Algorithms for the Binary XPFC Model

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1 Introduction

Presented here is an approach to integrating the Binary XPFC equations of motion in cases where the free energy of mixing coupling ω is large. In previous work done on the binary XPFC model the coupling has been quite small which effectively diagonalizes the linear contributions to the equation of motion so that the stepping of density and concentration fields can be considered separately.

2 Semi-Implicit Spectral Methods for Systems of First Order PDEs

To start, we consider the general case of time stepping a system of non-linear first-order PDE's. Specifically, we are going to look at a set of stochastic non-linear PDE's.

$$\frac{\partial \overline{\psi}(x,t)}{\partial t} = \mathcal{G}\left[\overline{\psi}(x,t)\right] + \overline{\xi}(x,t) \tag{1}$$

Where,

$\overline{\psi}(x,t)$ = is a set of fields of interest (ex: (n, c))
$\mathcal{G}$ = some functional of our fields of interest
$\overline{\xi}(x,t)$ = the stochastic driving force with variances given by a generalized Einstein relationship

To develop a semi-implicit method we start by splitting the functional $\mathcal{G}$ into linear and non-linear components,

$$\frac{\partial \overline{\psi}(x,t)}{\partial t} = \overline{\overline{\mathcal{L}}}(x,x') * \overline{\psi}(x',t) + \mathcal{NL}\left[\overline{\psi}\right] + \overline{\xi}(x,t) \tag{2}$$

Where,

$\overline{\overline{\mathcal{L}}}$ = is a matrix
$*$ = matrix multiplication and integration over the repeated variable
$\mathcal{NL}$ = the non-linear component of the the functional $\mathcal{G}$

In a special set of PDE's the kernel $\overline{\overline{\mathcal{L}}}$ is translationally invariant. When this is the case, the convolution theorem can be used to write the linear functional as an algebraic product in Fourier space.

$$\frac{\partial \overline{\psi}(k,t)}{\partial t} = \overline{\overline{\mathcal{L}}}(k)\overline{\psi}(k,t) + \mathcal{F}\left[\mathcal{NL}\left[\overline{\psi}\right]\right] + \overline{\xi}(k,t) \tag{3}$$

Where, $\mathcal{F}[\,\cdot\,]$ denotes a Fourier transform. We now consider our fields on a discrete grid with Δk spacing between Fourier modes and Δt spacing between times such that we might define,

$$\overline{\psi}_j^n \equiv \overline{\psi}(j\Delta k, n\Delta t). \tag{4}$$

To develop a generic approach to time stepping we consider evaluating our field between grid points in time (eg. at $\overline{\psi}_j^{n+\gamma}$ where $\gamma \in [0,1]$).

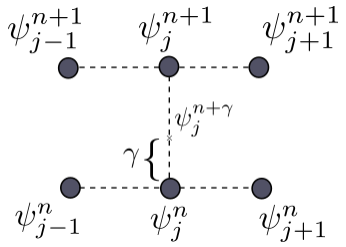

Figure 1: Schematic of time step

To first order we can approximate this value as a linear interpolation of the value at n and the value at $n+1$.

$$\overline{\psi}_j^{n+\gamma} = (1-\gamma)\overline{\psi}_j^n + \gamma\overline{\psi}_j^{n+1} \tag{5}$$

We can also approximate the time derivative $\partial_t\overline{\psi}$ as,

$$\frac{\partial\overline{\psi}}{\partial t} = \frac{\overline{\psi}_j^{n+1} - \overline{\psi}_j^n}{\Delta t} + \frac{1-2\gamma}{2}\frac{\partial^2\overline{\psi}}{\partial t^2}\Delta t + ... \tag{6}$$

Deriving different integration schemes is done by evaluating the equation of motion for various values of γ. For example, to recover simple Euler stepping we can evaluate the equation of motion with $\gamma = 0$. The semi-implicit scheme relays on evaluating the non-linear component of the equation of motion at $\gamma = 0$ while the rest of the equation is evaluated at $\gamma = 1$. In this treatment we will evaluate the non-linear component at $\gamma = 0$ but we will leave the rest of the equation unevaluated so that γ can be choosen freely at the end. Substituting these results into equation of motion we find the following result,

$$\frac{\overline{\psi}_j^{n+1} - \overline{\psi}_j^n}{\Delta t} + \frac{1-2\gamma}{2}\frac{\partial^2\overline{\psi}}{\partial t^2}\Delta t = \overline{\overline{\mathcal{L}}}\left((1-\gamma)\overline{\psi}_j^n + \gamma\overline{\psi}_j^{n+1}\right) + \mathcal{F}\left[\mathcal{N}\mathcal{L}\left[\overline{\psi}_j^n\right]\right] + \overline{\xi}_j^{n+\gamma} \tag{7}$$

