SOLUTIONS TO PROBLEM SET 3

1 Corrections to the macroscopic equation

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.

<u>*Solution:*</u>

Writing $\mathbf{x}(t) = \mathbf{x}_\mathrm{m}(t) + \boldsymbol{\varepsilon}(t)$ *with* $\boldsymbol{\varepsilon}(t) = \mathbf{x}(t) - \mathbf{x}_\mathrm{m}(t)$, *we may expand in* $\boldsymbol{\varepsilon}(t)$ *as follows:*

$$\mathbf{a}_1(\mathbf{x}(t)) = \mathbf{a}_1(\mathbf{x}_\mathrm{m}) + \boldsymbol{\varepsilon}(t) \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + + \frac{1}{2}\boldsymbol{\varepsilon}(t)\boldsymbol{\varepsilon}(t) : \frac{\partial^2 \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial\mathbf{x}_\mathrm{m}\partial\mathbf{x}_\mathrm{m}} + \mathcal{O}(\varepsilon^3),$$

whence

$$\frac{d\mathbf{x}_\mathrm{m}}{dt} = \langle\mathbf{a}_1(\mathbf{x}_\mathrm{m})\rangle + \langle\boldsymbol{\varepsilon}(t) \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}}\rangle + \frac{1}{2}\langle\boldsymbol{\varepsilon}(t)\boldsymbol{\varepsilon}(t) : \frac{\partial^2 \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial\mathbf{x}_\mathrm{m}\partial\mathbf{x}_\mathrm{m}}\rangle + \mathcal{O}(\varepsilon^3),$$

Using that $\mathbf{x}_\mathrm{m}$ *does not depend on* $\mathbf{x}$, *so that it may be taken outside of the average, we get:*

$$\frac{d\mathbf{x}_\mathrm{m}}{dt} = \mathbf{a}_1(\mathbf{x}) + \langle\boldsymbol{\varepsilon}(t)\rangle \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + \frac{1}{2}\langle\boldsymbol{\varepsilon}(t)\boldsymbol{\varepsilon}(t)\rangle : \frac{\partial^2 \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial\mathbf{x}_\mathrm{m}\partial\mathbf{x}_\mathrm{m}} + \mathcal{O}(\varepsilon^3),$$

But since $\langle\boldsymbol{\varepsilon}\rangle = \langle\mathbf{x} - \mathbf{x}_\mathrm{m}\rangle = \langle\mathbf{x} - \langle\mathbf{x}\rangle\rangle = 0$, *we have*

$$\frac{d\mathbf{x}_\mathrm{m}}{dt} = \mathbf{a}_1(\mathbf{x}) + \frac{1}{2}\langle(\mathbf{x}(t) - \mathbf{x}(t))(\mathbf{x}(t) - \mathbf{x}(t))\rangle : \frac{\partial^2 \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial\mathbf{x}_\mathrm{m}\partial\mathbf{x}_\mathrm{m}} + \mathcal{O}(\varepsilon^3),$$

which, upon identifying $\boldsymbol{\sigma}$, *is the desired equation.*

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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.

<u>Solution:</u>

We start with the given definition of $\boldsymbol{\sigma}(t)$ and take the time derivative:

$$\begin{aligned}
\frac{d}{dt}\boldsymbol{\sigma}(t) &= \frac{d}{dt}\int d\mathbf{x}\,(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))P(\mathbf{x}, t) \\
&= -\int d\mathbf{x}\,\frac{d\mathbf{x}_{\mathrm{m}}(t)}{dt}(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))P(\mathbf{x}, t) - \int d\mathbf{x}\,(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))\frac{d\mathbf{x}_{\mathrm{m}}(t)}{dt}P(\mathbf{x}, t) \\
&\quad + \int d\mathbf{x}\,(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))(\mathbf{x} - \mathbf{x}_{\mathrm{m}}(t))\frac{\partial}{\partial t}P(\mathbf{x}, t)
\end{aligned}$$

