Advanced Statistical Physics – CORRECTION OF THE JANUARY 2024 EXAM

1 Bridge processes : conditioning in the Langevin equation

We consider the process described by the SDE

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = F(x(t)) + \sqrt{2D}\,\eta(t) \tag{1}$$

where $\eta(t)$ is a normalised Gaussian white noise, $\langle\eta(t)\rangle = 0$ and $\langle\eta(t)\eta(t')\rangle = \delta(t-t')$.

1/ Correlator of the Wiener process :

$$\big\langle W(t)W(t')\big\rangle = \int_0^t \mathrm{d}\tau \int_0^{t'} \mathrm{d}\tau'\,\delta(\tau-\tau') = \int_0^{\min(t,t')} \mathrm{d}\tau = \min\big(t,t'\big)$$

We now consider the Brownian bridge starting and ending at $x_0 = x_f = 0$

$$x(t) = W(t) - \frac{W(t_f)}{t_f}\,t \quad \text{for } t\in[0,t_f] \tag{2}$$

The correlator is

$$C_B(t,t') = \big\langle W(t)W(t')\big\rangle - \frac{t}{t_f}\,\big\langle W(t_f)W(t')\big\rangle - \frac{t'}{t_f}\,\big\langle W(t)W(t_f)\big\rangle + \frac{t\,t'}{t_f^2}\,\big\langle W(t_f)^2\big\rangle = \min\big(t,t'\big) - \frac{t\,t'}{t_f}$$

which vanishes for $t = 0 = t_f$ and $t' = 0 = t_f$, as it should.

2/ The question "*Give the probability for the process to arrive at x_f at time t_f, conditioned to start from x_0 (at time 0) and pass at x at time $t\in]0,t_f[$*" was not fantastic ! In principle, the answer is

$$P_{1|2}(x_f,t_f\,|\,x,t;x_0,0) \overset{\text{Markov}}{=} P_{1|1}(x_f,t_f\,|\,x,t) \equiv P_{t_f-t}(x_f|x) \tag{3}$$

(we used that the process is homogeneous).
It would have been more useful for the following to ask the probability to be at x_f at time t_f and at x at time t, conditioned on the initial value x_0 :

$$P_{2|1}(x_f,t_f;x,t\,|\,x_0,0) = P_{1|2}(x_f,t_f\,|\,x,t;x_0,0)P_{1|1}(x,t\,|\,x_0,0) \overset{\text{Markov}}{=} P_{t_f-t}(x_f|x)P_t(x|x_0) \tag{4}$$

Hence this is the joint distribution of $x(t_f)$ and $x(t)$, conditioned to start from x_0.
** Both answers are accepted **

3/ We introduce

$$\mathscr{P}_t(x) = \frac{P_{t_f-t}(x_f|x)P_t(x|x_0)}{P_{t_f}(x_f|x_0)} = \frac{\text{joint distribution of } x(t_f)\ \&\ x(t)}{\text{distribution of } x(t_f)} \tag{5}$$

Using the Chapman-Kolmogorov equation we get $\int \mathrm{d}x\,\mathscr{P}_t(x) = 1$. The function $\mathscr{P}_t(x)$ is the distribution of $x(t)$, conditioned on both the intial value $x(0) = x_0$ and the final value $x(t_f) = x_f$.

4/ For convenience, we write

$$\mathscr{P}_t(x) = \frac{Q(x,t)\,P(x,t)}{P_{t_f}(x_f|x_0)} \qquad \text{where } \begin{cases} P(x,t) \equiv P_t(x|x_0) \\ Q(x,t) \equiv P_{t_f-t}(x_f|x) \end{cases} \tag{6}$$

Using the appendix, we have

$$\partial_t P(x,t) = -\partial_x\big[F(x)P(x,t)\big] + D\partial_x^2 P(x,t) \qquad \text{(forward FPE)} \tag{7}$$

$$-\partial_t Q(x,t) = +F(x)\,\partial_x Q(x,t) + D\partial_x^2 Q(x,t) \qquad \text{(backward FPE).} \tag{8}$$

We deduce

$$\begin{aligned} \partial_t(PQ) &= -Q\partial_x\big[FP\big] - PF\partial_x\big[Q\big] + D\overbrace{\big\{Q\partial_x^2 P - P\partial_x^2 Q\big\}}^{=\partial_x^2(QP)-2P\partial_x^2 Q - 2(\partial_x Q)(\partial_x P)} \\ &= -\partial_x\big[FQP\big] - 2D\underbrace{\partial_x\big[(\partial_x Q)P\big]}_{=\partial_x\left[\left(\partial_x \ln Q\right)QP\right]} + D\,\partial_x^2\big[QP\big] \end{aligned}$$

