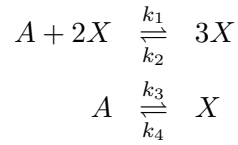# Fluctuating Hydrodynamics of Schlogl reaction-diffusion systems

Aleksandar Donev et. al.
Courant Institute

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The first Schlogl model [1, 2] is given by the reaction network

$$A + 2X \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad 3X$$

$$A \quad \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \quad X$$

where the concentration of A is kept constant externally. The system exhibits a bimodal distribution and metastability due to the cubic nonlinearity (which is quite artificial since tri-molecular reactions are essentially non-existent).

1 SDE

Let us consider now an out of equilibrium example without spatial dependence, i.e., focus on a single cell of volume V with the concentration of X denoted by $n_X = N_X/V$. The deterministic piece is assumed to be given by the law of mass action (LMA),

$$d\left(n_X\right) = -k_2 n_x^3 + k_1 n_X^2 n_A - k_4 n_x + k_3 n_A. \tag{1}$$

Note that it has been suggested to also include corrections to the deterministic terms of order V^{-1} (these come from the master equation containing terms like $N(N-1) = N^2 - N$ which are deterministically approximated with N^2) and use

$$\tilde{d}\left(n_X\right) = d\left(n_X\right) - V^{-1}\left(k_1 n_X n_A - 3n_x^2\right) \tag{2}$$

instead of d. This makes a big difference for the Schlogl model for small and moderate V (e.g., less than about 100 molecules per cell) but I do not think we want to do this since there is no really convincing (systematic) derivation of such corrections and I do not like the usual approaches to this (truncation ala Kramers-Moyal expansion or truncations of expansions of the generator in powers of V^{-1} since such truncation ruins long-term properties). It may however be that inclusion of such terms is in fact important to get the right physics (not clear what the right physics is however!) over a broad range of time scales.

1.1 Chemical Langevin

In the chemical Langevin equation (CLE) [3] the noise amplitude is

$$D_G\left(n_X\right) = \frac{1}{2}\left(k_1 n_X^2 n_A + k_3 n_A + k_2 n_x^3 + k_4 n_x\right), \tag{3}$$

1

and the noise is Ito, giving the SDE (in the physics notation),

$$\frac{dn_X}{dt} = d\left(n_X\right) + \sqrt{2V^{-1}D_G\left(n_X\right)}\,\mathcal{W}(t), \tag{4}$$

where $\mathcal{W}(t)$ denotes white noise. This equation can be derived in several ways (e.g., by truncation of the Kramers-Moyal expansion at the second level) of various level of rigor and applicability but formally it be seen as a central-limit theorem for the fluctuations in the limit $V \to \infty$.

1.2 Hanggi-Grabert

We believe that a better model is provided by an equation first proposed in [1], which takes the noise amplitude to be

$$D_H\left(n_X\right) = V^{-1}\frac{\left(k_1 n_X^2 n_A + k_3 n_A\right) - \left(k_2 n_x^3 + k_4 n_x\right)}{\ln\left(k_1 n_X^2 n_A + k_3 n_A\right) - \ln\left(k_2 n_x^3 + k_4 n_x\right)}, \tag{5}$$

and the noise interpretation to be the kinetic one, which can be written in the Ito sense as

$$\frac{dn_X}{dt} = d\left(n_X\right) + \sqrt{2V^{-1}D_H\left(n_X\right)} \diamond \mathcal{W}(t) = d\left(n_X\right) + \sqrt{2V^{-1}D_H\left(n_X\right)}\,\mathcal{W}(t) + V^{-1}\frac{dD_H\left(n_X\right)}{dn_X}. \tag{6}$$

A related from is provided by the Oettinger and Grmela [4] based on the GENERIC formalism [5],

$$\frac{dn_X}{dt} = d\left(n_X\right) + \sqrt{2V^{-1}\left(D_1\left(n_X\right) + D_2\left(n_X\right)\right)} \diamond \mathcal{W}(t), \tag{7}$$

where there is a now a noise term associated with each reaction,

$$D_1\left(n_X\right) = \frac{k_1 n_X^2 n_A - k_2 n_x^3}{\ln\left(k_1 n_X^2 n_A\right) - \ln\left(k_2 n_x^3\right)}, \quad \text{and} \quad D_2\left(n_X\right) = \frac{k_3 n_A - k_4 n_x}{\ln\left(k_3 n_A\right) - \ln\left(k_4 n_x\right)}.$$

