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A novel Eulerian model based on central moments to simulate age and reactivity continua interacting with mixing processes

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S1 Technical description of validation models

Here the numerical models that were used as independent means to validate the formulations and simulations using central moments are described.

S1.1 Application 1: Particle-tracking model

The simulated dynamics in the particle tracking model will correspond to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + P + R \tag{S1}$$

and also account for the aging of the particles. The model simulates diffusion as discrete jumps, conceptually following Crank (1956), whereby $D = 0.5 f \delta_x^2$. The spacing of grid cells matches the jumping distance (δ_x), and advection is not included, allowing for a spatially non-continuous Lagrangian model formulation that is only designed to validate the model based on centralized moments in the first application. The term P accounts for the production of new material with an age of zero, and the last term denotes a consumption reaction, which is implemented as $R = -kC$.

For all particles $i \in [1, n]$, a vector $\vec{C}$ stores the locations of particles, which are numbers corresponding to cell indices in a 1-D grid. Another vector $\vec{\chi}$ stores the ages of the particles. The boundary conditions, which are contained in the first and last cell of the one-dimensional domain, are defined as populations of particles with ages. For instance, we chose arbitrarily

$$\vec{\chi_L} = [\chi_1, \chi_2, \chi_3, \ldots, \chi_{2000}], \quad \text{where} \begin{cases} \chi_i \sim \mathcal{N}(0, 2^2) & \text{for the first 1000 elements,} \\ \chi_i \sim \mathcal{N}(-0.5, 1^2) & \text{for the next 500 elements,} \\ \chi_i \sim \mathcal{N}(0.5, 1^2) & \text{for the next 500 elements,} \end{cases} \tag{S2}$$

to represent the left boundary condition, which, for this example, means that 1000 samples were taken from a normal distribution of $\mu = 0$ and $\sigma = 2$, 500 samples from a normal distribution with $\mu = -0.5$ and $\sigma = 1$, and 500 samples from a normal distribution with $\mu = 0.5$ and $\sigma = 1$. The right boundary condition was set to

$$\vec{\chi_R} = [\chi_1, \chi_2, \chi_3, \ldots, \chi_{4000}], \quad \text{where} \begin{cases} \chi_i \sim \mathcal{N}(1, 0.2^2) & \text{for all 4000 elements.} \end{cases} \tag{S3}$$

Thus, 4000 samples from a normal distribution were taken with $\mu = 1$ and $\sigma = 0.2$. These populations at the boundaries do not change during simulations.

As initial conditions, it is assumed that all interior cells of the grid have the population of the left boundary condition

$$\vec{\chi}_0 = \left(\underbrace{\vec{\chi}_L}_{(m-1)\text{ times}}, \vec{\chi}_R \right) \tag{S4}$$

whereby subscript '0' indicates initial conditions, and m is the number of grid cells. Note that the first and last cell contain the boundary conditions. The corresponding vector with particle locations is

$$\vec{C}_0 = \left(\underbrace{[1, 2, \ldots, (m-1)]}_{|\vec{\chi_L}|}, \underset{|\vec{\chi_R}|}{m} \right) \tag{S5}$$

whereby the notation $|\vec{v}|$ indicates the length of $\vec{v}$. Here $|\vec{\chi_L}|$ and $|\vec{\chi_R}|$ are the number of times that the vector $[1, 2, \ldots, (m-1)]$ and scalar m are repeated in the array, respectively.

A discrete time-step is defined as $\Delta t = 1/f$ is the inverse particle jumping frequency. At each time step, the status of the particles is updated by

$$\vec{\chi} = \vec{\chi} + \Delta t \tag{S6}$$

$$\vec{C} = \vec{C} + s([-1, 1], n) \tag{S7}$$

Equation S6 accounts for aging, which can also be turned off. The function s in equation S7 is defined as $s(A, n) = (x_1, x_2, \ldots, x_n)$, whereby each x_i is independently sampled from the set A. It changes the location of particles randomly by ± 1, so that each particle is moved to an adjacent cell.

The boundary conditions are enforced by first removing all particles at the boundaries, i.e., removing all indices from $\vec{C}$ and $\vec{\chi}$ when $C_i = 1$ or $C_i = m$. Then the initial particles at the boundaries, as in equations S4 and S5, are concatenated to $\vec{C}$ and $\vec{\chi}$.