However, because $\langle \mathbf{x}(t) \rangle = \mathbf{x}_{\mathrm{m}}(t)$, the first two terms are zero. Now use the master equation in the remaining term:

$$\begin{aligned}
\frac{d}{dt}\boldsymbol{\sigma}(t) &= \int d\mathbf{x}\int d\mathbf{x}'\,(\mathbf{x} - \mathbf{x}_{\mathrm{m}})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\left[W(\mathbf{x}' \to \mathbf{x})P(\mathbf{x}', t) - W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t)\right] \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\left[(\mathbf{x}' - \mathbf{x}_{\mathrm{m}})(\mathbf{x}' - \mathbf{x}_{\mathrm{m}}) - (\mathbf{x} - \mathbf{x}_{\mathrm{m}})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\right]W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\left[\mathbf{x}'\mathbf{x}' - \mathbf{x}_{\mathrm{m}}\mathbf{x}' - \mathbf{x}'\mathbf{x}_{\mathrm{m}} - \mathbf{x}\mathbf{x} + \mathbf{x}_{\mathrm{m}}\mathbf{x} + \mathbf{x}\mathbf{x}_{\mathrm{m}}\right]W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\left[\mathbf{x}'\mathbf{x}' - \mathbf{x}\mathbf{x} - \mathbf{x}_{\mathrm{m}}(\mathbf{x}' - \mathbf{x}) - (\mathbf{x}' - \mathbf{x})\mathbf{x}_{\mathrm{m}}\right]W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\Bigg[\mathbf{x}'\mathbf{x}' - \mathbf{x}\mathbf{x} - \mathbf{x}(\mathbf{x}' - \mathbf{x}) + (\mathbf{x} - \mathbf{x}_{\mathrm{m}})(\mathbf{x}' - \mathbf{x}) \\
&\qquad\qquad - (\mathbf{x}' - \mathbf{x})\mathbf{x} + (\mathbf{x}' - \mathbf{x})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\Bigg]W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\left[\mathbf{x}'\mathbf{x}' - \mathbf{x}\mathbf{x}' - \mathbf{x}'\mathbf{x} + \mathbf{x}\mathbf{x} + (\mathbf{x} - \mathbf{x}_{\mathrm{m}})(\mathbf{x}' - \mathbf{x}) + (\mathbf{x}' - \mathbf{x})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\right] \\
&\qquad \times W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\int d\mathbf{x}'\,\left[(\mathbf{x}' - \mathbf{x})(\mathbf{x}' - \mathbf{x}) + (\mathbf{x} - \mathbf{x}_{\mathrm{m}})(\mathbf{x}' - \mathbf{x}) + (\mathbf{x}' - \mathbf{x})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\right] \\
&\qquad \times W(\mathbf{x} \to \mathbf{x}')P(\mathbf{x}, t) \\
&= \int d\mathbf{x}\,\left[\mathbf{a}_2(\mathbf{x}) + (\mathbf{x} - \mathbf{x}_{\mathrm{m}})\mathbf{a}_1(\mathbf{x}) + \mathbf{a}_1(\mathbf{x})(\mathbf{x} - \mathbf{x}_{\mathrm{m}})\right]P(\mathbf{x}, t) \\
&= \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
\end{aligned}$$

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

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

Solution:

Starting from the result of b. we write again $\mathbf{x} = \mathbf{x}_\mathrm{m} + \boldsymbol{\varepsilon}$ *with* $\boldsymbol{\varepsilon}(t) = \mathbf{x}(t) - \mathbf{x}_\mathrm{m}(t)$ *and expand in* $\boldsymbol{\varepsilon}(t)$*:*

