A. Different free energy concepts and Fixman potentials

The table below shows the various notions of free energy in this thesis and surveys their related Fixman potentials (for a more detailed overview, we refer to Section 3.5). As before $\Phi : \mathbf{R}^n \to \mathbf{R}^k$ is a smooth reaction coordinate, where *smooth* is meant such that the level sets $\Sigma_\xi = \Phi^{-1}(\xi)$ are $\mathcal{C}^2$-submanifolds of codimension k in $\mathbf{R}^n$ for all regular values $\xi \in \mathbf{R}^k$. The Jacobian is abbreviated as $J_\Phi = \mathbf{D}\Phi$. Following the previous nomenclature, $d\sigma$ labels the surface element (or Hausdorff measure) of $\Sigma_\xi \subset \mathbf{R}^n$, whereas $d\mathcal{H}$ denotes the surface element of the phase space submanifold $\Sigma_\xi \times \mathbf{R}^n \subset \mathbf{R}^n \times \mathbf{R}^n$. Note that standard and geometric free energies coincide, if the reaction coordinate is linear in the configurations. In this case also $A = D = F - G$ below.

free energy	second-order system	first-order system	Fixman potential
standard	$F = -\beta^{-1} \ln Z$ with $Z = \int \exp(-\beta H)(\mathrm{vol} J_\Phi)^{-1}\, d\mathcal{H}$	$F = -\beta^{-1} \ln Q$ with $Q = \int \exp(-\beta V)(\mathrm{vol} J_\Phi)^{-1}\, d\sigma$	$D = -\beta^{-1} \ln M\, (= F - G)$ with $M = \frac{1}{Q_\Sigma} \int (\mathrm{vol} J_\Phi)^{-1} \exp(-\beta V) d\sigma$
geometric	$G = -\beta^{-1} \ln Z_\Sigma$ with $Z_\Sigma = \int \exp(-\beta H)\, d\mathcal{H}$	$G = -\beta^{-1} \ln Q_\Sigma$ with $Q_\Sigma = \int \exp(-\beta V)\, d\sigma$	$W = \beta^{-1} \ln \mathrm{vol} J_\Phi$, e.g., $V \mapsto V + W$ for Blue Moon reweighting
optimal prediction	$E = \frac{1}{2} \langle I\eta, \eta \rangle + G$ with $I = \frac{1}{Q_\Sigma} \int J_\Phi^T J_\Phi \exp(-\beta V) d\sigma$		$A = -\beta^{-1} \ln \int \exp(-\beta E) d\eta - G$, where typically $A \neq F - G$
confinement			$U = \beta^{-1} \ln \sqrt{\det K}$, (K s.p.d.) if $K = J_\Phi^T J_\Phi$, then $U = W$

B. Coordinate expressions

We introduce the local coordinate expressions and expressions for the metric tensor that are used throughout this thesis. Let $\Sigma \subset \mathbf{R}^n$ be a smooth submanifold of codimension k in $\mathbf{R}^n$. Recall the definition of the normal bundle over Σ

$$N\Sigma = \{(\sigma, n) \,|\, \sigma \in \Sigma, n \in N_\sigma\Sigma\} \subset \mathbf{R}^n \times \mathbf{R}^n$$

with the natural diffeomorphism of $N\Sigma$ into $\mathbf{R}^n$ given by $\iota : (\sigma, n) \mapsto \sigma + n$. In a sufficiently small tubular neighbourhood $N\Sigma_\varepsilon$ of Σ with $\|n\| < \varepsilon$ we can pull back the Euclidean metric, considering $N\Sigma_\varepsilon$ as our configuration space. Then, given an orthonormal frame $\{n_1(\sigma), \ldots, n_k(\sigma)\}$, we can introduce local coordinates on $N\Sigma_\varepsilon$ by

$$\phi_1 : \mathbf{R}^n \to N\Sigma_\varepsilon,\ (x, y) \mapsto (\sigma(x),\, y^i n_i(\sigma(x)))\,, \tag{B.1}$$

By means of ϕ_1 we can represent any point $(\sigma, n) \in N\Sigma_\varepsilon$ in terms of the bundle coordinates (x, y), hence any point $q \in \mathbf{R}^n$ close to the submanifold Σ. We shall make the arrangement that all coordinates that belong to Σ are indexed by Greek letters $\alpha, \beta, \gamma, \ldots$, whereas the normal coordinates are indexed by Latin letters $i, j, k, \ldots$. Whenever it is necessary, we will use Latin indices $\ldots, l, m, n$ that run over all coordinates which, however, should become clear from the context.

We endow the tangent space $TN\Sigma_\varepsilon$ with the standard bases $\partial/\partial x^\alpha \in T_{\sigma,n}N\Sigma_\varepsilon$ and $\partial/\partial y^i \in T_{\sigma,n}N\Sigma_\varepsilon$ which give rise to local coordinates in the usual way. Let us abbreviate $z = (x, y)$. Then the local coordinate expression of the metric tensor is obtained by pulling back the Euclidean metric by the map $\phi = \iota \circ \phi_1$

$$g_{ij}(z) = \delta_{kl} \frac{\partial \phi^k}{\partial z^i} \frac{\partial \phi^l}{\partial z^j}\,, \quad i, j, k, l = 1, \ldots, n$$