To account for the consumption, the number of particles at each location (except not the cells at the boundaries) in a grid are counted, and the particle indices are stored in a vector $\vec{p_i}$ for cell i. The rate for each cell becomes $R_i = \lfloor k|\vec{p_i}|\rceil$, whereby $\lfloor \ldots \rceil$ indicates rounding to the nearest integer. Then the indices vector $\vec{p_i}$ is randomly shuffled, and the indices corresponding to the first R_i entries from the randomized $\vec{p_i}$ are the indices of $\vec{C}$ and $\vec{\chi}$ that will be removed.

Production (P in equation S1) is implemented by

$$\vec{C} = \left(\vec{C}, \underbrace{[2, 3, \ldots, (m-1)]}_{P}\right) \tag{S8}$$

$$\vec{\chi} = \left(\vec{\chi}, \underset{(m-2)P}{0}\right) \tag{S9}$$

whereby the production rate P needs to be a round number. Equation S8 adds at each location in the grid new particles to account for production. Equation S9 sets the age of the new particles to zero.

Finally, $n = |\vec{C}|$ updates the total number of particles. A single time step has finished, and it can be repeated until the simulation finishes.

S1.2 Application 2: Multi-G model

In this validation model, the reactivity distribution is divided in n bins, whereby the bin width $\Delta k = (\chi_{\max} - \chi_{\min})/n$. The reactivites for each bin for $i \in [1, n]$ are defined as

$$k_i = \Delta k(i - 0.5) \tag{S10}$$

and each bin i is also implemented as a state variable. The upper boundary is included in the upper domain cell, which does not change over time. The concentrations in this upper layer are set to

$$C_i^* = \int_{k_{\min}+(i-1)\Delta k}^{k_{\min}+i\Delta k} f(\chi)\, d\chi \tag{S11}$$

whereby $f(\chi)$ is the distribution function defined for the upper boundary. The upper boundary condition is also used as initial condition throughout the domain. The simulation solves

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_i}{\partial x} - \omega C_i\right) + k_i C_i \tag{S12}$$

which is discretized with finite differences (Soetaert and Meysman, 2012; R Core Team, 2022). A zero-gradient lower boundary condition was imposed. Using a 15 cm long domain divided into 50 evenly spaced cells, the simulation was run with the vode solver (Brown et al., 1989).

S1.3 Application 3: Age bins model

In this approach, bins are used for ages. A moving grid is used, meaning that the boundaries of the age grid, defining the boundaries of the age bins, change during the simulation. In this way, material in one bin does not have to be moved to another bin due to aging, which avoids numerical diffusion and preserves the moments of the age distribution.

S1.3.1 Age grid

A grid for ages is constructed for a simulation that runs for $t \in [t_0, t_f]$. There is a continuous age distribuion $f(\chi)$ defined as upper boundary condition, which has only non-zero values for $\chi \in [\chi_0, \chi_f]$. The grid is a vector $\vec{g}$ that corresponds to boundaries of age bins. The first indice corresponds to the highest age boundary. The age at the boundary during the simulation is

$$g(t, i = 1) = \chi_f + (t - t_0) \tag{S13}$$

The distance between nodes of $\vec{g}$ depends on the age distribution imposed as upper boundary condition and the number of age bins (o):

$$\Delta\chi = (\chi_f - \chi_0)/o \tag{S14}$$

The total number of bins in the simulation is set to

$$m = [\chi_f - \chi_0 + t_f - t_0]/\Delta\chi \tag{S15}$$

whereby the simulation time for t_f and t_0 is chosen in such a way that m becomes an integer. A function is defined to return the age at the boundaries defined by $\vec{g}$:

$$g(t,i) = \chi_f + (t - t_0) - \Delta\chi(i-1) \tag{S16}$$

for $i \in [1, m+1]$. The function can return negative values for g_i that are located in the future of the simulation. To avoid evaluating non-physical ages, it may be convenient to define

$$g^+(t,i) = \max\{g(t,i), 0\} \tag{S17}$$

The mean age of the bins can be defined

$$h(t,j) = \frac{g^+(t,j) + g^+(t,j+1)}{2} \tag{S18}$$

for $j \in [1, m]$. When $h(t,j) = 0$, the result is ignored.