We can interpret the two first terms as a drift term for the time dependent drift

$$\widetilde{F}(x,t) = F(x) + 2D\,\partial_x \ln Q(x,t) \tag{9}$$

i.e. the distribution obeys

$$\partial_t \mathscr{P}_t(x) = -\partial_x\big[\widetilde{F}(x,t)\mathscr{P}_t(x)\big] + D\,\partial_x^2\mathscr{P}_t(x) \tag{10}$$

whose solution describes the stochastic process constrained to reach x_f at time t_f.

5/ According to the appendix, this FPE corresponds to the SDE

$$\frac{\mathrm{d}x}{\mathrm{d}t} = F(x) + 2D\,\partial_x\big[\ln Q(x,t)\big] + \sqrt{2D}\,\eta(t) \qquad \text{for } t\in[0,t_f]\,. \tag{11}$$

(simulations of the figures correspond to this SDE for $F(x)=0$).

6/ Reminder of the **Ornstein-Uhlenbeck** process (linear force $F(x) = -\gamma\,x$). We integrate the SDE (1), leading to $x(t) = x_0\,\mathrm{e}^{-\gamma t} + \sqrt{2D}\int_0^t \mathrm{d}t_1\,\eta(t_1)\,\mathrm{e}^{-\gamma(t-t_1)}$. Averaging is easy (cf. lectures + tutorials) :

$$\langle x(t)\rangle = x_0\,\mathrm{e}^{-\gamma t} \tag{12}$$

$$\mathrm{Var}(x(t)) = \frac{D}{\gamma}\left(1-\mathrm{e}^{-2\gamma t}\right) \tag{13}$$

Using that the process is Gaussian, we deduce the distribution

$$P_t(x|x_0) = \sqrt{\frac{\gamma}{2\pi D(1-\mathrm{e}^{-2\gamma t})}}\,\exp\left\{-\frac{\gamma(x-x_0\,\mathrm{e}^{-\gamma t})^2}{2D(1-\mathrm{e}^{-2\gamma t})}\right\} \tag{14}$$

We use that $Q(x,t) = P_{t_f-t}(x_f|x)$, thus

$$2D\,\partial_x \ln Q(x,t) = \gamma\,\frac{x_f - x\,\mathrm{e}^{-2\gamma(t_f-t)}}{\sinh\gamma(t_f-t)} \tag{15}$$

i.e. the SDE for the constrained Ornstein-Uhlenbeck process is

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = -\gamma\,x(t) + \gamma\,\frac{x_f - x(t)\,\mathrm{e}^{-2\gamma(t_f-t)}}{\sinh\gamma(t_f-t)} + \sqrt{2D}\,\eta(t) \tag{16}$$

Some solutions of this SDE are represented on the figure.

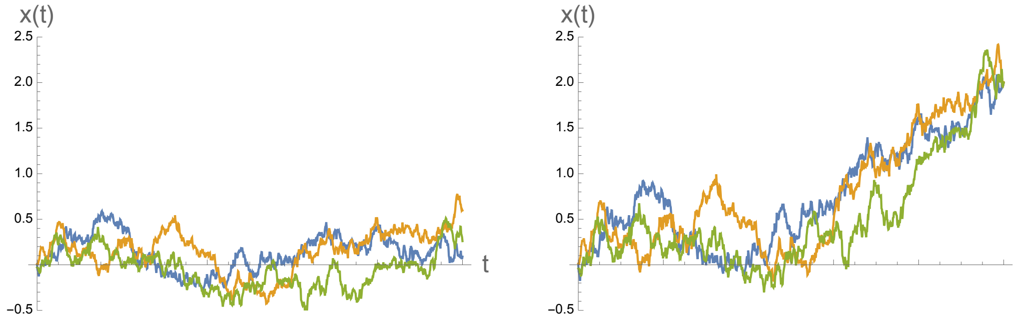


Figure 1: Left : *Unconstrained Ornstein-Uhlenbeck process* ($D = 1$, $\gamma = 3$). Right : *Ornstein-Uhlenbeck process constrained to reach* $x_f = 2$ *obtained by solving* (16).