Hence the metric tensor takes the form

$$g(x, y) = \begin{pmatrix} G(x) + C(x, y) & A(x, y) \\ A(x, y)^T & \mathbf{1} \end{pmatrix}. \tag{B.2}$$

where the matrix $G(x) \in \mathbf{R}^{d\times d}$, $d = n-k$ is the metric induced on Σ by restricting the Euclidean metric. Introducing the shorthand $X_\alpha = \partial\sigma/\partial x^\alpha$ for the vectors tangent to Σ, we have $G_{\alpha\beta} = \langle X_\alpha, X_\beta \rangle$. The matrix $C(x, y) \in \mathbf{R}^{d\times d}$ has the entries

$$C_{\alpha\beta} = 2\, y^k \langle dn_k(X_\alpha), X_\beta \rangle + y^k y^l \langle dn_k(X_\alpha), dn_l(X_\beta) \rangle\ ,$$

where $dn(X) = \nabla n \cdot X$ denotes the directional derivative of n along X.[29] Note that we have exploited the symmetry $\langle dn_k(X_\alpha), X_\beta \rangle = \langle X_\alpha, dn_k(X_\beta) \rangle$ in the last equation. Finally the elements of the off-diagonal matrix $A(x, y) \in \mathbf{R}^{d\times k}$ are given by

$$A_{i\beta} = y^j \langle n_i, dn_j(X_\beta) \rangle\ .$$

If the codimension of Σ in $\mathbf{R}^n$ is one, then the metric tensor takes a particularly simple form, and the matrices G, C can be given a nice geometrical meaning:

$$g(x, y) = \begin{pmatrix} G(x)(\mathbf{1} - M(x, y))^2 & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

where M denotes the matrix of the Weingarten map that is associated with the second fundamental form of the embedding $\Sigma \subset \mathbf{R}^n$ (cf. [81, 219]). It is defined by

$$M^\alpha_\gamma = y G^{\alpha\beta} \langle dn_1(X_\beta), X_\gamma \rangle\ .$$

[29] We will also sometimes use the common notation $dn(X) = \nabla_X n$.

The vanishing of the off-diagonal matrix A is related to the fact that the normal connection is identically zero for submanifolds of codimension one. This can be seen by differentiating the expression $\|n_1\|^2 = 1$ along Σ

$$0 = \frac{d}{dt}\|n_1(\sigma(t))\|^2\Big|_{t=0} = 2\,\langle dn_1(X), n_1\rangle\ ,$$

where $\sigma(t)$ is a curve in Σ with tangent X at $t = 0$. More generally, the coefficients $\omega^i_j(X) = \langle dn_i(X), n_j\rangle$ are 1-forms which are called the *normal fundamental forms*. By the same differentiation argument it is easy to check that these 1-forms are skew-symmetric, $\omega^i_j = -\omega^j_i$. For the details the reader is referred to [181, 183].

Hamiltonian and Lagrange function We now state the local expressions of the molecular Lagrangian and the corresponding Hamiltonian. Without loss of generality we set the atomic masses to unity. The Lagrangian $L : TN\Sigma_\varepsilon \to \mathbf{R}$ is considered first:

$$L(\sigma, n, \dot\sigma, \dot n) = \frac{1}{2}\,\langle(\dot\sigma, \dot n), (\dot\sigma, \dot n)\rangle - V(\sigma, n)\,.$$

Note that this is the ordinary Lagrangian (2.1) with $M = \mathbf{1}$, where the inner product of tangent vectors in $TN\Sigma_\varepsilon$ is defined by

$$\langle(X, Y), (X', Y')\rangle = \langle X + Y, X' + Y'\rangle\ ,$$

where $\langle\cdot,\cdot\rangle$ is the usual inner product in $\mathbf{R}^n$. The local coordinate expression of L is

$$L(x, y, \dot x, \dot y) = \frac{1}{2}\,\big\langle g(x, y)\cdot(\dot x, \dot y)^T, (\dot x, \dot y)\big\rangle - V(x, y)\,, \tag{B.3}$$

where $V(x, y) = V(\sigma(x) + y^i n_i(\sigma(x)))$, and the metric tensor (B.2) can be written as

$$g = \begin{pmatrix} G + C & A \\ A^T & \mathbf{1}\end{pmatrix} = P\cdot\begin{pmatrix} G + C - AA^T & \mathbf{0} \\ \mathbf{0} & \mathbf{1}\end{pmatrix}\cdot P^T$$

with the matrix

$$P = \begin{pmatrix} \mathbf{1} & A \\ \mathbf{0} & \mathbf{1}\end{pmatrix}\,.$$

The inverse metric tensor then takes the form

$$g^{-1} = P^{-T}\cdot\begin{pmatrix} (G + C - AA^T)^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1}\end{pmatrix}\cdot P^{-1}$$

with the inverse of P,

$$P^{-1} = \begin{pmatrix} \mathbf{1} & -A \\ \mathbf{0} & \mathbf{1}\end{pmatrix}\,.$$

Defining the conjugate momenta to (x, y) by

$$\begin{aligned} u_\alpha &= \frac{\partial L}{\partial \dot x^\alpha}\,, \quad \alpha = 1, \ldots, d \\ v_i\ &= \frac{\partial L}{\partial \dot y^i}\,, \quad i = 1, \ldots, k\,. \end{aligned}$$

we obtain the Hamiltonian as the Legendre transform of L

$$H(x, y, u, v) = \frac{1}{2}\,\big\langle g(x, y)^{-1}\cdot(u, v)^T, (u, v)\big\rangle + V(x, y)\,. \tag{B.4}$$