The form of these diffusion coefficients is strange but if one uses detailed balance to relate the forward and backward rates one can write the *logarithmic mean*

$$\Lambda\left(x,y\right) = \frac{x - y}{\left(\ln x - \ln y\right)} = \int_0^1 x^s y^{1-s} ds \geq 0$$

using chemical potentials as

$$\frac{e^{\mu_r} - e^{\mu_p}}{\mu_r - \mu_p} = \int_0^1 \exp\left(\gamma\mu_r + (1-\gamma)\mu_p\right) d\gamma, \tag{8}$$

which now looks like a thermodynamic entropy factor (volume in phase space), with γ interpreted as some sort of reaction coordinate. Here μ_r is the sum of chemical potentials of the reactants and μ_p of the products. We don't yet have an idea however where this particular thermodynamic weighting comes from physically. In this form it becomes obvious how to generalize this to general reaction networks in multispecies networks.

1.2.1 Fluctuation-Dissipation Balance

To leading order, the equilibrium distribution corresponding to the Schlogl model can be explicitly computed from the ME to be

$$P_{\text{eq}}(n_x) \approx C \, \exp\left[V \int_{s=0}^{n_x} \ln\left(\frac{\lambda_0(s)}{\mu_0(s)}\right) ds \right] \text{ with normalization } \int_{x=0}^{\infty} P_{\text{eq}}(x) dx = 1, \qquad (9)$$

where the rates are

$$\begin{aligned} \lambda_0(n_X) &= k_1 n_X^2 n_A + k_3 n_A \\ \mu_0(n_X) &= k_2 x^3 + k_4 n_x. \end{aligned}$$

If we now want to construct a Fokker-Planck equation that is in detailed balance (zero flux) with respect to (9), the FPE has to have the form,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial n_X}\left[D\left(-\frac{d}{D}P + \frac{\partial P}{\partial n_X} \right) \right] = 0, \qquad (10)$$

where the thermodynamic flux inside the parenthesis vanishes at steady state, giving the noise covariance

$$D = P_{\text{eq}}\left(\frac{\partial P_{\text{eq}}}{\partial n_X}\right)^{-1} d.$$

Taking the leading-order approximation (9) and *assuming* that the drift d has the form of the deterministic law of mass action (it is important to note that this assumption is not justified, but going beyond it requires a deep understanding of nonlinear effects and renormalization [6] which is beyond the present scope), we get (5),

$$D = V^{-1} \frac{\lambda_0(n_X) - \mu_0(n_X)}{\ln\left(\frac{\lambda_0(n_X)}{\mu_0(n_X)}\right)}.$$

One can include $O(V^{-1})$ corrections in (9), see equation (16) in Ref. [7], and for the Schlogl model keeping only one of the next-order correction terms (but this may be just a fluke and *not* generic!?!) seems to give a great approximation to the true steady-state distribution as predicted from the ME,

$$P_{\text{eq}}(n_x) \approx C \, \exp\left[V \int_{s=0}^{n_X} \ln\left(\frac{\lambda_0(s)}{\mu_0(s)}\right) ds - \frac{1}{2}\ln\left(\lambda_0(n_X)\mu_0(n_X)\right) \right], \qquad (11)$$

giving

$$P_{\text{eq}}^{-1}\frac{\partial P_{\text{eq}}}{\partial n_X} = V \ln\left(\frac{\lambda_0(n_X)}{\mu_0(n_X)}\right) - \frac{1}{2}\frac{\lambda_0'(n_X)}{\lambda_0(n_X)} - \frac{1}{2}\frac{\mu_0'(n_X)}{\mu_0(n_X)}.$$

At this point, however, one should also include terms of $O\left(V^{-1}\right)$ in d. One approach would be to try to match the short-time dynamics in addition to P_{eq}, and thus fix both D and d – this should probably be done by expanding the generator in powers as done in EVE's notes. Note however that terms of $O\left(V^{-1}\right)$ do not naturally fit a continuum (SPDE) Langevin description, at least if one wants to use white-in-space noise.