Separating $t = n+1$ terms on the left and $t = n$ terms on the right,

$$\left(\mathbb{1} - \Delta t\gamma\overline{\overline{\mathcal{L}}}\right)\overline{\psi}_j^{n+1} = \left(\mathbb{1} + \Delta t(1-\gamma)\overline{\overline{\mathcal{L}}}\right)\overline{\psi}_j^n + \Delta t\mathcal{F}\left[\mathcal{N}\mathcal{L}\left[\overline{\psi}_j^n\right]\right] + \Delta t\overline{\xi}_j^{n+\gamma} - \frac{1-2\gamma}{2}\frac{\partial^2\overline{\psi}}{\partial t^2}\Delta t^2 \tag{8}$$

Finally, we can isolate $\overline{\psi}_j^{n+1}$ by left multiplying by $\left(\mathbb{1} - \gamma\Delta t\overline{\overline{\mathcal{L}}}\right)^{-1}$,

$$\overline{\psi}_j^{n+1} = \left(\mathbb{1} - \Delta t\gamma\overline{\overline{\mathcal{L}}}\right)^{-1}\left(\left(\mathbb{1} + \Delta t(1-\gamma)\overline{\overline{\mathcal{L}}}\right)\overline{\psi}_j^n + \Delta t\mathcal{F}\left[\mathcal{N}\mathcal{L}\left[\overline{\psi}_j^n\right]\right] + \Delta t\overline{\xi}_j^{n+\gamma} - \frac{1-2\gamma}{2}\frac{\partial^2\overline{\psi}}{\partial t^2}\Delta t^2\right) \tag{9}$$

The final term on the right hand side emphasizes that if we choose $\gamma = 1/2$ we will have a algorithm that is accurate to second order in time (this is a kind of Crank-Nicolson method). If we choose $\gamma = 1$ we recover a semi-implicit method.

3 Applications to the Binary XPFC Model

The binary XPFC model is a good example of a system of first order PDE's like those discussed in the previous discussion. The equations of motion in real space are,

$$\frac{\partial c(x,t)}{\partial t} = M_c \nabla^2 \left((\omega\epsilon - W_c\nabla^2)c + \omega(1+n)\frac{\partial \Delta F_{mix}(c)}{\partial c} - \frac{1}{2}n\left(\frac{\partial C_{eff}}{\partial c} * n\right)\right) + \xi_c(x,t) \tag{10}$$

$$\frac{\partial n(x,t)}{\partial t} = M_n \nabla^2 \left((1 - C_{eff}*)\, n - \frac{\eta}{2}n^2 + \frac{\chi}{3}n^3 + \omega \Delta F_{mix}\right) + \xi_n(x,t) \tag{11}$$

Where,

$$\begin{aligned} * \quad &= \text{a convolution operation} \\ \Delta F_{mix} &= c\log\left(\tfrac{c}{c_0}\right) + (1-c)\log\left(\tfrac{1-c}{1-c_0}\right) \end{aligned}$$

With reference to the formalism we've already established our task is now to seperate out the linear and non-linear components of these equations of motion. To do this, we expand the concentration and density around constant references c_* and n_*. Doing so leads to an expression of $\overline{\overline{\mathcal{L}}}$,

$$\overline{\overline{\mathcal{L}}} = \begin{bmatrix} -M_c k^2 \left(\omega\left(\epsilon - \frac{1}{c_*^2 - c_*}\right) + W_c k^2\right) & -M_c k^2 \omega \log\left(\frac{(c_0-1)c_*}{c_0(c_*-1)}\right) \\ -M_n k^2 \omega \log\left(\frac{(c_0-1)c_*}{c_0(c_*-1)}\right) & -M_n k^2 \left(1 - C_{eff}|_{c_*}(k)\right) \end{bmatrix} \tag{12}$$

Important to note in the structure of $\overline{\overline{\mathcal{L}}}$ is that it is diagonal in the limit of small ω. In the approximation that it is diagonal, previous algorithms for the binary XPFC model are recovered where, to linear order, concentration and density may be independently integrated. Another interesting case is that of $M_n = M_c$ where the matrix is symmetric and thus has orthogonal eigenvectors.