Calculation of the Christoffel symbols Our averaging results rely on local coordinates. Hence we need to compute the (symmetric) Christoffel symbols

$$\Gamma^i_{jk} = \frac{1}{2} g^{il} \left(\frac{\partial g_{jl}}{\partial z^k} + \frac{\partial g_{kl}}{\partial z^j} - \frac{\partial g_{jk}}{\partial z^l} \right)$$

with $z = (x, y)$. Since we can assume that all curves $(\sigma(t), n(t))$ stay close to Σ it makes sense to consider only terms up to zeroth order in y (linear terms have mean zero anyway). At $y = 0$ the first $\alpha \leq n - k$ Christoffel symbols read

$$\begin{aligned} \Gamma^\alpha_{\beta\gamma} &= \frac{1}{2} G^{\alpha\delta} \left(\frac{\partial G_{\beta\delta}}{\partial x^\gamma} + \frac{\partial G_{\gamma\delta}}{\partial x^\beta} - \frac{\partial G_{\beta\gamma}}{\partial x^\delta} \right) \\ \Gamma^\alpha_{i\beta} &= G^{\alpha\gamma} S^i_{\gamma\beta} \\ \Gamma^\alpha_{ij} &= 0 \,, \end{aligned} \tag{B.5}$$

where $\Gamma^\alpha_{\beta\gamma}$ are simply the Christoffel symbols that are associated with the metric G on the surface Σ. The symmetric matrix that is associated with the second fundamental form in the local coordinate basis $X_\alpha = \partial\sigma/\partial x^\alpha$ has the entries

$$S^i_{\gamma\beta} = \langle dn_i(X_\gamma), X_\beta] \rangle \ .$$

The remaining Christoffel symbols for the normal coordinates ($i \leq k$) are given by

$$\begin{aligned} \Gamma^i_{\alpha\beta} &= -S^i_{\alpha\beta} \\ \Gamma^i_{j\alpha} &= \frac{1}{2} \left(\omega^j_{i\alpha} - \omega^i_{j\alpha} \right) \\ \Gamma^i_{jk} &= 0 \,. \end{aligned} \tag{B.6}$$

Notice that $\Gamma^i_{j\alpha}$ is skew-symmetric in the upper and lower indices, as follows from the definition of the skew-symmetric coefficients of the normal connection

$$\omega^i_{j\alpha} = \langle dn_i(X_\alpha), n_j \rangle \ .$$

C. More coordinate expressions and the mean curvature vector

We first address the problem how to parametrize the constraint manifold. A submanifold Σ of $\mathbf{R}^n$ defined by the vector-valued equation $\Phi(q) = 0$ is properly immersed, if $\mathbf{D}\Phi$ has maximum rank, i.e., is non-singular almost everywhere on the surface [182, 243]. According to Sard's Lemma [174] this can be guaranteed by choosing $\Phi : \mathbf{R}^n \to \mathbf{R}^k$, such that it belongs to the class $\mathcal{C}^{n-k+1}(\mathbf{R}^n)$. Then the points, at which $\mathbf{D}\Phi$ is rank-deficient, form a set of measure zero in $\mathbf{R}^{n-k}$, and the level sets $\Phi^{-1}(\xi)$ are regular submanifolds of codimension k in $\mathbf{R}^n$. The following Lemma holds:

Lemma C.1. *Let $q^* \in \Sigma$ be any non-singular point, and let $U_\delta(q^*)$ denote a sufficiently small tubular δ-neighbourhood including that point. Then there is a parametrization of Σ in $U_\delta(q^*)$ given by $\{q^1, \ldots, q^{n-k}; f^1, \ldots, f^k\}$ that is an embedding, where $f : \mathbf{R}^{n-k} \to \mathbf{R}^k$ is the local inverse of Φ as defined by $q^{n-k+l} = f^l(q^1, \ldots, q^{n-k})$.*

Proof. Let q^* be a non-singular point of Σ, and consider the square $k \times k$ minor K of $\mathbf{D}\Phi$ which is made by, say, cropping the Jacobian's first $n - k$ columns. Suppose $\det K \neq 0$ at $q^* \in \Sigma$. Then the *Implicit Function Theorem* guarantees that we can locally solve the equation $\Phi(q) = 0$ for the vector $(q^{n-k+1}, \ldots, q^n)$, obtaining smooth functions of the remaining coordinates. Let these function be denoted by

$q^{n-k+l} = f^l(q^1, \ldots, q^{n-k})$, such that $\Phi(q^1, \ldots, q^{n-k}; f^1, \ldots, f^k) = 0$. Consequently $\sigma = (q^1, \ldots, q^{n-k}; f^1, \ldots, f^k)^T$ is an immersion and moreover by the Inverse Function Theorem and smoothness of f an embedding of Σ into $\mathbf{R}^n$. □

Note that the specific choice of K does not affect our considerations, for we can always choose a different parametrization $\tilde{\sigma}$, with any k coordinates q^l being functions of the remaining $n-k$ coordinates. For instance if Φ is of class $\mathcal{C}^\infty$, then so are the transition functions $\psi = \sigma \circ \tilde{\sigma}^{-1}$. Thus Σ will be globally smooth.