7/ Consider now the free BM :

a) $Q(x,t) = \frac{1}{\sqrt{4\pi D(t_f - t)}} \exp\big\{ -(x_f - x)^2/4D(t_f - t)\big\}$. We get

$$2D\,\partial_x \ln Q(x,t) = (x_f - x)/(t_f - t)$$

We deduce the SDE for the constrained process

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{x_f - x(t)}{t_f - t} + \sqrt{2D}\,\eta(t) \tag{17}$$

which is indeed the $\gamma \to 0$ limit of the previous SDE.

b) As $t \to t_f^-$ the drift diverges, unless $x \to x_f$, being the reason why the constrained process eventually reaches x_f.

c) If we average the equation we find

$$\frac{\mathrm{d}\,\langle x(t)\rangle}{\mathrm{d}t} = \frac{x_f - \langle x(t)\rangle}{t_f - t} \qquad \Rightarrow \qquad \frac{\mathrm{d}\,\langle x(t)\rangle}{x_f - \langle x(t)\rangle} = \frac{\mathrm{d}t}{t_f - t} \tag{18}$$

leading to

$$\frac{x_f - \langle x(t)\rangle}{x_f - x_0} = 1 - \frac{t}{t_f} \qquad \Rightarrow \qquad \langle x(t)\rangle = x_0\left(1 - \frac{t}{t_f}\right) + x_f\,\frac{t}{t_f} \tag{19}$$

as expected.

d) We now study the variance from the constrained SDE. This time we use the modified FPE :

$$\frac{\partial}{\partial t}\left\langle x(t)^2\right\rangle = \int \mathrm{d}x\, x^2 \partial_t \mathscr{P}_t(x) = \int \mathrm{d}x\, x^2 \left(-\partial_x\big[\widetilde{F}\mathscr{P}_t(x)\big] + D\partial_x^2 \mathscr{P}_t(x)\right) \tag{20}$$

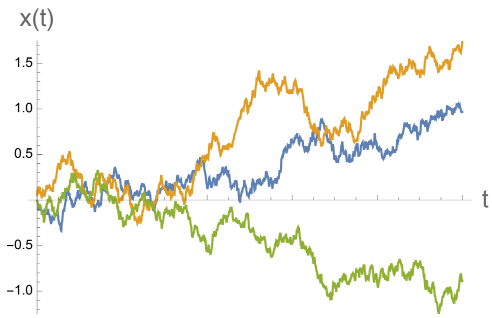
Integrations by parts give

$$\frac{\partial}{\partial t}\left\langle x(t)^2\right\rangle = 2\left\langle x(t)\widetilde{F}(x(t),t)\right\rangle + 2D \tag{21}$$

We apply the formula to the free BM and set $D = 1/2$ and $x_0 = x_f = 0$ for simplicity. We get

$$\frac{\partial}{\partial t}\left\langle x(t)^2\right\rangle = -2\frac{\left\langle x(t)^2\right\rangle}{t_f - t} + 1 \tag{22}$$

We check easily that $\left\langle x(t)^2\right\rangle = t(1 - t/t_f)$ is solution. This shows that the constrained SDE (and the constrained FPE) describes the Brownian bridge (2).



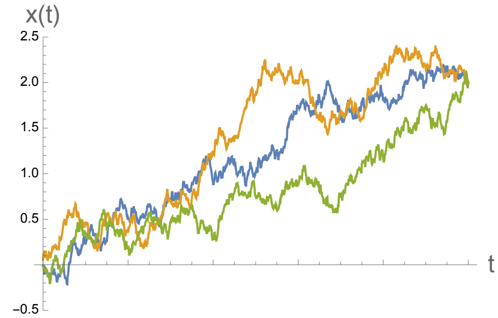


Figure 2: Left : *Unconstrained RW* ($D = 1/2$). Right : *RW constrained to reach* $x_f = 2$.

To learn more : S. N. Majumdar & H. Orland, "*Effective Langevin equations for constrained stochastic processes*", J. Stat. Mech. P06039 (2015).
This is also related to "conditioning and Doob h's transform".

2 Wetting transition

The substrate is at $z = 0$ and the fluid with density $n(z)$ above. The grand potential is

$$g_f[n(z)] = \int_0^\infty \mathrm{d}z \left[\frac{1}{2}B\left[\partial_z n(z)\right]^2 + W(n(z))\right] , \tag{23}$$

Additionally there is a surface term (interaction between the substrate and the fluid) :

$$g_s(n_s) = a_0 - a_1 \frac{n_s}{n_l - n_v} + \frac{1}{2}a_2 \frac{n_s^2}{(n_l - n_v)^2} + \dots \tag{24}$$

where $n_s = n(z = 0)$ is the density of the fluid at the solid surface.

