PROBLEM SET 3

Notes:

- This set contains 4 problems, with multiple parts to each problem.
- Please start each problem on a new page.
- Due date: **November 15, 2005**.

1 Corrections to the macroscopic equation

From the master equation

$$\frac{\partial P(\mathbf{x},t)}{\partial t} = \int d\mathbf{x}' \left[W(\mathbf{x}' \to \mathbf{x}) P(\mathbf{x}',t) - W(\mathbf{x} \to \mathbf{x}') P(\mathbf{x},t) \right]$$

it was derived in the lecture that the macroscopically observed value of $\mathbf{x}$, i.e., $\mathbf{x}_{\mathrm{m}}(t) = \langle \mathbf{x}(t) \rangle = \int d\mathbf{x}\, \mathbf{x}\, P(\mathbf{x},t)$, satisfies

$$\frac{d\mathbf{x}_{\mathrm{m}}}{dt} = \langle \mathbf{a}_1(\mathbf{x}) \rangle.$$

This is not a closed equation for the time evolution of $\mathbf{x}_{\mathrm{m}}$ because the first jump moment $\mathbf{a}_1(\mathbf{x})$ is in general a nonlinear function of $\mathbf{x}$, so that $\langle \mathbf{a}_1(\mathbf{x}) \rangle \neq \mathbf{a}_1(\langle \mathbf{x} \rangle) = \mathbf{a}_1(\mathbf{x}_{\mathrm{m}})$.

a. Under the assumption that fluctuations are small, expand the function $\mathbf{a}_1(\mathbf{x})$ around $\mathbf{x}_{\mathrm{m}}$ and show that

$$\frac{d\mathbf{x}_{\mathrm{m}}}{dt} = \mathbf{a}_1(\mathbf{x}_{\mathrm{m}}) + \frac{1}{2} \boldsymbol{\sigma}(t) : \frac{\partial^2 \mathbf{a}_1(\mathbf{x}_{\mathrm{m}})}{\partial \mathbf{x}_{\mathrm{m}} \partial \mathbf{x}_{\mathrm{m}}} + \ldots,$$

where

$$\boldsymbol{\sigma}(t) = \langle (\mathbf{x}(t) - \mathbf{x}_{\mathrm{m}}(t))(\mathbf{x}(t) - \mathbf{x}_{\mathrm{m}}(t)) \rangle = \int d\mathbf{x}\, (\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t)) P(\mathbf{x},t).$$

which is a measure of the width (or rather the width squared) of the distribution of $\mathbf{x}$ in the system, i.e., a measure of the fluctuations.

Note that because we took the fluctuations into account, we did not get a closed equation for $\mathbf{x}_{\mathrm{m}}$ (unless $\mathbf{a}$ is a linear function of $\mathbf{x}_{\mathrm{m}}$).

b. Show that $\boldsymbol{\sigma}$ satisfies

$$\frac{d\boldsymbol{\sigma}}{dt} = \langle \mathbf{a}_2(\mathbf{x}) \rangle + \langle (\mathbf{x} - \mathbf{x}_{\mathrm{m}}) \mathbf{a}_1(\mathbf{x}) \rangle + \langle \mathbf{a}_1(\mathbf{x}) (\mathbf{x} - \mathbf{x}_{\mathrm{m}}) \rangle$$

with $\mathbf{a}_2$ the second jump moment.

c. Show that expanding $\mathbf{x}$ around $\mathbf{x}_\mathrm{m}$ in this equation leads to

$$\frac{d\boldsymbol{\sigma}}{dt} = \mathbf{a}_2(\mathbf{x}_\mathrm{m}) + \frac{1}{2}\boldsymbol{\sigma} : \frac{\partial^2 \mathbf{a}_2(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m} \partial \mathbf{x}_\mathrm{m}} + \boldsymbol{\sigma} \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} \cdot \boldsymbol{\sigma} + \dots .$$

Note that we have derived a closed set of two coupled equations for $\mathbf{x}_\mathrm{m}$ and $\boldsymbol{\sigma}$, which could be the starting point of an investigation of the influence of small fluctuations.