Hence we can define local coordinates $\{x^1, \ldots, x^{n-k}\}$ with $x^\alpha = q^\alpha$ for $\alpha = 1, \ldots, n-k$, such that $\sigma = \sigma(x)$ is an embedding $\Sigma \subset \mathbf{R}^n$. Then we obtain from implicit differentiation of the equality $\Phi(x^1, \ldots, x^{n-k}; f^1, \ldots, f^k) = 0$

$$d\Phi = \left(\frac{\partial \Phi}{\partial x^\alpha} + \frac{\partial \Phi}{\partial f^l} \frac{\partial f^l}{\partial x^\alpha} \right) dx^\alpha = 0\,, \quad (f^l = q^{n-k+l})$$

where the sum is taken over $\alpha = 1, \ldots, n-k$ and $i = 1, \ldots, k$. Since the 1-forms dx^α are linearly independent, we demand that each of the brackets vanishes. For convenience we may bring the last equation into matrix vector form. We have

$$\mathbf{D}f = -(\mathbf{D}_2\Phi)^{-1}\mathbf{D}_1\Phi\,.$$

Here we used the symbol $\mathbf{D}_1$ to denote the derivative with respect to the first $n-k$ coordinates and $\mathbf{D}_2$ for the remaining slot. Clearly $K = \mathbf{D}_2\Phi$ is the invertible $k \times k$ minor of $\mathbf{D}\Phi$. In particular in the codimension $k = 1$ case, we can explicitly assert $\mathbf{D}f = -(\partial\Phi/\partial q^n)^{-1}\mathbf{D}_1\Phi$. Finally we obtain the restriction of the Euclidean metric to Σ as the metric that is induced by the embedding of Σ into $\mathbf{R}^n$,

$$G_{\alpha\gamma} = \langle \partial\sigma/\partial x^\alpha, \partial\sigma/\partial x^\gamma \rangle = \delta_{\alpha\gamma} + \sum_l \frac{\partial f^l}{\partial x^\alpha} \frac{\partial f^l}{\partial x^\gamma}$$

which can be equivalently written in the form

$$G = \mathbf{1} + (\mathbf{D}_1\Phi)^T(\mathbf{D}_2\Phi)^{-T}(\mathbf{D}_2\Phi)(\mathbf{D}_1\Phi)\,.$$

Mean curvature vector The map $\Phi : \mathbf{R}^n \to \mathbf{R}^k$ with the rank of $\mathbf{D}\Phi$ equal to k defines a foliation of $\mathbf{R}^n$ of codimension k by the collection of all connected components $\Sigma_\xi = \Phi^{-1}(\xi)$, where ξ varies throughout $\mathbf{R}^k$. In the calculation of the optimal prediction equations in Section 3.3.1 we have utilized a relation between the variation of the surface element $d\sigma_\xi$ with ξ and the components of the mean curvature vector of the leaf Σ_ξ. The justification is given now:

For each regular ξ value consider the normal bundle over $\Sigma = \Sigma_\xi$. We have seen in Appendix B that in a sufficiently small tubular neighbourhood we can pull back the Euclidean metric to the normal bundle $N\Sigma$. Using bundle coordinates (x, y) the pulled-back metric takes the form (B.2), viz.,

$$g(x,y) = \begin{pmatrix} G(x) + C(x,y) & A(x,y) \\ A(x,y)^T & \mathbf{1} \end{pmatrix}.$$

where the matrix G is the metric induced on Σ by the embedding. By

$$dV = \sqrt{\det g(x,y)}dxdy$$

we define the volume element on $N\Sigma$. Since $g(x,0) = G(x) \otimes \mathbf{1}$ the surface element $d\sigma_\xi = \sqrt{\det G_\xi(x)}dx$ of Σ in can be expressed accordingly as

$$d\sigma_\xi = \sqrt{\det g(x,0)}dx$$

where the subscript ξ is used to indicate the implicit dependence of the surface metric on the foliation parameter ξ (on the other hand, $g(x,0) = G(x) \otimes \mathbf{1}$ without subscript, since the normal coordinate $y = 0$ takes over the role of the parameter ξ).

Given an orthonormal frame $\{n_1(\sigma), \dots, n_k(\sigma)\}$ for the normal bundle we can write the map Φ in terms of the bundle coordinates $\Phi(x,y) - \xi = (J_\Phi^T Q)(\sigma(x))y$, where $Q \in \mathbf{R}^{n\times k}$ is the matrix $(n_1, \dots, n_k)$, and $J_\Phi = \mathbf{D}\Phi$ denotes the Jacobian. By chain rule we can evaluate the derivative of the surface metric G_ξ

$$\frac{\partial}{\partial \xi^i}\sqrt{\det G_\xi(x)} = (J_\Phi^T Q)^{ij}\frac{\partial}{\partial y^j}\sqrt{\det g(x,0)}\,.$$

Here $(J_\Phi^T Q)^{ij}$ are the elements of the inverse matrix $(J_\Phi^T Q)^{-1}$. Taking advantage of the identity $(\det g)' = \det g \cdot \operatorname{tr}(g^{-1}g')$ we find

$$\begin{aligned}\frac{\partial}{\partial \xi^i}\sqrt{\det G_\xi} &= \frac{1}{2}(J_\Phi^T Q)^{ij}\operatorname{tr}\left(g(x,0)^{-1}\left.\frac{\partial g}{\partial y^j}\right|_{y=0}\right)\sqrt{\det g(x,0)}\\ &= -(J_\Phi^T Q)^{ij}\operatorname{tr}\left(G^{-1}\mathfrak{S}_j\right)\sqrt{\det G}\,.\end{aligned}$$

From the particular form of the metric $g(x,y)$ we can conclude that $G^{-1}\mathfrak{S}_j$ with $\mathfrak{S}_j = -P_T dn_j(\cdot)$ are the matrices of the Weingarten maps with respect to the local basis of the tangent vectors $\partial\sigma/\partial x^\alpha \in T_\sigma\Sigma$, where $P_T : T_\sigma\mathbf{R}^n \to T_\sigma\Sigma$ is the tangential projection. The trace gives the negative components of the mean curvature vector

$$H(\sigma(x)) = \sum_{i=1}^{s}\kappa_i(x)n_i(x)\,,\quad \kappa_i = -\operatorname{tr}(G^{-1}\mathfrak{S}_i)\,,$$

with respect to the normal coordinates $y^1, \dots, y^k$ (or the respective normal frame). Accordingly $\partial_i\sqrt{\det G_\xi} = (J_\Phi Q)^{ij}\kappa_j$ is the mean curvature with respect to the foliation $\Phi^{-1}(\xi)$. The dependence on Φ via the Jacobian does not come as a surprise, since, as is known, the mean curvature is an extrinsic curvature measure.

