APPENDIX A

Langevin equation with space dependent mobility and its discretised form

A.1. Derivation of the general Langevin equation and numerical implementation

According to Gardiner [9] the many variable version of the Fokker Planck equation, which describes the time evolution of the probability density function of a stochast $\mathbf{x}$ is given as

$$\frac{\partial p(\mathbf{x},t|\mathbf{x}_0,t_0)}{\partial t} = -\sum_{i=1}^{n} \partial_i\big(p(\mathbf{x},t|\mathbf{x}_0,t_0)a_i(\mathbf{x})\big) + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \partial_i\partial_j\big(p(\mathbf{x},t|\mathbf{x}_0,t_0)D_{ij}(\mathbf{x})\big), \quad \text{(A-1)}$$

which is related to the stochastic differential equation

$$\mathrm{d}\mathbf{x} = \mathbf{a}(\mathbf{x})\mathrm{d}t + B(\mathbf{x})\mathrm{d}\mathbf{W}, \quad \text{(A-2)}$$

by $D(\mathbf{x}) = B(\mathbf{x})B(\mathbf{x})^T$. The drift vector $\mathbf{a}(\mathbf{x})$ and noise matrix $B(\mathbf{x})$ are obtained by requiring the stationary solution of the FPE $p_s(\mathbf{x})$ to be the Boltzmann distribution

$p_s(\mathbf{x}) = N \exp\left[-\beta\phi(\mathbf{x})\right]$. Setting $\frac{\partial p(\mathbf{x},t|\mathbf{x}_0,t_0)}{\partial t} = 0$ and substitute $p_s(\mathbf{x})$ for $p(\mathbf{x},t|\mathbf{x}_0,t_0)$ in the FPE gives

$$p_s(\mathbf{x})a_i(\mathbf{x}) = \frac{1}{2}\sum_{j=1}^{n}\partial_j\left(p_s(\mathbf{x})D_{ij}(\mathbf{x})\right) \tag{A-3}$$

$$= \frac{1}{2}\sum_{j=1}^{n}\left(D_{ij}(\mathbf{x})\partial_j p_s(\mathbf{x}) + p_s(\mathbf{x})\partial_j D_{ij}(\mathbf{x})\right) \tag{A-4}$$

$$= \frac{1}{2}\sum_{j=1}^{n}\left(-\beta D_{ij}(\mathbf{x})\partial_j\phi(\mathbf{x})p_s(\mathbf{x}) + p_s(\mathbf{x})\partial_j D_{ij}(\mathbf{x})\right) \tag{A-5}$$

$$\rightarrow$$

$$a_i(\mathbf{x}) = \frac{1}{2}\sum_{j=1}^{n}\left(-\beta D_{ij}(\mathbf{x})\partial_j\phi(\mathbf{x}) + \partial_j D_{ij}(\mathbf{x})\right). \tag{A-6}$$

This leads to the following SDE

$$\mathrm{d}\mathbf{x} = \frac{1}{2}\left[-\beta D(\mathbf{x})\nabla\phi(\mathbf{x}) + \nabla D(\mathbf{x})\right]\mathrm{d}t + B(\mathbf{x})\mathrm{d}W(t), \tag{A-7}$$

where $B(\mathbf{x})B^T(\mathbf{x}) = D(\mathbf{x})$ and $\beta^{-1} = k_B T$. After defining $D(\mathbf{x}) = 2k_B T M(\mathbf{x}) = 2k_B T L(\mathbf{x})L^T(\mathbf{x})$ one obtains

$$\mathrm{d}\mathbf{x} = \left[-M(\mathbf{x})\nabla\phi(\mathbf{x}) + k_B T\nabla\cdot M(\mathbf{x})\right]\mathrm{d}t + \sqrt{2k_B T}L(\mathbf{x})\mathrm{d}W(t), \tag{A-8}$$

where the noise term satisfies the fluctuation dissipation theorem. Equation (A-8) is equivalent to the SDE proposed by Hütter and Öttinger [39]

$$\mathrm{d}\mathbf{x} = \left[-M(\mathbf{x})\nabla\Phi(\mathbf{x})\right]\mathrm{d}t + \frac{1}{2}\left[M(\mathbf{x}+\mathrm{d}\mathbf{x})M(\mathbf{x})^{-1} + I\right]\sqrt{2k_B T}L(\mathbf{x})\mathrm{d}W(t). \tag{A-9}$$

This can easily proven by expanding $M(\mathbf{x} + \mathrm{d}\mathbf{x})$ around $\mathbf{x}$ and obeying the rules $\mathrm{d}W\mathrm{d}t = 0$ and $\mathrm{d}W\mathrm{d}W = \mathrm{d}t$.
The discretized form of the SDE proposed by Hütter and Öttinger is given below. The update for $\mathbf{x}_k$ at simulation step k is given as

$$\begin{aligned}\mathbf{x}_{k+1} = {} & \mathbf{x}_k - \frac{1}{2}\left[M(\mathbf{x}_k + \Delta\mathbf{x}_k^p)\nabla\Phi(\mathbf{x}_k + \Delta\mathbf{x}_k^p) + M(\mathbf{x}_k)\nabla\Phi(\mathbf{x}_k)\right]\Delta t \\ & + \frac{1}{2}\left[M(\mathbf{x}_k + \Delta\mathbf{x}_k^p)M^{-1}(\mathbf{x}_k) + I\right]\sqrt{2k_B T}L(\mathbf{x}_k)\Delta W_t,\end{aligned} \tag{A-10}$$

with the corresponding predictor step

$$\Delta \mathbf{x}_k^p = -M(\mathbf{x}_k)\nabla\Phi(\mathbf{x}_k)\Delta t + \sqrt{2k_B T}L(\mathbf{x}_k)\Delta W_t. \tag{A-11}$$

The approximate inverse Hessian $B(\mathbf{x}_k) = B_k$, which is taken as the mobility tensor $M(\mathbf{x}_k)$, can be obtained using the DFP update

$$B_{k+1} = B_k - \frac{B_k \mathbf{y}_k \mathbf{y}_k^T B_k}{\mathbf{y}_k^T B_k \mathbf{y}_k} + \frac{\mathbf{s}_k \mathbf{s}_k^T}{\mathbf{y}_k^T \mathbf{s}_k}, \tag{A-12}$$

where,

$$\mathbf{s}_k = \mathbf{x}_{k+1} - \mathbf{x}_k \quad \text{and} \quad \mathbf{y}_k = \nabla\Phi(\mathbf{x}_{k+1}) - \nabla\Phi(\mathbf{x}_k). \tag{A-13}$$