$$\begin{aligned} \frac{d}{dt}\boldsymbol{\sigma}(t) &= \langle \mathbf{a}_2(\mathbf{x}_\mathrm{m})\rangle + \langle \varepsilon \rangle \cdot \frac{\partial \mathbf{a}_2(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + \frac{1}{2}\langle \varepsilon\varepsilon \rangle \frac{\partial^2 \mathbf{a}_2(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m} \partial \mathbf{x}_\mathrm{m}} \\ &\quad + \langle \varepsilon \rangle \mathbf{a}_1(\mathbf{x}_\mathrm{m}) + \langle \varepsilon\varepsilon \rangle \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + \mathbf{a}_1(\mathbf{x}_\mathrm{m})\langle \varepsilon \rangle + \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} \cdot \langle \varepsilon\varepsilon \rangle + \ldots \\ &= \langle \mathbf{a}_2(\mathbf{x}_\mathrm{m})\rangle + \frac{1}{2}\langle \varepsilon\varepsilon \rangle \frac{\partial^2 \mathbf{a}_2(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m} \partial \mathbf{x}_\mathrm{m}} + \langle \varepsilon\varepsilon \rangle \cdot \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} + \frac{\partial \mathbf{a}_1(\mathbf{x}_\mathrm{m})}{\partial \mathbf{x}_\mathrm{m}} \cdot \langle \varepsilon\varepsilon \rangle + \ldots \end{aligned}$$

which, using $\langle \varepsilon\varepsilon \rangle = \boldsymbol{\sigma}$*, leads to the desired result.*

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2 Transition probability rates for reactions in dilute solutions

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

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

Solution:

Imagine the volume to be divided up into small cells (subvolume) of size v_r*. There are* V/v_r *such cells. The probability for any of the molecules to be in a specific cell is* v_r/V*, and thus the probability for that molecule not to be in that specific cell is* $1 - v_r/V$*. For not too-high densities, we may neglect possible correlations between the molecules. Then, the probability to find precisely* s_j *molecules of species* j *in a specific cell is the probability to find* s_j *of these molecules in that cell, i.e.* $(v_r/V)^{s_j}$*, times the probability to find the other ones not in this cell, i.e.* $(1 - v_r/V)^{N_j - s_j}$*, times the number of ways to pick* s_j *molecules from the* N_j *available ones, i.e.* $\binom{N_j}{s_j}$*. The molecules of different components are also uncorrelated, so that the probabilities multiply, and we get for the probability that* s_j *molecules of components* N_j *are in a specific cell:*

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

Realizing that this may occur in any of the cells, of which there are v_r/V many, leads to the desired formula.

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

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

<u>*Solution:*</u>

$$\begin{aligned}
P &= \frac{V}{v_r} \prod_{j=1}^{J} \binom{N_j}{s_j} \left(\frac{v_r}{V}\right)^{s_j} \left(1 - \frac{v_r}{V}\right)^{N_j - s_j} \\
&= \frac{V}{v_r} \prod_{j=1}^{J} \left(\frac{v_r}{V}\right)^{s_j} \frac{N_j!}{(N - s_j)! s_j!} \left(1 - \frac{(N_j - s_j)v_r/V}{N_j - s_j}\right)^{N_j - s_j} \\
&\overset{\text{large } N_j}{\longrightarrow} \frac{V}{v_r} \prod_{j=1}^{J} \left(\frac{v_r}{V}\right)^{s_j} \frac{N_j!}{(N - s_j)! s_j!} e^{-(N_j - s_j)v_r/V} \\
&\overset{\text{large } V}{\longrightarrow} \frac{V}{v_r} \prod_{j=1}^{J} \left(\frac{v_r}{V}\right)^{s_j} \frac{N_j!}{(N - s_j)! s_j!} e^{-N_j v_r/V}
\end{aligned}$$

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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.

<u>*Solution:*</u>

The transition rate $W(\{N_j\} \to \{N_j + r_j - s_j\})$ is proportional to P, times a collision cross section, times a probability for the reaction to actually occur when the molecules meet. The latter two do not depend on the number of molecules nor on the volume of the system. Thus, we may absorb into the constant k_+ everything except the dependence on N_j and V, which gives

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

The result for the reverse reaction simply follows by considering it as a forward reaction, replacing r_j and s_j.