1.3 SPDE: Fluctuating Hydrodynamics

With diffusion we get the reaction-diffusion SPDE for the local concentration $dn_X(\boldsymbol{r},t)$,

$$
\begin{aligned}
\partial_t n_X(\boldsymbol{r},t) &= d\left(n_X(\boldsymbol{r},t)\right) + \sqrt{2\Delta A^{-1}D_H\left(n_X(\boldsymbol{r},t)\right)} \diamond \mathcal{W}(\boldsymbol{r},t) + \\
&+ \chi\boldsymbol{\nabla}^2 n_X(\boldsymbol{r},t) + \boldsymbol{\nabla}\cdot\left(\sqrt{2\Delta A^{-1}\chi n_X(\boldsymbol{r},t)}\,\mathcal{Z}(\boldsymbol{r},t)\right),
\end{aligned} \tag{12}
$$

where $\mathcal{W}(\boldsymbol{r},t)$ and $\mathcal{Z}(\boldsymbol{r},t)$ are independent spatio-temporal white-noise processes. Here ΔA is an additional scaling that depends on dimensionality: in 1D we interpret ΔA as the surface cross-section of the one-dimensional channel, in 2D we interpret ΔA as the thickness in the third direction, and in 3D we interpret ΔA as unity. Here χ is the diffusion coefficient, assumed constant. Note that this SPDE is only defined formally as it does not really make sense mathematically. It only becomes sensible after discretization or regularization of the noise at molecular scales. In this way we see that for the discretized noise to scale like ΔV^{-1}, where ΔV is the volume of a finite-volume cell, we need to add an additional scaling in the noise in the SPDE corresponding to the cross-section so that $\Delta x \Delta A = \Delta V$.

We can similarly write an SPDE corresponding to the CLE,

$$
\begin{aligned}
\partial_t n_X(\boldsymbol{r},t) &= d\left(n_X(\boldsymbol{r},t)\right) + \sqrt{2\Delta A^{-1}D_G\left(n_X(\boldsymbol{r},t)\right)}\,\mathcal{W}(\boldsymbol{r},t) + \\
&+ \chi\boldsymbol{\nabla}^2 n_X(\boldsymbol{r},t) + \boldsymbol{\nabla}\cdot\left(\sqrt{2\Delta A^{-1}\chi n_X(\boldsymbol{r},t)}\,\mathcal{Z}(\boldsymbol{r},t)\right),
\end{aligned} \tag{13}
$$

which we will compare to the above SPDE. One can also compare to Master Equation descriptions but those are computationally infeasible for large numbers of molecules...

As explained in [8] (using ME rather than Langevin), for certain choices of the parameters, the above reaction-diffusion dynamics exhibits an interesting switch in the relative height of the two peaks in the bimodal distribution for a finite system in one dimension and intermediate values of χ (such that diffusion cannot mix the whole system over a typical reaction time). The transition states between the spatially-uniform metastable minima exhibit diffusive propagating fronts and are different from classical nucleation.

1.4 Linearized Fluctuating Hydrodynamics

For the case of a monomodal well-localized distribution, the fluctuations will be essentially Gaussian and a simple linearized theory is applicable and leads to some illustrative observations. Let us now consider a Schlögl reactive system that also has diffusion, and denote the vector of n_X's with $\boldsymbol{n}$ (dropping the subscript X for simplicity of notation). If we linearize the hydrodynamic SPDE around a constant state $\boldsymbol{n} = \bar{\boldsymbol{n}} + \delta\boldsymbol{n}$ we get

$$
\partial_t\left(\delta\boldsymbol{n}\right) = \left[\left(\boldsymbol{\nu}\cdot\frac{\partial d\left(\bar{\boldsymbol{n}}\right)}{\partial\boldsymbol{n}}\right)\delta\boldsymbol{n} + \boldsymbol{\nu}\sqrt{2\Delta A^{-1}D\left(\bar{\boldsymbol{n}}\right)}\check{\mathcal{W}}\right] + \left[\chi\boldsymbol{\nabla}^2\left(\delta\boldsymbol{n}\right) + \boldsymbol{\nabla}\cdot\left(\sqrt{2\Delta A^{-1}\chi\boldsymbol{n}_0}\,\mathcal{Z}\right)\right],
$$

where now the noise is additive so the stochastic interpretation does not matter. Note that near a stable simple equilibrium it does not matter which choice of the S(P)DE we use, since

$$
D_G\left(n_0\right) = D_H\left(n_0\right)
$$

because $d\left(n_0\right) = 0$.

1.4.1 Static Structure Factor

Assume that one the dominant peak is at $n_X = \bar{n}$, and linearize the equations around the peak, and then take the Fourier transform, to get an Ornstein-Uhlenbeck equation for each Fourier mode,

$$\partial_t \hat{n}_k = -\left(-d_0' + \chi k^2\right) \hat{n}_k + \sqrt{2D_0}\,\hat{\mathcal{W}}_k(t) + ik\,\sqrt{2\chi n_0}\,\hat{\mathcal{Z}}_k(t),$$

where $D_0 = D(\bar{n})$ and $d_0' = d'(\bar{n})$ is the slope of $d(n_X)$ at $n_X = \bar{n}$ ($d_0' < 0$ for stable states). This gives the equilibrium spectrum, or static structure factor (note that this has factors of inverse volume taken out already in the definition) [9],

$$S(k) = \frac{D_0 + \bar{n}\chi k^2}{-d_0' + \chi\,k^2} \rightarrow \begin{cases} \bar{n} & \text{for diffusion-dominated} \\ -D_0/d_0' & \text{for reaction-dominated} \end{cases}. \tag{14}$$