2 Transition probability rates for reactions in dilute solutions

Consider a reaction between J components $X_1 \dots X_J$:

$$s_1 X_1 + s_2 X_2 + \dots + s_J X_J \rightleftharpoons r_1 X_1 + r_2 X_2 + \dots + r_J X_J$$

The quantity of interest here is the transition probability rate W associated with this reaction in a uniform dilute solution. Let the volume of the solution be V, and let there be N_j molecules of compound j present in that volume. Assume that for the reaction to happen, the reactants have to all be inside the same (small) reaction volume v_r.

a. Show that the probability for having s_1 molecules of X_1, s_2 molecules of X_2, etc., being inside the same volume v_r (which may be anywhere in the system) is equal to

$$P = \frac{V}{v_r} \prod_{j=1}^{J} \binom{N_j}{s_j} \left(\frac{v_r}{V}\right)^{s_j} \left(1 - \frac{v_r}{V}\right)^{N_j - s_j}$$

b. Show that in the limit $V \to \infty$ with N_j/V and v_r fixed, this leads to

$$P = \frac{V}{v_r} \prod_{j=1}^{J} \left(\frac{v_r}{V}\right)^{s_j} \frac{N_j!}{(N_j - s_j)!} \frac{e^{-v_r N_j/V}}{s_j!}.$$

c. Argue now that the transition rates for the forward and reverse reaction in dilute solutions are given by

$$\begin{aligned} W(\{N_j\} \to \{N_j + r_j - s_j\}) &= k_+ V \prod_{j=1}^{J} \frac{N_j!}{(N_j - s_j)!} \frac{1}{V^{s_j}} \\ W(\{N_j\} \to \{N_j + s_j - r_j\}) &= k_- V \prod_{j=1}^{J} \frac{N_j!}{(N_j - r_j)!} \frac{1}{V^{r_j}}, \end{aligned}$$

respectively, where k_+ and k_- are independent of the N_j.

3 Derivation of the Kramers' equation

Consider the evolution of the Kramers' particle (representing a reaction coordinate) in the Langevin description:

$$\begin{aligned}\frac{dx(t)}{dt} &= v(t) \\ \frac{dv(t)}{dt} &= -U'\big(x(t)\big) - \alpha v + \xi(t).\end{aligned}$$

where

$$\begin{aligned}\langle \xi(t) \rangle &= 0 \\ \langle \xi(t)\xi(t') \rangle &= 2kT\alpha\delta(t-t').\end{aligned}$$

For simplicity the particle has been given a mass of one here.
Instead of this stochastic differential equation one can use a description of the system in terms of a probability distribution function $P(x, v, t)$, for which an equation needs to be derived. The starting point is the master equation

$$\frac{\partial P(x,v,t)}{\partial t} = \int dx'\,dv' \Big[W\big((x',v') \to (x,v)\big) P(x',v',t) - W\big((x,v) \to (x',v')\big) P(x,v,t) \Big],$$

where $W\big((x',v') \to (x,v)\big)dx\,dv$ is the transition probability per unit time to go from the state (x', v') to another state between (x, v) and $(x + dx, v + dv)$.

a. Write $W\big((x',v') \to (x,v)\big) = \tilde{W}(x',v';x-x',v-v')$ and show that the master equation can be written as

$$\frac{\partial P(x,v,t)}{\partial t} = \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty}{}' \frac{(-1)^{\mu+\nu}}{\mu!\nu!} \frac{\partial^{\mu+\nu}}{\partial x^{\mu} \partial v^{\nu}} \left[a_{\mu\nu}(x,v) P(x,v,t) \right],$$

where the prime on the summation denotes that the case $\mu = \nu = 0$ is excluded, and the jump moments $a_{\mu\nu}$ are given by

$$a_{\mu\nu}(x,v) = \int d\Delta x\, d\Delta v\, \tilde{W}(x,v;\Delta x,\Delta v) \Delta x^{\mu} \Delta v^{\nu}.$$

This is called the Kramers-Moyal expansion of the master equation.

b. Argue that jump moments can be expressed as

$$a_{\mu\nu}(x,v) = \lim_{\Delta t \to 0} (\Delta t)^{-1} \langle [\Delta x(\Delta t)]^{\mu} [\Delta v(\Delta t)]^{\nu} \rangle$$

where $\Delta x(\Delta t)$ and $\Delta v(\Delta t)$ are the change in position and velocity, respectively, starting from (x, v).