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3 Derivation of the Kramers' equation

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

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

<u>Solution:</u>

Substituting $\tilde{W}$ gives

$$\begin{aligned}\frac{\partial P(x,v,t)}{\partial t} &= \int dx'\, dv' \left[\tilde{W}(x',v';x-x',v-v')P(x',v',t) - \tilde{W}(x,v;x'-x,v'-v)P(x,v,t)\right]\\ &= \int dx'\, dv' \Big[\tilde{W}(x',v';x-x',v-v')P(x+x'-x,v+v'-v,t)\\ &\qquad -\tilde{W}(x,v;x'-x,v'-v)P(x,v,t)\Big]\end{aligned}$$

Changing integration variables to $\Delta x = x - x'$ and $\Delta v = v - v'$ leads to

$$\begin{aligned}\frac{\partial P(x,v,t)}{\partial t} &= \int d\Delta x\, d\Delta v \Big[\tilde{W}(x-\Delta x,v-\Delta v;\Delta x,\Delta v)P(x-\Delta x,v-\Delta v,t)\\ &\qquad -\tilde{W}(x,v;-\Delta x,-\Delta v)P(x,v,t)\Big]\end{aligned}$$

but changing $\Delta x \to -\Delta x$ and $\Delta v \to -\Delta v$ in the last term gives

$$\begin{aligned}\frac{\partial P(x,v,t)}{\partial t} &= \int d\Delta x\, d\Delta v \Big[\tilde{W}(x-\Delta x,v-\Delta v;\Delta x,\Delta v)P(x-\Delta x,v-\Delta v,t)\\ &\qquad -\tilde{W}(x,v;\Delta x,\Delta v)P(x,v,t)\Big]\end{aligned}$$

Expanding the first term gives

$$\begin{aligned}
\frac{\partial P(x,v,t)}{\partial t} &= \int d\Delta x\, d\Delta v \Bigg[\sum_{\mu=0}^{\infty} \frac{[-\Delta x]^\mu}{\mu!} \sum_{\nu=0}^{\infty} \frac{[-\Delta v]^\nu}{\nu!} \frac{\partial^{\mu+\nu}}{\partial x^\mu \partial v^\nu} \left\{ \tilde{W}(x,v;\Delta x,\Delta v) P(x,v,t) \right\} \\
&\qquad - \tilde{W}(x,v;\Delta x,\Delta v) P(x,v,t) \Bigg] \\
&= \int d\Delta x\, d\Delta v \sum_{\mu=0}^{\infty} {\sum_{\nu=0}^{\infty}}' \frac{[-\Delta x]^\mu}{\mu!} \frac{[-\Delta v]^\nu}{\nu!} \frac{\partial^{\mu+\nu}}{\partial x^\mu \partial v^\nu} \left\{ \tilde{W}(x,v;\Delta x,\Delta v) P(x,v,t) \right\} \\
&= \sum_{\mu=0}^{\infty} {\sum_{\nu=0}^{\infty}}' \frac{(-1)^{\mu+\nu}}{\mu!\nu!} \frac{\partial^{\mu+\nu}}{\partial x^\mu \partial v^\nu} \left\{ \int d\Delta x\, d\Delta v\, \Delta x^\mu \Delta v^\nu \tilde{W}(x,v;\Delta x,\Delta v) P(x,v,t) \right\} \\
&= \sum_{\mu=0}^{\infty} {\sum_{\nu=0}^{\infty}}' \frac{(-1)^{\mu+\nu}}{\mu!\nu!} \frac{\partial^{\mu+\nu}}{\partial x^\mu \partial v^\nu} \left[a_{\mu\nu}(x,v) P(x,v,t) \right].
\end{aligned}$$

q.e.d.

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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).

<u>Solution:</u>

$\tilde{W}$ is the probability to jump a distance $(\Delta x, \Delta v)$ per unit time, i.e., for an infinitesimal small time Δt, the probability to jump is $\tilde{W}\Delta t$. The average of $\Delta x^\mu \Delta v^\nu$ in that time interval is

$$\langle [\Delta x(\Delta t)]^\mu [\Delta v(\Delta t)]^\nu \rangle = \int d\Delta x \int d\Delta v\, \tilde{W}(x,v;\Delta x,\Delta v)\Delta t = a_{\mu\nu}(x,v)\Delta t$$

which leads to

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

Since Δt was infinitesimal, we can take the limit $\Delta t \to 0$ and get the result we were after. Note that in taking the average here, x and v are kept fixed.