Note that in order to take discretization artifacts into account one should replace k^2 by $\tilde{k}^2$, the Fourier symbol of the three-point discrete Laplacian,

$$\tilde{k} = \frac{\exp\left(ik\Delta x/2\right) - \exp\left(-ik\Delta x/2\right)}{i\Delta x} = \frac{\sin\left(k\Delta x/2\right)}{(\Delta x/2)}.$$

Note that it is not hard to also compute dynamic correlation function functions (dynamic structure factor).

An interesting observation is that in the case of a simple monomodal distribution, i.e., when $d(n) = -(n^2 + \alpha^2)(n - \bar{n})$ has a single real root $\bar{n}$, we get that $D_0/\bar{n} = -d_0' = \bar{n}^2 + \alpha^2$, which implies that $S(k) = \bar{n}$ is flat independent of k. This is exactly the same spectrum as we get if there is no chemical reactions and there is only diffusion; it corresponds to a Poisson distribution for the number of particles. This means that in the simple monomodal case there is nothing interesting happening. But the linearized theory presented here also applies even in the more interesting bimodal case if one looks at fluctuations around one of the two peaks.

We can get the variance in one dimension by integrating the spectrum, in one dimension,

$$\sigma^2 = (2\pi)^{-1}\,\Delta A^{-1} \int_{-\pi/\Delta x}^{\pi/\Delta x} S(k)dk = \frac{\bar{n}}{\Delta V} + \frac{D_0\lambda^2 - \chi\bar{n}}{\pi\lambda\Delta A\chi}\arctan\left(\frac{\pi\lambda}{\Delta x}\right),$$

where $\lambda = \sqrt{-\chi/d_0'}$ is a correlation length scale. Note that as $\lambda \to \infty$ (approaching the bifurcation point $d_0' = 0$), we have $\sigma^2 \to D_0\lambda/(2\chi\Delta A) \to \infty$. This means nonlinearities and finite-size effects will be crucial to make the variance bounded.

The result (14) gives us several important conclusions. Firstly, note that $S(k = 0)$ is simply the variance of the *average* concentration (density) multiplied by the total volume of the system. If there is no reaction, than $S(k = 0) = 0$ since the average is conserved by diffusion. But when there is a reaction, independent of the value of the diffusion coefficient, $S(0) = -D_0/d_0'$. This means that the variance of the average concentration is *unaffected* by diffusion, and only depends on the total volume of the system V and not on how it is divided into cells, which is physically sensible. The system will be well-mixed at a length-scale k^{-1} if in the numerator χk^2 dominates, $k^2 \gg -d_0'/\chi$. This means that if

$$\left(\frac{\pi}{\Delta x}\right)^2 \gg -\frac{d_0'}{\chi}, \quad \text{equivalently, if} \quad \chi \gg -\frac{d_0'\Delta x^2}{\pi^2} \tag{15}$$

we can consider each cell to be "well-mixed" and it is not necessary to further increase the resolution. The whole system will be well mixed if

$$\left(\frac{2\pi}{L}\right)^2 \gg -\frac{d_0'}{\chi}, \quad \text{equivalently, if} \quad \chi \gg -\frac{d_0'L^2}{4\pi^2}. \tag{16}$$

Another thing we learn is that if $\chi \to \infty$, $S(k > 0) \to \bar{n}$, which means that mixing entropy fluctuations completely dominate at all k's except for $k = 0$ where chemistry is the only actor. In this case the local fluctuations of n_X will be the same as if there were no reactions; they will be the usual Poisson-like (in this theory Gaussian) density fluctuations. In an SSA model this can be simulated by, after every reactive step, distributing the particles randomly uniformly through the system. If $\chi \to 0$, then we get that $S(k) = -D_0/d_0'$ for all k. This is because each cell fluctuates independently of all others, so the field looks like white noise in space. The variance of the local concentration will be $-D_0/(d_0'\Delta V)$ and of the average concentration over the whole system it is $-D_0/(d_0'V)$.