D. A co-area formula for Dirac's delta function

We briefly outline how to write the conditional probability (3.6) as an ordinary surface integral (3.7). Some definitions first: a function $f : \mathbf{R}^n \to \mathbf{R}$ is *quickly decaying* if

$$\lim_{\|z\|\to\infty} z^\alpha f(z) = 0\,,\quad \forall\alpha \in \mathbf{N}_0\,,$$

where z^α is declared component-wise [306]. Then the space of quickly decaying functions $f \in \mathcal{C}^\infty(\mathbf{R}^n)$ with quickly decaying derivatives is called Schwartz space and is denoted by $\mathscr{S}(\mathbf{R}^n)$. Let $\Phi : \mathbf{R}^n \to \mathbf{R}^k$ be a smooth function, such that the fibres $\Sigma_\xi = \Phi^{-1}(\xi)$ are smooth submanifolds of codimension k in $\mathbf{R}^n$. Then for any function $f \in \mathscr{S}(\mathbf{R}^n)$ we define the Dirac measure $\delta(\Phi(z) - \xi)$ by

$$\int_{\mathbf{R}^n} f(z)\delta(\Phi(z) - \xi)\,dz = \int_{\Sigma_\xi} f\,(\operatorname{vol}J_\Phi)^{-1}\,d\sigma_\xi\,. \tag{D.1}$$

Here $J_\Phi = \mathbf{D}\Phi$ denotes the Jacobian of Φ, and $d\sigma_\xi$ is the Hausdorff measure (surface element) of $\Sigma_\xi \subset \mathbf{R}^n$. The matrix volume for the rectangular matrix J_Φ is given by

$$\operatorname{vol}J_\Phi(z) = \sqrt{\det J_\Phi^T(z)J_\Phi(z)}$$

Without loss of generality we set $\xi = 0$ and omit the argument ξ from now on. In order to show that the definition (D.1) makes sense let us introduce a non-negative function

$\varphi : \mathbf{R}^k \to \mathbf{R}$ that has compact support and which satisfies $\varphi(0) > 0$. Moreover for $\varepsilon > 0$ we define the family of functions $\delta_\varepsilon(y) = \varepsilon^{-1}\varphi(\varepsilon^{-1}y)$. The following is standard: for a test function $h \in \mathscr{S}(\mathbf{R}^k)$ we introduce the Dirac distribution $\delta(y)$ by

$$\lim_{\varepsilon\to 0}\int_{\mathbf{R}^k} \delta_\varepsilon(y)h(y)\,dy = \int_{\mathbf{R}^k} h(y)\delta(y)\,dy\,,$$

where the rightmost integral is defined as the point evaluation [307]

$$h(0) = \int_{\mathbf{R}^k} h(y)\delta(y)\,dy\,.$$

Here we face a slightly different problem: Using (D.1) we have to show that

$$\lim_{\varepsilon\to 0}\int_{\mathbf{R}^n} \delta_\varepsilon(\Phi(z))f(z)\,dz = \int_{\mathbf{R}^n} f(z)\delta(\Phi(z))\,dz\,. \tag{D.2}$$

By definition, the support of δ_ε shrinks as ε goes to zero. Therefore we can restrict the integration domain to a tubular neighbourhood $N\Sigma_\varepsilon$ of Σ with local coordinates given by the map $\phi(x,y) = \sigma(x) + y^i n_i(\sigma(x))$. Hence we have

$$\begin{aligned}\lim_{\varepsilon\to 0} &\int_{N\Sigma_\varepsilon\cap\mathbf{R}^n} \delta_\varepsilon(\Phi(z))f(z)\,dz \\ &= \lim_{\varepsilon\to 0}\int_{\mathbf{R}^n} f(x,y)\delta_\varepsilon(B(x)y)\,\sqrt{g(x,y)}dxdy\end{aligned}$$

with the abbreviation $\sqrt{g} = \sqrt{\det g}$. Note that we have used the somehow abusive notation $f(x,y)$ for the pull-back $(f\circ\phi)(x,y))$. The matrix $B = Q^T J_\Phi \in \mathbf{R}^{k\times k}$ with $Q = (n_1,\ldots,n_k)$ stems from the local representation of $(\Phi\circ\phi)(x,y) = B(x)y$. We introduce a new variable ζ by setting $\zeta = B(x)y$. Thus by the above definition of the Dirac distribution $\delta(\zeta)$ the last equation becomes

$$\begin{aligned}\lim_{\varepsilon\to 0} &\int_{\mathbf{R}^n} f(x,B(x)^{-1}\zeta)\delta_\varepsilon(\zeta)(\det B(x))^{-1}\,\sqrt{g(x,B(x)^{-1}\zeta)}dxd\zeta \\ &= \int_{\mathbf{R}^n} f(x,B(x)^{-1}\zeta)\delta(\zeta)(\det B(x))^{-1}\,\sqrt{g(x,B(x)^{-1}\zeta)}dxd\zeta \\ &= \int_{\mathbf{R}^{n-k}} f(x,0)(\det B(x))^{-1}\,\sqrt{g(x,0)}dx\,,\end{aligned}$$

It follows from the particular form of the metric (B.2) that $\sqrt{g(x,0)} = \sqrt{G(x)}$, where G is the metric of Σ. Observing further that $\det B(x) = \mathrm{vol}J_\Phi(\sigma(x))$ we obtain

$$\lim_{\varepsilon\to 0}\int_{N\Sigma_\varepsilon\cap\mathbf{R}^n} \delta_\varepsilon(\Phi(z))f(z)\,dx = \int_\Sigma f\,(\mathrm{vol}J_\Phi)^{-1}\,d\sigma\,,$$

which gives the assertion (D.2). We conclude by noting that the definition (D.1) is independent of the choice of any compactly supported function φ.