1/ The form (23) is a Ginzburg-Landau functional and (24) is a Landau expansion.

2/ Field equation is

$$\frac{\delta g_f}{\delta n(z)} = -B\, n''(z) + W'(n(z)) = 0 \tag{25}$$

We denote $n_*(z)$ its solution.

3/ We identify a conserved quantity :

$$\mathcal{E} = \frac{B}{2}\left[n_*'(z)\right]^2 - W(n_*(z)) \tag{26}$$

(independent of z). At infinity the density is that of the vapor, $n_*(z \to \infty) = n_v$, hence $\mathcal{E} = -W(n_v) = 0$. As a result, the solution satisfies $n_*'(z) = \pm\sqrt{2\,W(n_*(z))/B}$. Note that the vapor density is the lowest, hence $n_*(z)$ decreases with z.

4/ We deduce

$$g_f[n_*] = B\int_0^\infty \mathrm{d}z\,\left[n_*'(z)\right]^2 = -B\int_0^\infty \mathrm{d}z\,\frac{\mathrm{d}n_*(z)}{\mathrm{d}z}\sqrt{\frac{2}{B}W(n_*(z))} = \sqrt{2B}\int_{n_v}^{n_s}\mathrm{d}n\sqrt{W(n)} \tag{27}$$

A. Thin-film profile.— We choose the simple form $W(n) = c\,(n - n_v)^2(n - n_l)^2$ for $n_v < n_s < n_l$.

5/ The field equation leads to the

$$n'(z) = -\sqrt{\frac{2c}{B}}\,(n_l - n)(n - n_v) \tag{28}$$

6/ Integration is easy. We write

$$\frac{\mathrm{d}n}{(n_l - n)(n - n_v)} = -\sqrt{\frac{2c}{B}}\,\mathrm{d}z \quad \text{i.e.} \quad \int_{n_s}^{n_*(z)} \mathrm{d}z \left(\frac{1}{n_l - n} + \frac{1}{n - n_v}\right) = -z/\xi \tag{29}$$

where $\xi = \sqrt{\frac{B}{2c}}(n_l - n_v)^{-1}$. We get

$$\frac{n_*(z) - n_v}{n_l - n_*(z)} = \underbrace{\frac{n_s - n_v}{n_l - n_s}}_{=\Delta}\ \mathrm{e}^{-z/\xi} \tag{30}$$

i.e

$$n_*(z) = \frac{n_v + n_l\,\Delta\,\mathrm{e}^{-z/\xi}}{1 + \Delta\,\mathrm{e}^{-z/\xi}} \tag{31}$$

We check that it decreases from $n_*(0) = n_s$ to $n_*(z \to \infty) = n_v$.

7/ If $n_s \gg n_v$, then $n_*(z) \simeq n_l \left[1 + \mathrm{e}^{(z-z_0)/\xi}\right]^{-1}$ where $z_0 = \xi \log\left(\frac{n_s}{n_l - n_s}\right)$. It is a step function where the drop of the density occurs around z_0, on a scale ξ. Hence z_0 can be interpreted as the height of the liquid/gas interface (this makes sense for $z_0 \gg \xi$).

B. Wetting transitions.— We define the vapor-liquid interfacial energy $\gamma = \int_{n_v}^{n_l} \mathrm{d}n\,\sqrt{2\,B\,W(n)}$.

8/ Consider a liquid/gas interface :

$$\gamma = g_f[n_*] = \sqrt{2B}\int_{n_v}^{n_l} \mathrm{d}n\sqrt{W(n)} = \sqrt{2Bc}\int_{n_v}^{n_l} \mathrm{d}n\,(n_l - n)(n - n_v)$$
$$= \sqrt{2Bc}\int_0^{n_l - n_v} \mathrm{d}x\,(n_l - n_v - x)\,x = \sqrt{2\,B\,c}\,(n_l - n_v)^3\left(\frac{1}{2} - \frac{1}{3}\right) = \frac{\sqrt{2\,B\,c}}{6}\,(n_l - n_v)^3$$

9/ In the general case where $n_s \neq n_l$,

$$g_f[n_*(z)] = \sqrt{2B}\int_{n_v}^{n_s} \mathrm{d}n\sqrt{W(n)} = \sqrt{2\,B\,c}\,(n_l - n_v)^3\left[\frac{1}{2}\left(\frac{n_s - n_v}{n_l - n_v}\right)^2 - \frac{1}{3}\left(\frac{n_s - n_v}{n_l - n_v}\right)^3\right] \tag{32}$$