S1.3.2 Implementation of diffusion, advection, reactions, boundary and initial conditions

The depth domain for $z \in [0, L]$ in the model is divided into N evenly spaced layers. The matrix describing the state of the simulations has m columns to account different age bins and N rows to account for different depth. A standard finite differences scheme is applied for each column to simulate

$$\left.\frac{\partial C}{\partial t}\right|_{\text{column}} = \frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z} - wC\right) + R \tag{S19}$$

The equation was discretized by finite differences. For advection, both upwind and central differences have been tested. In the test runs, the central differences gave best results when diffusion was turned on, but when $D = 0$ it gives unphysical oscillations. The upwind scheme avoids these oscillations, but leads to the moments of variance and higher moments to be off due to numerical diffusion. Since diffusion is normally turned on, central differences are used per default.

For the reaction,

$$R(\chi) = R(h(t,j)) = f(\chi)C(\chi) \tag{S20}$$

When $h(t,j) = 0$, the expression may be ignored. It should be noted that $f(0)$ is not necessarily zero, but $C(0)$ should in principle be zero.

Dirichlet upper boundary conditions are implemented. The age distribution at the upper boundary condition is defined by a function

$$f(p,\chi)_{z=0} = f(p_0,\chi) \tag{S21}$$

whereby p_0 are the parameters for the distribution function at the upper boundary. In the state matrix, the first column represents material with age $g(t,1) \le \chi \le g(t,2)$. For all columns,

$$C_j^* = \frac{1}{g^+(t,j) - g^+(t,j+1)} \int_{g^+(t,j+1)}^{g^+(t,j)} f(p_0,\chi)\,d\chi \tag{S22}$$

defines the concentration at the upper boundary of the domain when $g^+(t,j) > 0$ and else $C_j^* = 0$. The integration was performed numerically in R (R Core Team, 2022; Piessens et al., 1983).

As initial conditions, at all depths (i.e, for all columns of the state matrix) the age distribution was set to the upper boundary distribution (eqns. S21, S22). All age bins were of uniform width, spanning 1 year each. For the age bins, differences of 1 year were used. The simulations were run by the vode solver (Brown et al., 1989).

S2 Mathematical validation of partial differential equations for the diffusion of central moments

Here it will be showed that the equations for variance and other higher central moments are consistent with the equations for non-central moments derived by Delhez and Deleersnijder (2002).

S2.1 Validation for the variance PDE

The noncentralized and centralized second moments are defined as

$$C\mu_2 = \sum_{i=1}^{C} \chi_i^2 \tag{S23}$$

$$C\sigma^2 = \sum (\chi_i - \mu)^2 \tag{S24}$$

The following

$$\sum (\chi_i - \mu)^2 = \sum \chi_i^2 - C\mu^2 \tag{S25}$$

implies

$$\sum \chi_i^2 = C(\sigma^2 + \mu^2) \tag{S26}$$

which can also be obtained by applying the binomial theorem. The derivative is

$$\frac{\partial(\sum \chi_i^2)}{\partial t} = \frac{\partial(C\sigma^2)}{\partial t} + 2\mu C \frac{\partial \mu}{\partial t} + \mu^2 \frac{\partial C}{\partial t} \tag{S27}$$

One can write

$$\frac{\partial \mu}{\partial t} = \left(\frac{\partial(C\mu)}{\partial t} - \mu \frac{\partial C}{\partial t} \right) / C \tag{S28}$$

$$2C\mu \frac{\partial \mu}{\partial t} = 2\mu \frac{\partial(C\mu)}{\partial t} - 2\mu^2 \frac{\partial C}{\partial t} \tag{S29}$$

yielding

$$\frac{\partial(\sum \chi_i^2)}{\partial t} = \frac{\partial(C\sigma^2)}{\partial t} + 2\mu \frac{\partial(C\mu)}{\partial t} - \mu^2 \frac{\partial C}{\partial t} \tag{S30}$$

Inserting the expressions derived in the manuscript yields

$$\begin{aligned} \frac{\partial(\sum \chi_i^2)}{\partial t} = {} & \frac{\partial}{\partial x}\left(D \frac{\partial(C\sigma^2)}{\partial x} \right) + 2DC \left(\frac{\partial \mu}{\partial x} \right)^2 + \\ & 2\mu \frac{\partial}{\partial x}\left(D \frac{\partial(C\mu)}{\partial x} \right) - \mu^2 \frac{\partial C}{\partial t} \end{aligned} \tag{S31}$$