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

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

Solution:

First we determine for an infinitesimal Δt*, as in the notes:*

$$\begin{aligned}\Delta r(\Delta t) &= v\Delta t \\ \Delta v(\Delta t) &= -U'(x)\Delta t - \alpha v\Delta t + \int_0^{\Delta t} dt'\,\xi(t')\end{aligned}$$

Thus,

$$\begin{aligned}a_{10}(x,v) &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle \Delta x(\Delta t)\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle v\Delta t\rangle = v \\ a_{01}(x,v) &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle \Delta v(\Delta t)\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle -U'(x)\Delta t - \alpha v\Delta t + \int_0^{\Delta t} dt'\,\xi(t')\rangle = -U'(x) - \alpha v \\ a_{02}(x,v) &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle [-U'(x)\Delta t - \alpha v\Delta t + \int_0^{\Delta t} dt'\,\xi(t')]^2\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle [\int_0^{\Delta t} dt'\,\xi(t')]^2\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle \int_0^{\Delta t} dt'\,\xi(t') \int_0^{\Delta t} dt''\,\xi(t'')\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\int_0^{\Delta t} dt' \int_0^{\Delta t} dt''\langle \xi(t')\xi(t'')\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\int_0^{\Delta t} dt' \int_0^{\Delta t} dt''\,2kT\alpha\delta(t'-t'') \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\int_0^{\Delta t} dt'\,2kT\alpha = 2kT\alpha\end{aligned}$$

where we used that $\langle\xi\rangle = 0$ *and* $\langle \xi(t')\xi(t'')\rangle = 2kT\alpha\delta(t'-t'')$*.*

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d. Prove that

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

Solution:

Skipping a few steps, we get

$$\begin{aligned}a_{04}(x,v) &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle [-U'(x)\Delta t - \alpha v\Delta t + \int_0^{\Delta t} dt'\,\xi(t')]^4\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\langle [\int_0^{\Delta t} dt'\,\xi(t')]^4\rangle \\ &= \lim_{\Delta t\to 0}(\Delta t)^{-1}\int_0^{\Delta t} dt_1 \int_0^{\Delta t} dt_2 \int_0^{\Delta t} dt_3 \int_0^{\Delta t} dt_4 \langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4)\rangle.\end{aligned}$$

Using the factorization gives

$$a_{04}(x,v) = 2kT\alpha \lim_{\Delta t\to 0}(\Delta t)^{-1}\int_0^{\Delta t}dt_1\int_0^{\Delta t}dt_2\int_0^{\Delta t}dt_3\int_0^{\Delta t}dt_4\Big[\delta(t_1-t_2)\delta(t_3-t_4) + \delta(t_1-t_3)\delta(t_2-t_4)+\delta(t_1-t_4)\delta(t_2-t_3)\Big]$$

For each term, the two delta functions get rid of two integrals, so that two integrals remain, giving Δ^2*. Times the factor* $(\Delta t)^{-1}$*, we get* Δt*, whose* $\Delta \to 0$ *limit is zero:*

$$a_{04} = 0.$$

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

Solution:

First notice that products of an odd number of $\xi(t)$*'s average to zero, since they cannot be fully factorized, so that there is always a factor* $\langle \xi(t_i)\rangle = 0$*. For an even number* n *of factors of* ξ*, the result is a product of* $n/2$ *delta functions. Each jump moment* $a_{\mu\nu}$ *can be written as sum of terms in which there is a product of* k *fluctuating forces, with* k *at most* ν*. Thus it gives* $k/2$ *delta functions, and* ν *integrals, i.e.,* $k - k/2 = k/2$ *factors of* Δt*. The rest gives another factor proportional of* $\Delta t^{\mu+\nu-k}$*, so we get* $\Delta t^{\mu+\nu-k/2}$*, or, times* $(\Delta t)^{-1}$*,* $\Delta t^{\mu+\nu-k/2-1}$*. The smallest exponent of* Δt *we can get is for* $k = \nu$ *(or* $k = \nu - 1$ *if* ν *is odd), i.e.,* $\Delta t^{\mu+\lceil\nu/2\rceil-1}$*. The exponent is always positive, unless* $(\mu,\nu) = (1,0)$*,* $(0,1)$ *or* $(0,2)$*, when it is zero. If the exponent is positive, the limit* $\Delta t \to 0$ *gives zero, so all jump moments are zero except the cases* $(\mu,\nu) = (1,0)$*,* $(0,1)$ *or* $(0,2)$*.*

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4 Kramers' escape problem for moderate friction

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).

Solution:

In we insert the solution into the Kramer's equations, it would appear that the naive solution is an exact solution. The approximation lies in the fact that if we take it to hold everywhere, i.e., for x *from* 0 *to* ∞*, the function is not properly normalized,* $P(x\to\infty, v) \to \exp(-v^2/2kT)$*, so the normalization integral would diverge. Hence, we restrict our solution to have this value only up to the point* m *say (this would mean that the normalization is right to good approximation). Inside the metastable basin,* *this would make $\partial P/\partial t = 0$. However, because there is a probability flux $J(m) \neq 0$ at m, this solution will be 'drained', i.e., it will slowly leak probability, across the barrier and to infinity. Therefore, it is only approximately stationary.*

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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

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

<u>*Solution:*</u>

Call

$$E = \exp\left[\frac{|U''(b)|(x-b)^2 - v^2}{2kT}\right]$$

From the Ansatz, it follows that

$$\begin{aligned}
\frac{\partial P}{\partial t} &= 0 \\
\frac{\partial P}{\partial x} &= \left[\frac{\partial}{\partial x} f\big(v-\omega(x-b)\big) + \frac{(x-b)|U''(b)|}{kT} f\big(v-\omega(x-b)\big)\right] E \\
&= \left[-\omega f'\big(v-\omega(x-b)\big) + \frac{(x-b)|U''(b)|}{kT} f\big(v-\omega(x-b)\big)\right] E \\
\frac{\partial P}{\partial v} &= \left[\frac{\partial}{\partial v} f\big(v-\omega(x-b)\big) - \frac{v}{kT} f\big(v-\omega(x-b)\big)\right] E \\
&= \left[f'\big(v-\omega(x-b)\big) - \frac{v}{kT} f\big(v-\omega(x-b)\big)\right] E \\
\frac{\partial^2 P}{\partial v^2} &= \left[\frac{\partial^2}{\partial v^2} f\big(v-\omega(x-b)\big) - \frac{2v}{kT}\frac{\partial}{\partial v} f\big(v-\omega(x-b)\big) + \frac{v^2 - kT}{(kT)^2} f\big(v-\omega(x-b)\big)\right] E \\
&= \left[f''\big(v-\omega(x-b)\big) - \frac{2v}{kT} f'\big(v-\omega(x-b)\big) + \frac{v^2 - kT}{(kT)^2} f\big(v-\omega(x-b)\big)\right] E
\end{aligned}$$

Substituting these into the Kramer's equation, setting $v - \omega(x-b)$ to z, and dividing by E leads to the desired result.

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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

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

<u>*Solution:*</u>

We can rewrite the equation as

$$\omega v - |U''(b)|(x-b) - \alpha v = -\alpha kT f''(z)/f'(z).$$

Since the right-hand side depends only on z, so should the left-hand side. We substitute in the left-hand side $v = z + \omega x - \omega b$, and get

$$\begin{aligned}&\omega(z + \omega x - \omega b) - |U''(b)|(x-b) - \alpha(z + \omega x - \omega b)\\ &= (\omega - \alpha)z + (\omega^2 - |U''(b)| - \alpha\omega)(x-b)\end{aligned}$$