c. Show that first few jump moments are given by:

$$a_{10}(x,v) = v, \quad a_{01}(x,v) = -\alpha v - U'(x), \quad a_{02}(x,v) = 2kT\alpha.$$

The random force $\xi(t)$ has the Gaussian property that multi-time correlations are equal to the sum of all possible ways to factorize them:

$$\langle \xi(t_1)\xi(t_2)\cdots\xi(t_N)\rangle = \prod_{\text{all factorizations}} \langle \xi(t_i)\xi(t_j)\rangle$$

E.g., in particular

$$\begin{aligned}\langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4)\rangle &= \langle \xi(t_1)\xi(t_2)\rangle\langle \xi(t_3)\xi(t_4)\rangle + \langle \xi(t_1)\xi(t_3)\rangle\langle \xi(t_2)\xi(t_4)\rangle \\ &\quad +\langle \xi(t_1)\xi(t_4)\rangle\langle \xi(t_2)\xi(t_3)\rangle \\ &= 2kT\alpha\Big[\delta(t_1-t_2)\delta(t_3-t_4)+\delta(t_1-t_3)\delta(t_2-t_4) \\ &\qquad +\delta(t_1-t_4)\delta(t_2-t_3)\Big]\end{aligned}$$

d. Prove that

$$a_{04}(x,v) = 0.$$

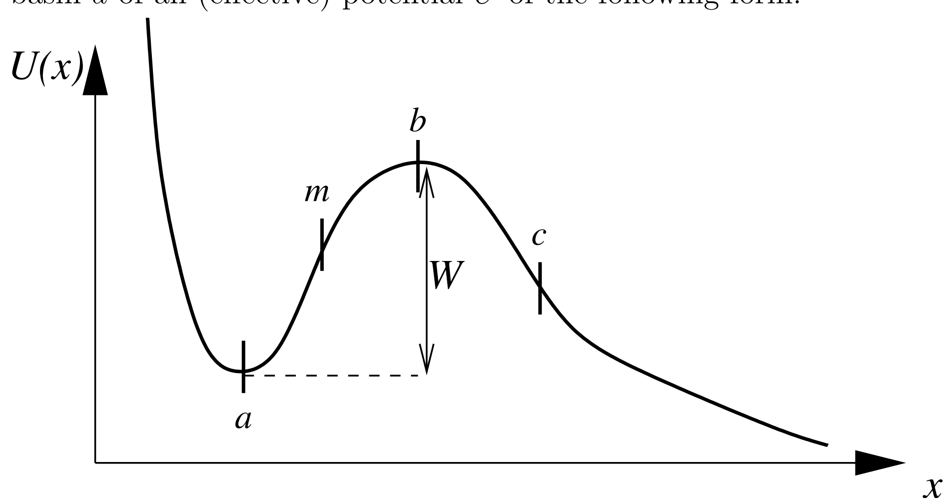
e. Argue now that all higher order jump moments are zero.

Thus the expansion of the master equation reduces to the Kramers' equation:

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{\partial}{\partial v}\Big[(\alpha v + U')P\Big] + kT\alpha\frac{\partial^2 P}{\partial v^2}.$$

4 Kramers' escape problem for moderate friction

The Kramers' problem consists of finding the time for a Kramers' particle to escape from a metastable basin a of an (effective) potential U of the following form:



As in problem 3, we will set the mass of the Kramers' particle equal to one.
To determine the escape time, one can use that the probability distribution $P(x, v, t)$ will be quasi-stationary inside the basin, with a small net flow out of the basin through the top of the barrier b, given by

$$\frac{1}{\tau} = \int_{-\infty}^{\infty} dv\, v P(b, v).$$

The problem then reduces to finding an approximation to the quasi-stationary distribution $P(x, v)$.
In the lecture, a naive expression for the quasi-stationary distribution was found, i.e.,

$$P_{\text{naive}}(x, v) = \frac{\sqrt{U''(a)}}{2\pi kT} \exp\left[-\frac{\frac{1}{2}v^2 + U(x) - U(a)}{kT}\right],$$

which lead to $\tau_{\text{naive}} = [2\pi/\sqrt{U''(a)}]\exp[W/kT]$, where $W = U(b) - U(a)$ is the barrier height.