4 Algorithm for the Concentration $c(x,t)$

To construct algorithm for the equation of motion of the concentration field we follow the outline of Danzig on pg 195. The equation of motion is,

$$\partial_t \tilde{c} = -M_c k^2 \left(\omega\epsilon\tilde{c} + W_c k^2 \tilde{c} + \mathcal{F}\{NL(c)\}\right) + \tilde{\zeta}. \tag{13}$$

Where $NL(c)$ is the non-linear term and ζ is the drive noise.

$$NL(c) = \omega(1+n)\left(\ln\left(\frac{c}{c_0}\right) - \ln\left(\frac{1-c}{1-c_0}\right)\right) - \frac{1}{2}n\left(C_{eff}^n * n\right) \tag{14}$$

Now if we think about the solution to this equation at time $t^{n+\xi}$ time between t^n and t^{n+1} we express the solution as an interpolation between the solutions at the earlier and later times.

$$\tilde{c}_k^{n+\xi} = (1-\xi)\tilde{c}_k^n + \xi\tilde{c}_k^{n+1} \tag{15}$$

We also find that we can express the time derivative as finite difference plus a correction term.

$$\partial_t \tilde{c} = \frac{\tilde{c}_k^{n+1} - \tilde{c}_k^n}{\Delta t} + \frac{1-2\xi}{2}\frac{\partial^2 \tilde{c}}{\partial t^2}\Delta t + ... \tag{16}$$

Using each of these ideas we can rewrite the equation of motion completely, with the exception of the nonlinear term, which we evaluate a the time t^n in keeping with many of the semi-implicit methods published.

$$\frac{\tilde{c}_k^{n+1} - \tilde{c}_k^n}{\Delta t} + \frac{1-2\xi}{2}\frac{\partial^2 \tilde{c}}{\partial t^2}\Delta t = \Lambda(k)\left[(1-\xi)\tilde{c}_k^n + \xi\tilde{c}_k^{n+1}\right] - M_c k^2 \mathcal{F}\{NL(c^n)\} + \tilde{\zeta}_k^n \tag{17}$$

where,

$$\Lambda(k) = -M_c k^2\left(\omega\epsilon + W_c k^2\right). \tag{18}$$

Moving future times to the left and past times to the right we find,

$$\tilde{c}_k^{n+1} = \hat{P}\tilde{c}_k^n + \hat{Q}\mathcal{F}\{NL(c^n)\}_k + \hat{L}\tilde{\zeta}_k^n + \frac{2\xi - 1}{2}\frac{\partial^2 \tilde{c}}{\partial t^2}\Delta t^2 \tag{19}$$

Where the operators $\hat{P}$, $\hat{Q}$ and $\hat{L}$ are,

$$\hat{P} = 1 + \frac{\Delta t \Lambda(k)}{1 - \xi\Delta t\Lambda(k)} \tag{20}$$

$$\hat{Q} = -\frac{M_c k^2 \Delta t}{1 - \Delta t\xi\Lambda(k)} \tag{21}$$

$$\hat{L} = \frac{\Delta t}{1 - \Delta t\xi\Lambda(k)} \tag{22}$$

Different values of ξ lead to different integration schemes. The $\xi = 0$ corresponds to euler time stepping in fourier space, while $\xi = 1$ yields the often used semi-implicit fourier method. There is an import case in which we choose $\xi = 1/2$ where the algorithm becomes accurate to second order in time. This is the Crank-Nicholson fourier method.

5 Algorithm for the Total Density $n(x,t)$

We can develop an algorithm for the equation of motion fo the total density in the same way that we did with concentration. The equation of motion for the total density in fourier space looks like,

$$\partial_t \tilde{n}(k,t) = -M_n k^2\left(\tilde{n} + \mathcal{F}\{NL(n)\}\right) + \tilde{\zeta} \tag{23}$$

Where now the nonlinear term is,

$$NL(n) = -\eta\frac{n^2}{2} + \chi\frac{n^3}{3} + \Delta f_{mix}(c) - C_{eff}^n * n \tag{24}$$

Note that the convolution term is nonlinear because of an implicit dependance on the concentration. Now, in principle, you could compute that pair correlation function every time step for a more accurate linear propagator, but here we will not consider that.

Here again, we find the same structure as previously:

$$\tilde{n}_k^{n+1} = \hat{P}\tilde{n}_k^n + \hat{Q}\mathcal{F}\{NL(n^n)\}_k + \hat{L}\tilde{\zeta}_k \tag{25}$$

Here, the operators $\hat{P}$, $\hat{Q}$ and $\hat{L}$ are:

$$\hat{P} = 1 - \frac{\Delta t M_n k^2}{1 + \xi \Delta t M_n k^2} \tag{26}$$

$$\hat{Q} = -\frac{M_c k^2 \Delta t}{1 + \Delta t \xi M_n k^2} \tag{27}$$

$$\hat{L} = \frac{\Delta t}{1 + \Delta t \xi M_n k^2} \tag{28}$$