A special case to consider is the case when we omit the stochastic mass flux due to diffusion and drop the stochastic forcing term $\boldsymbol{\nabla} \cdot \left(\sqrt{2\Delta A^{-1}\chi \boldsymbol{n}_0}\, \mathcal{Z} \right)$. In this case, we get

$$ S(k) = \frac{D_0}{-d_0' + \chi\, k^2}. $$

Now, in the limit $\chi \to \infty$ we get $S(k > 0) \to 0$ which means $S(k)$ is a delta function; this means that the concentration is constant through the system (no Poisson fluctuations any more) and only the average concentration fluctuations due to reactions. In this case there should be no difference between the distribution of the local and the average concentrations, they should both be Gaussians with mean $\bar{n}$ and variance $-D_0/(d_0'V)$. Note that the condition for this well-mixed limit to apply is exactly the same as (16), since (16) implies that $S(k) \le S(k_{\min} = 2\pi/L) \ll -D_0/d_0'$ for all nonzero k. In SSA this sort of well-mixed limit can be simulated by equally distributing the particles among the cells after every reactive event.

1.4.2 Static correlations

From the discrete spectrum one can obtain the spatial correlation function by an inverse Fourier transform. In the continuum setting, Maple gives

$$ C(L) = \langle \delta x(0)\delta x(L) \rangle = \bar{n}\delta\left(L\right) + \frac{(\bar{n} + D_0/d_0')}{2\lambda} \exp\left(-\frac{L}{\lambda}\right) \text{ for } L > 0, $$

where $\lambda = \sqrt{-\chi/d_0'}$ is a correlation length scale. Note that in three dimensions one needs to perform the inverse Fourier transform differently, assuming isotropy,

$$ C(r) = \bar{n}\boldsymbol{\delta}\left(r\right) + (2\pi)^{-3} \int_{k=0}^{\infty} 4\pi k^2 \operatorname{sinc}\left(kr\right)\left[S(k) - \bar{n}\right] dk = \bar{n}\boldsymbol{\delta}\left(r\right) + \frac{(\bar{n}d_0' + D_0)}{4\pi\chi r} \exp\left(-\frac{r}{\lambda}\right). $$

In three dimensions we get a variance $\sigma^2 \sim D_0/(\chi\Delta x)$ as $\lambda \to \infty$, which seems like it would be smaller so nonlinear effects would be weaker (consistent with other cases such as giant fluctuations).

We can directly compare this to the theory in Ref. [10], taking into account that those authors work in three dimensions. First, we note that we can write

$$ \bar{n} + \frac{D_0}{d_0'} = \frac{2J}{d_0'} = \frac{2\left(k_1 a\bar{n}^2 - k_2\bar{n}^3\right)}{d_0'}, $$

where $J = (da/dt)_0$ is the steady-state influx of a required to keep the reaction out of equilibrium. At true thermodynamic equilibrium both reactions are balanced *individually*, and $J = 0$, giving purely local correlations and a flat spectrum $S(k) = \bar{n}$, as expected. We can therefore write the formula for the correlation function in the form

$$ C(L) = \bar{n}\delta\left(L\right) + \frac{\lambda J}{(\lambda^2 d_0')} \exp\left(-\frac{\bar{n}}{\lambda}\right) = \bar{n}\delta\left(L\right) - \frac{\lambda J}{\chi} \exp\left(-\frac{L}{\lambda}\right), $$

which is identical to (3.13) in Ref. [10] in three dimensions,

$$C(r) = \bar{n}\boldsymbol{\delta}(r) + \frac{J}{4\pi\chi r}\exp\left(-\frac{r}{\lambda}\right).$$

As explained in Ref. [10], the physical meaning of the correlation length λ is the typical distance a molecule X diffuses between reactions.

1.5 SSA

Let us now consider the equilibrium distribution of the Master Equation description of the Schlogl model and the associated SSA algorithm. In this simple 1D example balance (constant probability flux) implies detailed balance (zero probability flux), and the equilibrium distribution of the number of X molecules N is given by [see Ref. ([2]) for details],

$$p(N) = p(0)\prod_{i=1}^{n}\frac{\lambda(i-1)}{\mu(i)} \text{ with normalization } \sum_{k=0}^{\infty}p(k) = 1, \tag{17}$$

where the transition rates from $N \to N+1$ and $N \to N-1$ are, respectively,

$$\begin{aligned}
\lambda(N;V) &= \frac{N_A k_1 N(N-1)}{V} + N_A k_3 V \approx \frac{N_A k_1 N^2}{V} + N_A k_3 V \\
\mu(N;V) &= \frac{k_2 N(N-1)(N-2)}{V^2} + N k_4 \approx \frac{k_2 N^3}{V^2} + N k_4.
\end{aligned}$$