Delhez and Deleersnijder (2002) gave

$$\frac{\partial \sum \chi_i^2}{\partial t} = 2C\mu + \frac{\partial}{\partial x}\left(D \frac{\partial(\sum \chi_i^2)}{\partial x} \right) \tag{S32}$$

and here we shall test if equations S31 and S32 are mathematically equivalent. Starting with the last term on the right-hand side,

$$D \frac{\partial(\sum \chi_i^2)}{\partial x} = D \frac{\partial}{\partial x} \left(C\sigma^2 + C\mu^2 \right) \tag{S33}$$

$$\begin{aligned} \frac{\partial(\sum \chi_i^2)}{\partial x} &= \frac{\partial(C\sigma^2)}{\partial x} + \frac{\partial(C\mu^2)}{\partial x} \\ &= \frac{\partial(C\sigma^2)}{\partial x} + 2C\mu \frac{\partial \mu}{\partial x} + \mu^2 \frac{\partial C}{\partial x} \end{aligned} \tag{S34}$$

$$\begin{aligned} \frac{\partial}{\partial x}\left(D \frac{\partial(\sum \chi_i^2)}{\partial x} \right) = {} & \frac{\partial}{\partial x}\left(D \frac{\partial(C\sigma^2)}{\partial x} \right) + 2 \frac{\partial}{\partial x}\left(DC\mu \frac{\partial \mu}{\partial x} \right) + \\ & \frac{\partial}{\partial x}\left(D\mu^2 \frac{\partial C}{\partial x} \right) \end{aligned} \tag{S35}$$

The comparison of the last results with equation S31 is

$$\frac{\partial}{\partial x}\left(D\frac{\partial(C\sigma^2)}{\partial x}\right) + 2DC\left(\frac{\partial\mu}{\partial x}\right)^2 + 2\mu\frac{\partial}{\partial x}\left(D\frac{\partial(C\mu)}{\partial x}\right) - \mu^2\frac{\partial C}{\partial t} \stackrel{?}{=} 2C\mu + \frac{\partial}{\partial x}\left(D\frac{\partial(C\sigma^2)}{\partial x}\right) + 2\frac{\partial}{\partial x}\left(DC\mu\frac{\partial\mu}{\partial x}\right) + \frac{\partial}{\partial x}\left(D\mu^2\frac{\partial C}{\partial x}\right) \tag{S36}$$

Removing equal terms and substituting $\partial C/\partial t$ yields

$$2DC\left(\frac{\partial\mu}{\partial x}\right)^2 + 2\mu\frac{\partial}{\partial x}\left(D\frac{\partial(C\mu)}{\partial x}\right) - \mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \stackrel{?}{=} 2C\mu + 2\frac{\partial}{\partial x}\left(DC\mu\frac{\partial\mu}{\partial x}\right) + \frac{\partial}{\partial x}\left(D\mu^2\frac{\partial C}{\partial x}\right) \tag{S37}$$

Clearly, the second and third terms on the left and right-hand side, respectively, are very similar. Applying again the product rule:

$$\frac{\partial}{\partial x}\left(D\mu^2\frac{\partial C}{\partial x}\right) = \mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} \tag{S38}$$

and

$$2\frac{\partial}{\partial x}\left(DC\mu\frac{\partial\mu}{\partial x}\right) = 2\mu\frac{\partial}{\partial x}\left(DC\frac{\partial\mu}{\partial x}\right) + 2DC\left(\frac{\partial\mu}{\partial x}\right)^2 \tag{S39}$$

We see that the second term of equation S39 on the right-hand side cancels out with the first term on the left-hand side of equation S37. The first term on the right-hand side of equation S38 does not cancel out with third term of the left-hand side of equation S37 due to the different sign, but it can be brought over to the other side.

$$2\mu\frac{\partial}{\partial x}\left(D\frac{\partial(C\mu)}{\partial x}\right) - 2\mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \stackrel{?}{=} 2C\mu + 2\mu\frac{\partial}{\partial x}\left(DC\frac{\partial\mu}{\partial x}\right) + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} \tag{S40}$$