In this problem, you will improve upon this result by deriving a better approximation for the quasi-stationary probability distribution function for not too small α.

a. Show that inside the basin, i.e., close enough to a, the above naive distribution $P_{\text{naive}}(x, v)$ is approximately a stationary solution of the Kramers' equation (found at the end of the previous problem).

We will assume that the naive approximation is valid up to the point m (see figure) while for $m < x < c$ the potential $U(x)$ may be approximated by the inverted parabola

$$U(x) \approx U(b) - \frac{1}{2}|U''(b)|(x - b)^2 \quad \text{for } x > m.$$

b. Make the *Ansatz* that in the parabolic region $m < x < c$, $P(x, v)$ is of the form

$$P(x, v) = f\big(v - \omega(x - b)\big) \exp\left[\frac{|U''(b)|(x - b)^2 - v^2}{2kT}\right]$$

with so far a general ω. Show that $f(z) = f\big(v - \omega(x - b)\big)$ must satisfy

$$\big[\omega v - |U''(b)|(x - b) - \alpha v\big] f'(z) + \alpha kT f''(z) = 0.$$

c. Argue that for this *Ansatz* to work, the coefficient of $f'(z)$ must be a function of $z = v - \omega(x - b)$ only. Show that this requires that $\omega^2 - \alpha\omega - |U''(b)| = 0$ so that either

$$\omega = \frac{1}{2}\alpha + \frac{1}{2}\sqrt{\alpha^2 + 4|U''(b)|}$$

or

$$\omega = \frac{1}{2}\alpha - \frac{1}{2}\sqrt{\alpha^2 + 4|U''(b)|}.$$

d. Show that the resulting equation for f is now

$$(\omega - \alpha) z f'(z) + \alpha k T f''(z) = 0,$$

and show that this is solved in general by

$$f(z) = A + B \,\mathrm{erf}\left(\sqrt{\frac{\omega - \alpha}{2\alpha k T}}\; z\right)$$

where erf is the error function, which is defined by

$$\mathrm{erf}(\xi) = \frac{2}{\sqrt{\pi}} \int_0^{\xi} d\eta\, e^{-\eta^2}.$$

The error function has the properties that it blows up for large imaginary ξ, and that $\lim_{\xi \to \pm\infty} \mathrm{erf}(\xi) = \pm 1$.

e. Argue that for $P(x, v)$ to vanish for $x \to \infty$ (normalization condition), we should use the positive value of ω, and A should be equal to B.

f. Taking the results together gives

$$P(x,v) \approx \begin{cases} \dfrac{\sqrt{U''(a)}}{2\pi k T} \exp\left[-\dfrac{\frac{1}{2}v^2 + U(x) - U(a)}{kT}\right] & \text{for } 0 < x < m \\[2ex] A\left[1 + \mathrm{erf}\left(\sqrt{\dfrac{\omega - \alpha}{2\alpha k T}}\,\big(v - \omega(x - b)\big)\right)\right] \exp\left[-\dfrac{\frac{1}{2}v^2 + U(x) - U(b)}{kT}\right] & \text{for } m < x < c. \end{cases}$$

Show that the two parts match at the point $x = m$ if one chooses

$$A = \frac{\sqrt{U''(a)}}{4\pi k T} \exp\left[-\frac{W}{kT}\right].$$

Hint: use that m is far away from the top b of the barrier, i.e., $(b - m) \gg 1$.

g. Calculate finally the escape time:

$$\frac{1}{\tau} = \int_{-\infty}^{\infty} dv\, v P(b, v) = \frac{\sqrt{U''(a)|U''(b)|}}{\pi\left(\alpha + \sqrt{\alpha^2 + 4|U''(b)|}\right)} \exp\left[-\frac{W}{kT}\right].$$

Hint: use that $\int_{-\infty}^{\infty} dv\, v\, \mathrm{erf}(av) \exp(-bv^2) = [b\sqrt{1 + b/a^2}]^{-1}$.

Note: The method used here to find the escape time is an alternative to the mean first passage time technique. Indeed, for large α, the result found here is in agreement with the result

$$\frac{1}{\tau_{\mathrm{fp}}} = \frac{\sqrt{U''(a)|U''(b)|}}{2\pi\alpha} \exp\left[-\frac{W}{kT}\right]$$

that was obtained using the mean first passage time for large friction.