E. Three-scale problems

The common structure of the systems considered in Section 6 is that they involve three time scales rather than two time scales as in typical slow-fast systems. Hence we consider a generic three-scale system (for simplicity we assume that $(x,y) \in \mathbf{R}\times\mathbf{R}$)

$$\begin{aligned}\dot{x}_\epsilon(t) &= \frac{1}{\epsilon}f(x_\epsilon(t),y_\epsilon(t)) + g(x,y) \\ \dot{y}_\epsilon(t) &= -\frac{1}{\epsilon^2}h(x_\epsilon(t),y_\epsilon(t)) + \frac{\sigma}{\epsilon}\,\dot{W}_2(t)\end{aligned} \tag{E.1}$$

which is basically the former slow-fast system after a rescaling of time according to $t \mapsto t/\epsilon$, such that the right hand side of the slow equation has the same order of magnitude as the diffusion term in the fast equation [23, 34]; see also [308, 298].

In order to derive the limit equation for $\epsilon \to 0$, we shall employ a perturbation-like argument. To this end consider the backward equation associated with (E.1):

$$\partial_t v^\epsilon(x,y,t) = \mathcal{A}^\epsilon v^\epsilon(x,y,t) \tag{E.2}$$

with

$$\mathcal{A}^\epsilon = \epsilon^{-2}\mathcal{A}_1 + \epsilon^{-1}\mathcal{A}_2 + \mathcal{A}_3\,,$$

and the three generators

$$\begin{aligned}\mathcal{A}_1 &= \frac{\sigma^2}{2}\partial_y^2 + g(x,y)\partial_y \\ \mathcal{A}_2 &= f(x,y)\partial_x \\ \mathcal{A}_3 &= g(x,y)\partial_x\,.\end{aligned}$$

Suppose that the fast process, generated by $\mathcal{A}_1$, has a unique invariant measure $\mu_x(dy) = \rho(x,y)dy$, where the density ρ satisfies $\mathcal{A}_1\rho = 0$.

We expand the solution of the backward equation into a perturbation series according to $v^\epsilon = v_0 + \epsilon v_1 + \epsilon^2 v_2 + \dots$ choosing an initial density $v^\epsilon(x,y,0) = v^\epsilon(x,0)$ that only depends on the slow variable [35]. Plugging v^ϵ into (E.2) equating powers of ϵ yields a hierarchy of equations, the first three of which are

$$\epsilon^{-2} : \mathcal{A}_1 v_0 = 0\,, \tag{E.3}$$

$$\epsilon^{-1} : \mathcal{A}_1 v_1 = -\mathcal{A}_2 v_0\,, \tag{E.4}$$

$$\epsilon^{0} \;\; : \mathcal{A}_1 v_2 = \partial_t v_0 - \mathcal{A}_2 v_1 - \mathcal{A}_3 v_0\,. \tag{E.5}$$

As the operator $\mathcal{A}_1$ acts on function in the fast variable only, and its kernel is one-dimensional, we can conclude that v_0 depends on x only. In order to unveil the lowest order time evolution (E.5) we define the projection $\Pi : L^2(\mu_x) \to \ker(\mathcal{A}_1) \subset L^2(\mu_x)$ onto the nullspace of $\mathcal{A}_1$ as the map

$$(\Pi u)(x) = \int u(x,y)\mu_x(\mathrm{d}y)\,. \tag{E.6}$$

In fact Π is the conditional expectation with respect to $\mu_x(\mathrm{d}y)$. We address the next equation (E.4). For it to be uniquely solvable in $L^2(\mu_x)$, it is helpful to see that [309]

$$u \in \operatorname{ran}\mathcal{A}_1 \quad\Longleftrightarrow\quad u \in (\ker\mathcal{A}_1)^\perp \quad\Longleftrightarrow\quad \Pi u = 0\,.$$

Hence orthogonality to the kernel amounts to averaging of $\mathcal{A}_2 v_0$ to zero under the fast dynamics, which can be equivalently expressed by $\Pi\mathcal{A}_2\Pi = 0$, because the kernel of $\mathcal{A}_1$ is one-dimensional. If the centering condition (6.11) holds, this condition is clearly satisfied, such that we can invert $\mathcal{A}_1$ on the second equation:

$$v_1 = -\mathcal{A}_1^{-1}\mathcal{A}_2 v_0\,.$$

If we insert this expression into the evolution equation (E.5), and apply the orthogonal projection onto the nullspace of $\mathcal{A}_1$, we obtain the diffusive limit equation

$$\partial_t v_0(x,t) = \bar{\mathcal{A}} v_0(x,t) \quad \text{with} \quad \bar{\mathcal{A}} = \Pi\mathcal{A}_3\Pi - \Pi\mathcal{A}_2\mathcal{A}_1^{-1}\mathcal{A}_2\Pi\,. \tag{E.7}$$

