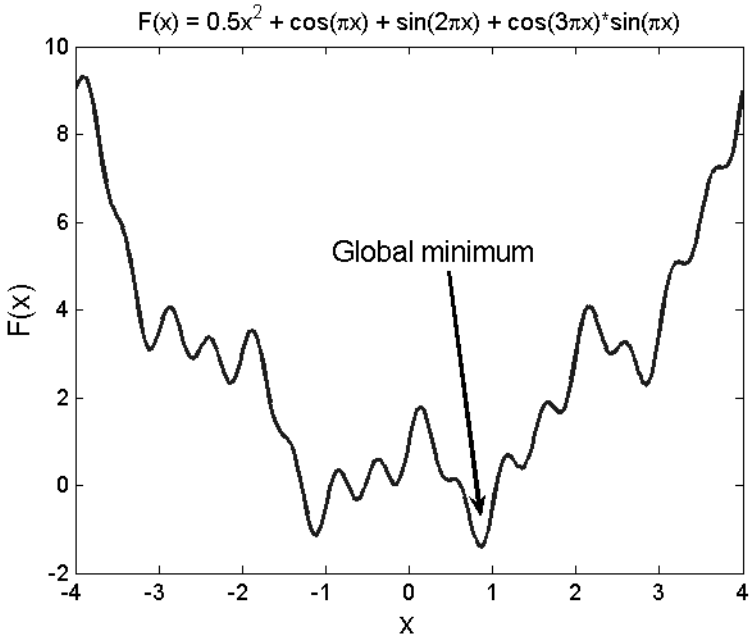
where again you use periodic BC to maintain the particle within $0 \le x \le 1$.

<u>Problem 3.</u> Simulated Annealing

Consider the cost function

$$F(x) = 0.5x^2 + \cos(\pi x) + \sin(2\pi x) + \cos(3\pi x)\sin(\pi x) \qquad \text{(EQ 19)}$$

plotted in the figure below.



Clearly, the cost function has many local minima, and it would be very difficult to find the global minimum using the deterministic techniques that we developed in chapter 5. Unfortunately, such irregular cost functions are not uncommon, especially when attempting to compute the minimum energy geometry of a molecule or a crystal.

Write a program that uses simulated annealing to identify the global minimum from a random initial guess. Store your program as *username_HW8_P3.m* and provide directions for its use.

Problem 4. Monte Carlo Integration

Solve problem 4.A.2 of the text, storing your program as *username_HW8_P4.m*.