10/ We set $\psi = \frac{n_l - n_s}{n_l - n_v}$. For $n_s \in [n_v, n_l]$ we have $\psi \in [0, 1]$ ($\psi = 1$ for the vapor and $\psi = 0$ for the liquid). We write

$$\frac{n_s - n_v}{n_l - n_v} = 1 - \psi \tag{33}$$

hence

$$g_f[n_*] = \gamma\left(1 - 3\psi^2 + 2\psi^3\right)\,. \tag{34}$$

11/ We write the surface contribution in terms of the new parameter

$$g_s(n_s) = g_s(n_l) + \left(a_1 - a_2\frac{n_l}{n_l - n_v}\right)\psi + \tfrac{1}{2}\,a_2\,\psi^2\,. \tag{35}$$

As a result, the total grand potential is

$$g_{tot}(n_s) = \gamma + g_s(n_l) + \left(a_1 - a_2 \frac{n_l}{n_l - n_v}\right)\psi + \left(\frac{1}{2}a_2 - 3\gamma\right)\psi^2 + 2\gamma\,\psi^3 \tag{36}$$

which has the form of a Landau expansion, in terms of the order parameter $\psi \in [0, 1]$.

12/ We introduce $\epsilon = (n_l - n_s)/n_s$. We find

$$\frac{1}{\psi} = \left(1 - \frac{n_v}{n_l}\right)\left(1 + \frac{1}{\epsilon}\right) \tag{37}$$

Above, we have introduced $e^{z_0/\xi} = \Delta = -1 + 1/\psi$. Hence there is a mapping between the order parameter ψ and the position of the interface z_0. In the liquid phase $\psi \to 0$ and the position of the interface diverges (wetting). In the vapor phase (no wetting) $\psi \lesssim 1$ and the position of the interface is $z_0 \lesssim 0$, density is low at the interface.

For $\psi \ll 1$ we have $\epsilon \simeq \psi \simeq e^{-z_0/\xi}$.

13/ Because $\epsilon \simeq \psi$ we find a similar expansion

$$g_{tot} = \gamma + g_s(n_l) + \alpha\,\epsilon + \beta\,\epsilon^2 + \theta\,\epsilon^3 + \ldots \tag{38}$$

(no need to compute the coefficients).

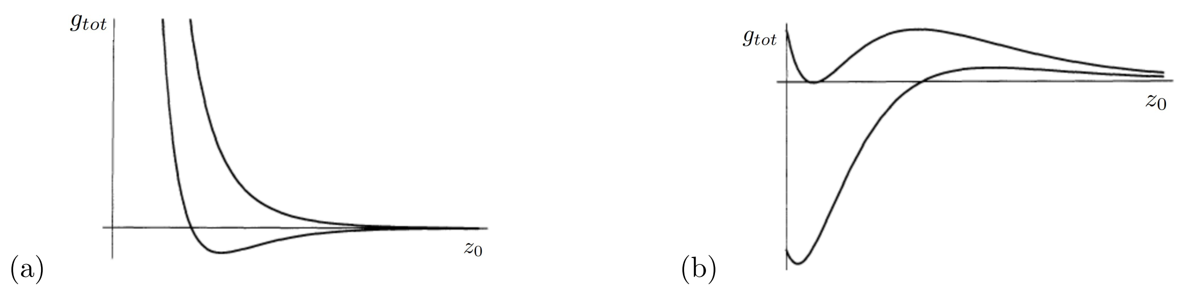


Figure 3: Plot of the system grand potential g_{tot} as a function of the parameter z_0 for two different temperatures for a given set of microscopic coefficients. (a) $\beta > 0$. (b) with another set of parameters with $\beta < 0$

14/ The figure shows the grand potential as a function of z_0 (instead of ϵ or ψ). In the figure (a), the top curve has a minimum for $z_0 = \infty$ (liquid, $n_s = n_l$) and the other curve has a minimumu for z_0 finite ($n_s < n_l$). This describes the transition between a wet substrate and non-wet substrate.

15/ Figure (a) : the transition looks second order as we go continuously from one situation to the other.

Figure (b) : clearly the minimum jumps discontinuously when one goes from one curve to the other. The transition is first order.

Apparently, wetting transition is more likely first order (coefficients corresponding to second scenario).