Applying again the product rule yields

$$2\mu\frac{\partial}{\partial x}\left(D\mu\frac{\partial C}{\partial x} + DC\frac{\partial\mu}{\partial x}\right) - 2\mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \stackrel{?}{=} 2C\mu + 2\mu\frac{\partial}{\partial x}\left(DC\frac{\partial\mu}{\partial x}\right) + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} \tag{S41}$$

leaving

$$2\mu\frac{\partial}{\partial x}\left(D\mu\frac{\partial C}{\partial x}\right) - 2\mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \stackrel{?}{=} 2C\mu + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} \tag{S42}$$

Applying the product rule again

$$2\mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} - 2\mu^2\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \stackrel{?}{=} 2C\mu + 2\mu D\frac{\partial C}{\partial x}\frac{\partial\mu}{\partial x} \tag{S43}$$

leaves

$$0 \neq 2C\mu \tag{S44}$$

The term $2C\mu$, causing the inequality, is an additional term used by Delhez and Deleersnijder (2002) to account for aging. This can be shown, starting from

$$\frac{\partial(\mu C)}{\partial t} = C\frac{\partial\mu}{\partial t} + \mu\frac{\partial C}{\partial t} \tag{S45}$$

Aging does not change the concentration, and $\partial\mu/\partial t = 1$, since a particle gains 1 unit age per one unit time. This leaves $\partial(\mu C)/\partial t = C$. The temporal derivative of the second non-central moment is

$$\frac{\partial \sum \chi_i^2}{\partial t} = 2\sum \chi_i \frac{\partial \chi_i}{\partial t} \tag{S46}$$

Since $\sum \chi_i = C\mu$ and $\partial\chi_i/\partial t = 1$, we obtain

$$\frac{\partial \sum \chi_i^2}{\partial t} = 2C\mu \tag{S47}$$

for aging. Ignoring this term shows that the result of Delhez and Deleersnijder (2002) is in agreement with the PDE for diffusion of the second centralized moment.

S2.2 Initial value problem with a delta distribution as analytical validation test

This section aims to validate the PDE derived for the skewness and all higher moments, but it will only be specifically tested for the skewness. For this, the temporal derivative of the skewness for a theoretical initial δ-distribution will be solved analytically.

Following Delhez and Deleersnijder (2002), a density function is defined as $\rho(x, t, \chi)$. For the initial value problem, the skewed initial distribution

$$\rho(x, t = 0, \chi) = 2\delta(\chi) + \delta(\chi - ax^2) \tag{S48}$$

was chosen, whereby $\delta(\chi)$ denotes Dirac's distribution, which is symmetric ($\delta[\chi] = \delta[-\chi]$). When these appear in integrals, the integrations can be performed as follows

$$\int_{-\infty}^{\infty} \delta(\chi)\, d\chi = 1 \tag{S49}$$

$$\int_{-\infty}^{\infty} \delta(a - \chi) f(\chi)\, dx = f(a) \tag{S50}$$

The derivative $\delta' = \partial\delta/\partial\chi$ is antisymmetric

$$\delta'(\chi) = -\delta'(-\chi) \tag{S51}$$

and allows integration by parts

$$\int_{-\infty}^{\infty} \delta'(\chi) f(\chi)\, d\chi = [\delta(\chi) f(\chi)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \delta(\chi) f'(\chi)\, d\chi \tag{S52}$$

$$= -\int_{-\infty}^{\infty} \delta(\chi) \frac{\partial f(\chi)}{\partial \chi}\, d\chi \tag{S53}$$

$$= -\frac{\partial f(\chi)}{\partial \chi} \tag{S54}$$

The term in the square brackets vanishes because $\delta(\chi)$ is zero at the integration boundaries. This integration by parts also works with higher-order derivatives of δ, which means that the integral over $\delta'(\chi)$, $\delta''(\chi)$, and other derivatives are zero.

S2.2.1 Diffusion of the delta distribution

The diffusion equation for the density distribution is

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial \rho}{\partial x}\right) . \tag{S55}$$

In density function (ρ), only the term $\delta(\chi - ax^2)$ depends on x. Its derivative inside the parentheses is calculated by the chain rule

$$\frac{\partial\rho}{\partial x} = \frac{\partial}{\partial x}\delta(\chi - ax^2) \tag{S56}$$

$$= \delta'(\chi - ax^2)(-2ax) \tag{S57}$$

For the outer derivative, the product rule is applied for three factors.