For this to be independent of x, the expression $(\omega^2 - |U''(b)| - \alpha\omega)$ needs to be zero, 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

$$(\omega - \alpha)zf'(z) + \alpha kT f''(z) = 0,$$

and show that this is solved in general by

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

<u>*Solution:*</u>

All that remains of the prefactor of $f'(z)$ is $(\omega-\alpha)z$, so we get the mentioned equation. We rewrite this as

$$f''(z) = -\frac{\omega-\alpha}{\alpha kT} z f'(z)$$

which has the following general solution for $f'(z)$:

$$f'(z) = \tilde{B}\exp\left[-\frac{\omega-\alpha}{2\alpha kT}z^2\right]$$

So that

$$f(z) = A + \tilde{B}\int_0^z d\tilde{z}\exp\left[-\frac{\omega-\alpha}{2\alpha kT}\tilde{z}^2\right].$$

Substituting $\eta = \sqrt{(\omega-\alpha)/(2\alpha kT)}\tilde{z}$ as a new integration variable, redefining B and using the definition of the error function, leads to the desired result.

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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.

<u>Solution:</u>

For P to be normalizable, it should at least not diverge for large v (and thus z). An imaginary argument of the error function is therefore not allowed. The two roots for ω are such that one is negative and one is positive. The positive one is furthermore larger than α, so selecting that one assure that the argument of the error function is real.

Consider now, for real arguments, the limit $z \to -\infty$ (and thus $x \to \infty$). $P(x, v)$ should vanish in that limit (otherwise there would be an overwhelming probability to be to the right of the barrier rather than to be in the metastable state), and since in this $z \to -\infty$ limit, the error function becomes -1, this means that A must be equal to B, so f goes to 0 as it should.

---

f. Taking the results together gives

$$P(x, v) \approx \begin{cases} \dfrac{\sqrt{U''(a)}}{2\pi kT} \exp\left[-\dfrac{\frac{1}{2}v^2 + U(x) - U(a)}{kT}\right] & \text{for } 0 < x < m \\ A\left[1 + \operatorname{erf}\left(\sqrt{\dfrac{\omega - \alpha}{2\alpha kT}}\,(v - \omega(x - b))\right)\right] \exp\left[-\dfrac{\frac{1}{2}v^2 + U(x) - U(b)}{kT}\right] & \\ & \text{for } m < x < c. \end{cases}$$

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

$$A = \frac{\sqrt{U''(a)}}{4\pi kT} \exp\left[-\frac{W}{kT}\right].$$

<u>Solution:</u>

At the point m, the argument of the error function has become large and positive, so we may replace it by 1. Matching then

$$\frac{\sqrt{U''(a)}}{2\pi kT} \exp\left[-\frac{\frac{1}{2}v^2 + U(m) - U(a)}{kT}\right]$$

and

$$A\left[1 + \operatorname{erf}\left(\sqrt{\frac{\omega - \alpha}{2\alpha kT}}\,(v - \omega(m - b))\right)\right] \exp\left[-\frac{\frac{1}{2}v^2 + U(m) - U(b)}{kT}\right]$$
$$\approx 2A \exp\left[-\frac{\frac{1}{2}v^2 + U(m) - U(b)}{kT}\right]$$

leads to

$$A = \frac{\sqrt{U''(a)}}{4\pi kT} \exp\left[-\frac{W}{kT}\right].$$

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g. Calculate finally the escape time:

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

Solution:

This requires just straightforward substitution of

$$P(b,v) = \frac{\sqrt{U''(a)}}{4\pi kT} \exp\left[\frac{-W}{kT}\right] \left[1 + \operatorname{erf}\left(\sqrt{\frac{\omega - \alpha}{2\alpha kT}}\, v)\right)\right] \exp\left[-\frac{v^2}{2kT}\right]$$

into

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

This gives

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

where we used the hint that $\int_{-\infty}^{\infty} dv\, v \operatorname{erf}(av) \exp(-bv^2) = [b\sqrt{1 + b/a^2}]^{-1}$.