Now, it is not hard to see that splitting the cell into smaller cells with an equal number of molecules per cell will *not* change the transition rates and thus has no effect on the steady state distribution for large-enough volumes. Consider there being N molecules of X in a system with volume V split into M cells. Assume that diffusion is so fast that it uniformly spreads the molecules among the cells, so that each cell has $N' = N/M$ molecules. The effective transition from N to $N+1$ molecules here will be that any one of the cells increments its local counter by one, giving an effective rate

$$\lambda'(N) = M\lambda\left(\frac{N}{M};\frac{V}{M}\right) = \lambda(N), \tag{18}$$

which is exactly the same as if there were only one well-mixed cell. The same goes for $\mu'(N) = \mu(N)$. So it does not matter how one splits the domain into cells. SSA simulations confirm this.

1.6 Infinite Diffusion

We expect that as the diffusion coefficient becomes infinite, the whole system becomes well-mixed and acts as one big cell. This is true for Ito equations but it is not true for kinetic SDEs as I explain now.

Consider a system of volume V divided into M cells. Assume that diffusion is infinite and its action is to make the concentrations in all M cells equal to the average concentration (this is not quite true since there will be additional Poisson-like fluctuations due to the random jumping process among the cells, this is a secondary effect). So what we will be doing is effectively solving a system of M identical SDEs, each driven by its own independent Wiener process. For Ito noise, this means that the average follows the same SDE but with a noise whose variance is now M times

smaller. So for CLE (4) we get for the average concentration

$$\frac{d\bar{n}}{dt} = \frac{1}{M}\sum_{i=1}^{M} d\left(n_i \approx \bar{n}\right) + \frac{1}{M}\sum_{i=1}^{M}\sqrt{2\frac{M}{V}D_G\left(n_i \approx \bar{n}\right)}\,\mathcal{W}_i(t),$$

$$\rightarrow d\left(\bar{n}\right) + \sqrt{2V^{-1}D_G\left(\bar{n}\right)}\,\mathcal{W}(t)$$

the same equation as if the system were not divided into cells. But for the Hanggi equation (6) we get

$$\frac{d\bar{n}}{dt} \rightarrow d\left(\bar{n}\right) + \sqrt{2V^{-1}D_H\left(\bar{n}\right)}\,\mathcal{W}(t) + \frac{M}{V}D'_H\left(\bar{n}\right)$$

which now has a different stochastic drift term and leads to a different equilibrium distribution from what one would get if there were only cell of volume V. I confirmed numerically by hacking the drift term in the code to divide by it by M that it is this enlargement of the thermal drift term by a factor of M that is the source of the problem.

Note that this only matters in more exotic cases where the distribution is not a well-peaked Gaussian, such as for example near the bifurcation point of the Schlogl model where the distribution becomes a very smeared "peak". Near bifurcation changing the drift term matters a lot, and omitting it gives a completely wrong answer, e.g., the distribution is not even peaked around the unstable point. Using the CLE gives also a very wrong distribution so it is not an improvement. In fact, near bifurcation, for the parameters we are using in the numerical simulations, $D_G(n) \approx D_H(n)$ for $n > 0.4$ so that in fact the CLE is essentially the same as the Hanggi equation but with the noise being Ito and not kinetic. From this perspective, for our purposes, the main difference between (4) and (6) is not so much the form of the noise amplitude but rather the noise interpretation.

What to do about this? What we want is that

$$\frac{1}{M}\sum_{i=1}^{M}\sqrt{2\frac{M}{V}D_H\left(n_i\right)} \diamond \mathcal{W}_i(t) \rightarrow \sqrt{2V^{-1}D_H\left(\bar{n}\right)} \diamond \mathcal{W}(t)$$

which does not happen in the present formulation. Mathematically, my feeling is that the issue here has to do with the fact that multiplicative noise terms with these types of stochastic drift terms arise in the process of taking some overdamped limit, so there is in them a hidden time scale that has been assumed small. When we now also take diffusion to infinity it becomes an issue of a double limit and the order matters. If diffusion really is the fastest process then the stochastic drift term amplitude should be $1/V$ and not $1/\Delta V$. It appears this is intimately connected to the fact that the Hanggi equation cannot apply at short times.

2 Results

We set $n_A = n_B = 1$ in these runs.

2.1 Monomodal Distributions

Here we study the case when there is only a single equilibrium state (only one root of the cubic polynomial d) at $n_X = \bar{n} = 1$. We consider a system of length $L = 4$, total volume $V = 1000$, split into different number of cells $M = 1, 2, 4, 8$.