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial x}\left(D\delta'(\chi - ax^2)\cdot(-2ax)\right) \tag{S58}$$

$$= \left[\frac{\partial D}{\partial x}\delta'(\chi - ax^2)\cdot(-2ax) + D\delta''(\chi - ax^2)\cdot(-2ax)^2 + D\delta'(\chi - ax^2)\cdot(-2a)\right] \tag{S59}$$

Now the expressions and their temporal derivatives can be calculated.

S2.2.2 The PDE for concentration

The concentration is

$$C = \int_{-\infty}^{\infty} \rho(x,t,\chi)\,d\chi = 3 \tag{S60}$$

Its temporal derivative can be solved by

$$\frac{\partial}{\partial t}C = \int_{-\infty}^{\infty} \frac{\partial}{\partial t}\rho(x,t,\chi)\,d\chi \tag{S61}$$

$$= \int_{-\infty}^{\infty} \left[\frac{\partial D}{\partial x}\delta'(\chi - ax^2)\cdot(-2ax) + D\delta''(\chi - ax^2)\cdot(-2ax)^2 + D\delta'(\chi - ax^2)\cdot(-2a)\right]\,d\chi \tag{S62}$$

Since only the derivatives of δ depend on χ, the integral yields zero.

S2.2.3 The PDE for the mean

The mean is

$$\mu = \frac{1}{C}\left(\int_{-\infty}^{\infty} \chi\rho(x,t,\chi)\,d\chi\right) = \frac{ax^2}{3} \tag{S63}$$

and its temporal derivative

$$\frac{\partial}{\partial t}\mu = \frac{1}{C}\left(\int_{-\infty}^{\infty} \chi\frac{\partial}{\partial t}\rho(x,t,\chi)\,d\chi\right) \tag{S64}$$

This equation is valid because $\partial C/\partial t = 0$.

$$\frac{\partial}{\partial t}\mu = \frac{1}{C}\int_{-\infty}^{\infty} \chi\left[\frac{\partial D}{\partial x}\delta'(\chi - ax^2)\cdot(-2ax) + D\delta''(\chi - ax^2)\cdot(-2ax)^2 + D\delta'(\chi - ax^2)\cdot(-2a)\right]\,d\chi \tag{S65}$$

Integrating by parts implies switching the sign, integrating the delta distribution, and differentiating the rest with respect to χ

$$\begin{aligned}\frac{\partial}{\partial t}\mu &= -\frac{1}{C}\int_{-\infty}^{\infty}\left[\frac{\partial D}{\partial x}\delta(\chi - ax^2)\cdot(-2ax)+\right.\\ &\quad \left. D\delta'(\chi - ax^2)\cdot(-2ax)^2 + D\delta(\chi - ax^2)\cdot(-2a)\right]\,d\chi \end{aligned} \tag{S66}$$

Since only the delta function and its derivative depend on χ, the integral over δ is one and the integral over δ' is zero, which gives

$$\frac{\partial}{\partial t}\mu = \frac{2ax}{3}\frac{\partial D}{\partial x} + \frac{2a}{3}D\,. \tag{S67}$$

For a constant D, the first-moment equation can be tested

$$\frac{\partial}{\partial t}\mu \stackrel{?}{=} \frac{\partial}{\partial x}\left(D\frac{\partial\mu}{\partial x}\right) \tag{S68}$$

Since $\partial\mu/\partial x = 2ax/3$, the equation holds for this example.

S2.2.4 The PDE for variance

The definition of the centralized variance

$$\phi_2 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \mu)^2 \tag{S69}$$

can also be written with the notation of Delhez and Deleersnijder (2002) as

$$\phi_2 = \frac{1}{C}\int_{-\infty}^{\infty}\rho(x,t,\chi)(\chi-\mu)^2\,d\chi \tag{S70}$$

For $t = 0$,

$$\phi_2 = \frac{1}{C}\left[2\cdot(0-\mu)^2 + (ax^2-\mu)^2\right] \tag{S71}$$

and given $\mu = ax^2/3$

$$\begin{aligned}\phi_2 &= \frac{1}{C}\left[2\left(\frac{ax^2}{3}\right)^2 + \left(\frac{2ax^2}{3}\right)^2\right]\\ &= \frac{2}{9}a^2x^4\end{aligned} \tag{S72}$$

is obtained. This result will be used in the following test for the skewness but is not worked further out since the PDE for variance was already validated (sect. S2.1).