In view of the fact that $\mathcal{A}_2$ and $\mathcal{A}_3$ are first-order differential operator, and $\mathcal{A}_1$ does not involve any x-derivatives at all, we can interpret the last equation again as a backward equation in $L^1(\mathrm{d}x)$ with a generator that can be cast into standard form

$$\bar{\mathcal{A}} = A(x)\partial_x^2 + B(x)\partial_x\,,$$

and to which the following Itô stochastic differential equation is associated [33]

$$\dot{x}(t) = B(x(t)) + \sqrt{2A(x(t))}\dot{W}(t)\,.$$

We will show below how the coefficients A, B are to be computed. Generally speaking, the procedure works by solving (E.4) which is an ordinary differential equation:

$$\mathcal{A}_1^{-1}\mathcal{A}_2 v_0 = \mathcal{A}_1^{-1} f(x,y)\partial_x v_0 =: w(x,y)\partial_x v_0\,,$$

where the function $w(x,y)$ solves the *cell problem*

$$\mathcal{A}_1 w(x,y) = f(x,y) \quad \text{with} \quad w(x,\cdot) \in (\ker \mathcal{A}_1)^\perp\,. \tag{E.8}$$

Note that the initial conditions and the respective integration constants of the cell problem are chosen such that $w(x,\cdot)$ does not lie in the nullspace of $\mathcal{A}_1$. Solving the equation subject to consistent initial conditions, $\bar{\mathcal{A}}$ can be written as

$$\begin{aligned}\bar{\mathcal{A}} v_0 = &-\int f(x,y) w(x,y) \mu_x(dy)\, \partial_x^2 v_0 \\ &+ \int \left(g(x,y) - f(x,y)\partial_x w(x,y)\right) \mu_x(dy)\, \partial_x v_0\end{aligned} \tag{E.9}$$

using the definition of the conditional expectation with respect to μ_x. It remains to show that the covariance matrix of the diffusion is positive definite. Indeed by means of (E.8) the first term under the integral can be rewritten as the quadratic expression

$$f(x,y)w(x,y) = w(x,y)\mathcal{A}_1 w(x,y)\,,$$

which is strictly negative, since the spectrum of $\mathcal{A}_1$, considered on functions that are orthogonal to the kernel of $\mathcal{A}_1$, lies entirely on the negative real axis.

Integral representation of the averaged generator Extracting the coefficients a, b by solving the cell problem (E.8) may not be possible in general. An alternative approach [25] uses an explicit integral representation $\mathcal{A}^{-1}$. Thus let $g(x,\cdot)$ be orthogonal to the kernel of $L^2(\mu_x)$, i.e., $\Pi g = 0$. Then the function

$$G(x,y) = -\int_0^\infty \exp(t\mathcal{A}_1) g(x,y)\, dt$$

is an integral representation of $\mathcal{A}_1^{-1} g$, for

$$\begin{aligned}\mathcal{A}_1 G &= -\int_0^\infty \mathcal{A}_1 \exp(t\mathcal{A}_1) g\, dt \\ &= -\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}t} \exp(t\mathcal{A}_1) g\, dt \\ &= (1 - \lim_{t\to\infty} \exp(t\mathcal{A}_1)) g\,,\end{aligned}$$

and $\mathcal{A}_1$ is negative-definite for all functions $g \in (\ker \mathcal{A}_1)^\perp$. Hence $\exp(t\mathcal{A}_1) \to 0$ and

$$w(x,y) = -\int_0^\infty \exp(t\mathcal{A}_1) f(x,y)\, dt\,,$$

which gives upon substitution into (E.9)

$$\begin{aligned}\bar{\mathcal{A}} v_0 = &\int f(x,y) \int_0^\infty \exp(t\mathcal{A}_1) f(x,y)\, dt\, \mu_x(dy)\, \partial_x^2 v_0 \\ &+ \int f(x,y)\, \partial_x \int_0^\infty \exp(t\mathcal{A}_1) f(x,y)\, dt\, \mu_x(dy)\, \partial_x v_0 \\ &+ \int g(x,y)\, \mu_x(dy)\, \partial_x v_0\,.\end{aligned}$$

Exploiting the semigroup property of $\exp(t\mathcal{A}_1)$ the coefficients become

$$A(x) = \int f(x,y) \int_0^\infty \mathbf{E}_y f(x, y_x(t))\, dt\, \mu_x(dy)$$
$$B(x) = \int \left(g(x,y) + f(x,y) \int_0^\infty \mathbf{E}_y \partial_x f(x, y_x(t))\, dt \right) \mu_x(dy)\,,$$

where $y_x(t)$ denotes the fast process at time t starting at $y_x(0) = y$, and $\mathbf{E}_y$ labels the average over all realizations up to time t conditional on the initial value y.