2.1.1 Stable states (Gaussian)

In this case we set

$$k_1 = k_2 = k_3 = k_4 = 1,$$

which means that the roots of d are $\pm i$ and 1, and we have $D_0 = 2$ and $d_0' = -2$; recall that for the monomodal case $S(k) = 1$ constant for any χ and k. If $\Delta x = 1$ ($M = 4$, $\Delta V = 250$) the condition for a well-mixed cell is $\chi \gg 0.2$. For the whole system to be well mixed we require $\chi \gg 0.8$. In our simulations we use $\chi = 15$ which should be more then large-enough to ensure the whole system is well-mixed. For comparison we also do a small $\chi = 0.1$. As explained above, when stochastic mass fluxes are included there is no difference between different χ's because the static structure factor (static distribution) is independent of χ. When stochastic mass fluxes are omitted there is however a difference; for large χ there should be no difference between local and average concentrations (as seen in the figure below), and for small χ there should be a difference but the average concentration should still have the same Gaussian distribution with variance $1/V$, as seen in the figure.
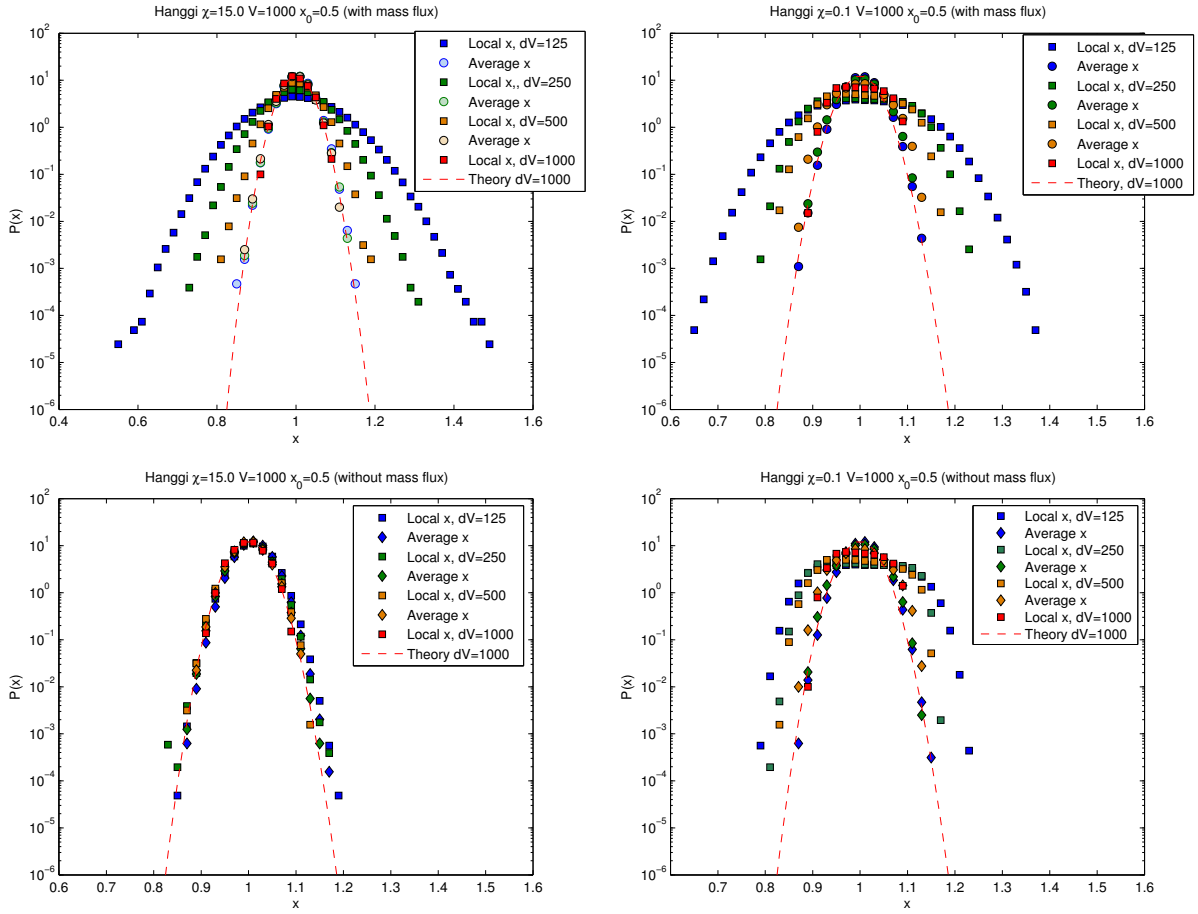

Figure 1: Distributions for simple Gaussian case for the local concentration (in each cell) and for the average concentration. Top row includes stochastic mass fluxes, bottom row does not. Left column is for fast diffusion $\chi = 15$, right column is for slow diffusion, $\chi = 0.1$.