S2.2.5 The PDE for skewness

The definition of the centralized skewness

$$\phi_3 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \mu)^3 \tag{S73}$$

can also be written as

$$\phi_3 = \frac{1}{C}\int_{\chi=-\infty}^{\infty}\rho(x,t,\chi)(\chi-\mu)^3\,d\chi \tag{S74}$$

For $t = 0$,

$$\phi_3 = \frac{1}{C}\left(2\cdot(0-\mu)^3 + (ax^2-\mu)^3\right) \tag{S75}$$

is obtained. Inserting $\mu = ax^2/3$ yields

$$\begin{aligned}\phi_3 &= \frac{1}{C}\left(-2\cdot\left(\frac{ax^2}{3}\right)^3 + \left(\frac{2ax^2}{3}\right)^3\right) \\ &= \frac{2}{27}a^3x^6\end{aligned} \tag{S76}$$

Applying the product rule allows

$$\begin{aligned}\frac{\partial\phi_3}{\partial t} &= \frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} + \frac{\partial\phi_3}{\partial\mu}\frac{\partial\mu}{\partial t} \\ &= \frac{1}{C}\int\limits_{-\infty}^{\infty}\left[\frac{\partial\rho(x,t,\chi)}{\partial t}(\chi-\mu)^3 + \rho(x,t,\chi)\left(-3(\chi-\mu)^2\right)\frac{\partial\mu}{\partial t}\right]d\chi\end{aligned} \tag{S77}$$

to be written. The former part can be calculated as

$$\begin{aligned}\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= \frac{1}{C}\int\limits_{-\infty}^{\infty}\frac{\partial\rho(x,t,\chi)}{\partial t}(\chi-\mu)^3\,d\chi \\ &= \frac{1}{C}\int\limits_{-\infty}^{\infty}\left[\frac{\partial D}{\partial x}\delta'(\chi-ax^2)\cdot(-2ax)+\right. \\ &\qquad \left. D\delta''(\chi-ax^2)\cdot(-2ax)^2 + D\delta'(\chi-ax^2)\cdot(-2a)\right](\chi-\mu)^3\,d\chi\end{aligned} \tag{S78}$$

Integration by parts gives

$$\begin{aligned}\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= -\frac{1}{C}\int\limits_{-\infty}^{\infty}\left[\frac{\partial D}{\partial x}\delta(\chi-ax^2)\cdot(-2ax)+\right. \\ &\qquad \left. D\delta'(\chi-ax^2)\cdot(-2ax)^2 + D\delta(\chi-ax^2)\cdot(-2a)\right]\cdot 3(\chi-\mu)^2\,d\chi\end{aligned} \tag{S79}$$

Integrating the terms with δ yields

$$\begin{aligned}\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= -\frac{1}{C}\frac{\partial D}{\partial x}\cdot(-2ax)\cdot 3(ax^2-\mu)^2 - \frac{1}{C}D\cdot(-2a)\cdot 3(ax^2-\mu)^2 - \\ &\qquad \frac{1}{C}\int\limits_{-\infty}^{\infty} D\delta'(\chi-ax^2)\cdot(-2ax)^2\cdot 3(\chi-\mu)^2\,d\chi\end{aligned} \tag{S80}$$

Integrating by parts again yields

$$\begin{aligned}\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= -\frac{1}{C}\frac{\partial D}{\partial x}\cdot(-2ax)\cdot 3(ax^2-\mu)^2 - \frac{1}{C}D\cdot(-2a)\cdot 3(ax^2-\mu)^2 + \\ &\qquad \frac{1}{C}\int\limits_{-\infty}^{\infty} D\delta(\chi-ax^2)\cdot(-2ax)^2\cdot 6(\chi-\mu)\,d\chi\end{aligned} \tag{S81}$$

and the δ integral is solved

$$\begin{aligned}\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= -\frac{1}{C}\frac{\partial D}{\partial x}\cdot(-2ax)\cdot 3(ax^2-\mu)^2 - \frac{1}{C}D\cdot(-2a)\cdot 3(ax^2-\mu)^2 + \\ &\qquad \frac{1}{C}D\cdot(-2ax)^2\cdot 6(ax^2-\mu)\end{aligned} \tag{S82}$$

Now $C=3$ and $\mu = ax^2/3$ are inserted

$$\begin{aligned}
\frac{\partial\phi_3}{\partial\rho}\frac{\partial\rho}{\partial t} &= -\frac{1}{3}\frac{\partial D}{\partial x}\cdot(-2ax)\cdot 3(\frac{2}{3}ax^2)^2 - \frac{1}{3}D\cdot(-2a)\cdot 3(\frac{2}{3}ax^2)^2 + \\
&\quad \frac{1}{3}D\cdot(-2ax)^2\cdot 6(\frac{2}{3}ax^2) \\
&= \frac{\partial D}{\partial x}\cdot(2ax)\cdot(\frac{2}{3}ax^2)^2 - D\cdot(-2a)\cdot(\frac{2}{3}ax^2)^2 + D\cdot(-2ax)^2\cdot 2(\frac{2}{3}ax^2) \\
&= \frac{8}{9}\frac{\partial D}{\partial x}\cdot(ax)\cdot(ax^2)^2 + \frac{8}{9}D\cdot a\cdot(ax^2)^2 + \frac{16}{3}D\cdot(ax)^2\cdot(ax^2) \\
&= \frac{8}{9}a^3x^5\frac{\partial D}{\partial x} + \frac{56}{9}a^3x^4D
\end{aligned} \tag{S83}$$

Solving the other part

$$\frac{\partial\phi_3}{\partial\mu}\frac{\partial\mu}{\partial t} = \frac{1}{C}\int_{\infty}^{\infty}\rho(x,t,\chi)\left(-3(\chi-\mu)^2\frac{\partial\mu}{\partial t}\right)d\chi \tag{S84}$$

Inserting $\rho(t=0)$ gives

$$\frac{\partial\phi_3}{\partial\mu}\frac{\partial\mu}{\partial t} = \frac{1}{C}\left[2\left(-3(0-\mu)^2\right) + \left(-3(ax^2-\mu)^2\right)\right]\frac{\partial\mu}{\partial t} \tag{S85}$$

and with $C=3$, $\mu = ax^2/3$ and $\frac{\partial\mu}{\partial t} = \frac{2ax}{3}\frac{\partial D}{\partial x} + \frac{2a}{3}D$, one obtains

$$\begin{aligned}
\frac{\partial\phi_3}{\partial\mu}\frac{\partial\mu}{\partial t} &= \left[2\left(-(\frac{ax^2}{3})^2\right) + \left(-(\frac{2ax^2}{3})^2\right)\right]\left(\frac{2ax}{3}\frac{\partial D}{\partial x} + \frac{2a}{3}D\right) \\
&= -\frac{2}{3}a^2x^4\left(\frac{2ax}{3}\frac{\partial D}{\partial x} + \frac{2a}{3}D\right) \\
&= -\frac{4}{9}a^3x^5\frac{\partial D}{\partial x} - \frac{4}{9}a^3x^4D
\end{aligned} \tag{S86}$$

So, together the parts give

$$\frac{\partial\phi_3}{\partial t} = \frac{4}{9}a^3x^5\frac{\partial D}{\partial x} + \frac{52}{9}a^3x^4D \tag{S87}$$

as the analytical result.

The PDE accounting for the diffusion of the third centralized moment that we want to test reads for a constant concentration

$$\frac{\partial\phi_3}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial\phi_3}{\partial x}\right) + 6D\frac{\partial\phi_2}{\partial x}\frac{\partial\mu}{\partial x} \tag{S88}$$

Recalling

$$\begin{aligned}
\mu &= \frac{1}{3}ax^2 \\
\phi_2 &= \frac{2}{9}a^2x^4 \\
\phi_3 &= \frac{2}{27}a^3x^6
\end{aligned}$$

and substituting these expressions into the last equation gives

$$\begin{aligned}
\frac{\partial\phi_3}{\partial t} &= \frac{\partial}{\partial x}\left(D\frac{4}{9}a^3x^5\right) + 6D\frac{8}{9}a^2x^3\frac{2}{3}ax \\
&= \frac{4}{9}a^3x^5\frac{\partial D}{\partial x} + \frac{20}{9}a^3x^4D + \frac{32}{9}a^3x^4D \\
&= \frac{4}{9}a^3x^5\frac{\partial D}{\partial x} + \frac{52}{9}a^3x^4D
\end{aligned} \tag{S89}$$

which matches equation S87.

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