2.1.2 Critical states (bifurcation)

In this case we set $k_1 = 3$, $k_2 = k_3 = 1$ and $k_4 = 3$ giving the triple root $x = 1$. In this case $D_0 = 4$ and $d'_0 = 0$, so the linearized theory does not really apply since it predicts a diverging spectrum at all and we expect completely non-Gaussian behavior with nonlinearities and finite-size effects becoming very important.

Now we see that the average concentration follows a different distribution depending on the number of cells, which indicates non-universal behavior depending on the grid choice. When there is no stochastic mass flux the local and global distributions overlap, since diffusion just quickly equalizes the concentration across the sample, but they are still different for different grid choices. Interestingly, for larger M (more grid cells) the distribution peaks around a value that is different from $x = 1$ (looks like 1.4 or so)? This seems wrong and makes no sense – it is also in disagreement with SSA results in which after each step we redistribute the particles uniformly among the M cells [**Donev: UNFINISHED...conjecture at present...**]. The explanation for this failure of the Langevin descri is in Section 1.6.
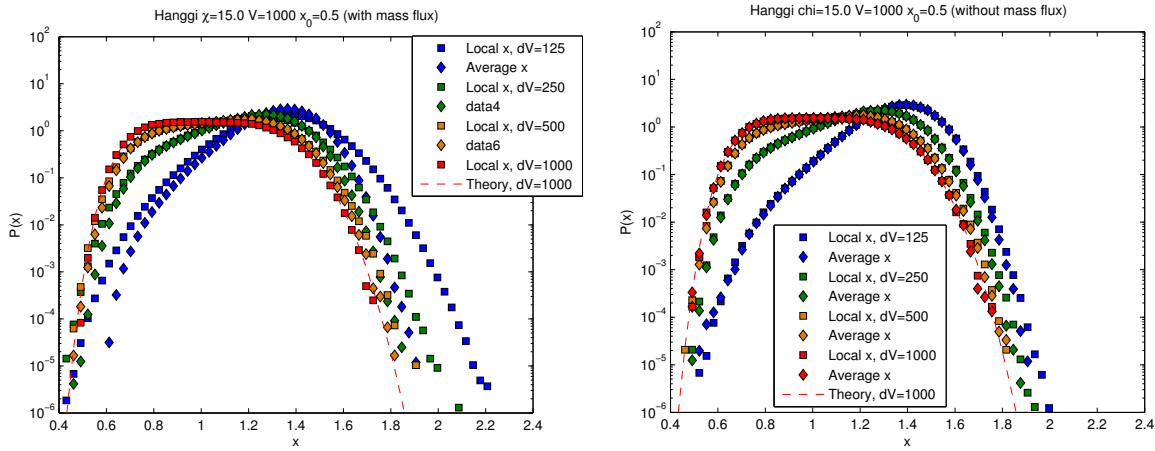

Figure 2: Distributions for simple Gaussian case for the local concentration (in each cell) and for the average concentration for fast diffusion $\chi = 15$. Left panel includes stochastic mass fluxes, right panel does not.

2.2 Bimodal Distributions

In this case we set $k_1 = 3.1$, $k_2 = 1$, $k_2 = 0.8$ and $k_4 = 2.9$ giving three roots: first peak at $\bar{n} = 0.5$, second peak at $\bar{n} = 1.6$ and saddle point at $n_X = 1$. If we are looking at small fluctuations around the first peak at $\bar{n} = 0.5$ than we can use the linearized theory with $D_0 = 1.575$ and $d'_0 = -0.55$. The condition for having a well-mixed system of length $L = 4$ is now $\chi \gg 0.25$. If we are looking at small fluctuations around the second peak at $\bar{n} = 1.6$ than we can use the linearized theory with $D_0 = 8.74$ and $d'_0 = -0.66$. The condition for having a well-mixed system of length $L = 4$ is similar, $\chi \gg 0.3$. Numerically we observe that we need $\chi > 10$ to really get a fully mixed system.

The interesting observation, however, is that even in the supposed well-mixed limit we see an effect of how exactly the system is divided into cells, i.e., we see an effect of M and ΔV rather than a result that only depends on $M\Delta V$...[**figures not completed but statement has been confirmed**]

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