F. Van Kampen's approximation

We shall demonstrate how studying the normalized deviations leads to a three-scale problem of the type (E.1). To this end consider the scaled deviation

$$\xi_\epsilon(t) = \frac{x_\epsilon(t) - x(t)}{\sqrt{\epsilon}}\,. \tag{F.1}$$

For the sake of convenience we restrict our attention to the case $\xi_\epsilon \in \mathbf{R}$. We augment the system (6.1) by the (redundant) differential equation (6.3) for ξ_ϵ. In other words, we replace (6.1) by the joint system for $(x, \xi_\epsilon, y_\epsilon) \in \mathbf{R} \times \mathbf{R} \times \mathbf{R}$:

$$\begin{aligned}
\dot{x} &= -\partial_x G(x) + \sigma \dot{W}_1 \\
\dot{\xi}_\epsilon &= -\frac{1}{\sqrt{\epsilon}} \partial_x \left(V(x, y_\epsilon) - G(x) \right) - \partial_x^2 V(x, y_\epsilon) \xi_\epsilon + \mathcal{O}(\epsilon^\infty) \\
\dot{y}_\epsilon &= -\frac{1}{\epsilon} \partial_y V(x, y_\epsilon) + \frac{\sigma}{\sqrt{\epsilon}}\, \dot{W}_2\,.
\end{aligned}$$

Clearly the averaged equation for x is decoupled from the rest, but we keep it, since otherwise the system would become time inhomogeneous. The associated backward equation then has the form

$$\partial_t u^\epsilon(x, \xi, y, t) = \mathcal{A}^\epsilon u^\epsilon(x, \xi, y, t)$$

with

$$\mathcal{A}^\epsilon = \epsilon^{-1} \mathcal{A}_1 + \epsilon^{-1/2} \mathcal{A}_2 + \mathcal{A}_3\,,$$

where the single generators are given by

$$\begin{aligned}
\mathcal{A}_1 &= \frac{\sigma^2}{2} \partial_y^2 - \partial_y V(x,y) \partial_y \\
\mathcal{A}_2 &= -\partial_x \left(V(x,y) - G(x) \right) \partial_\xi \\
\mathcal{A}_3 &= \frac{\sigma^2}{2} \partial_x^2 - \left(\partial_x V(x,y) + \partial_x^2 V(x,y) \xi \right) \partial_x\,.
\end{aligned}$$

In contrast to the previous section the nullspace of $\mathcal{A}_1$ now consists of function that depend on x as well as ξ (the slow coordinates). Accordingly the projection $\Pi : L^2(\mu_x) \to \ker \mathcal{A}_1$ maps to functions $g(x, \xi)$. Quite remarkably the operator $\mathcal{A}_2$ meets the solvability condition $\Pi \mathcal{A}_2 \Pi = 0$. The powers of $\sqrt{\epsilon}$ in the backward equation suggests that we shall expand its solution as follows

$$u^\epsilon = u_0 + \sqrt{\epsilon} u_{1/2} + \epsilon u_1 + \dots\,.$$

Equating powers of $\sqrt{\epsilon}$ yields a hierarchy of equations, the first three of which are

$$\begin{aligned}
\epsilon^{-1} &: \mathcal{A}_1 u_0 = 0\,, \\
\epsilon^{-1/2} &: \mathcal{A}_1 u_{1/2} = -\mathcal{A}_2 u_0\,, \\
\epsilon^{0} &: \mathcal{A}_1 u_1 = \partial_t u_0 - \mathcal{A}_2 u_{1/2} - \mathcal{A}_3 u_0\,.
\end{aligned}$$

Repeating the procedure from the last section taking into account the solvability condition and the fact that the projection Π commutes with the Ornstein-Uhlenbeck generator $\mathcal{A}_3$ gives the familiar limit equation

$$\partial_t u_0 = \bar{\mathcal{A}} u_0 \quad \text{with} \quad \bar{\mathcal{A}} = -\Pi \mathcal{A}_2 \mathcal{A}_1^{-1} \mathcal{A}_2 \Pi + \Pi \mathcal{A}_3 \Pi \,.$$

By running through the calculation from the last section, Appendix E, it can be shown that the term containing $\mathcal{A}_1^{-1}$ yields the diffusion expression for the normalized deviation ξ without further drift (see below), whereas the rightmost term yields the averaged equation for the slow variable x and the drift $G''(x)\xi$ of the error. That is, $\bar{\mathcal{A}}$ turns out out to be the generator of the skew system (6.6).

Calculation of the diffusion coefficient Consider the family of cell problems (E.8) for functions $w(x, \xi, \cdot) \in (\ker \mathcal{A}_1)^\perp$. In particular we take a look at

$$f(x, \xi, y) = -\frac{\partial}{\partial x} \left(\frac{\lambda(x)^2}{2} y^2 - \frac{\sigma^2}{2} \ln \lambda(x) \right)$$

from Example 6.1 above. The cell problem is then independent of ξ,

$$\frac{\sigma^2}{2} \frac{d^2 w}{dy^2} - y\lambda(x)^2 \frac{dw}{dy} + \left(y^2 \lambda'(x)\lambda(x) - \frac{\sigma^2}{2} \frac{\lambda'(x)}{\lambda(x)} \right) = 0 \,.$$

Hence $w(x, \xi, y) = w(x, y)$. The solution of the homogeneous problem is easily found:

$$w_0(x, y) = C_2(x) + \frac{\sigma\sqrt{\pi}}{2} \frac{C_1(x)}{\lambda(x)} \mathrm{Erfi}\left[\frac{\lambda(x) y}{\sigma} \right] ,$$

where C_1, C_2 are integration constants, that may or may not depend on the slow variable x, and $\mathrm{erfi}[z]$ is the *complex error function* that is defined by

$$\mathrm{erfi}[z] = -i \,\mathrm{erf}[iz] \quad \text{with} \quad \mathrm{erf}[z] = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\zeta^2)\, d\zeta \,.$$

Variation of constants including the solvability condition (6.11) finally leads to

$$w(x, y) = C_2(x) + \frac{\sigma\sqrt{\pi}}{2} \frac{C_1(x)}{\lambda(x)} \mathrm{Erfi}\left[\frac{\lambda(x) y}{\sigma} \right] + \frac{1}{2} \frac{\lambda'(x)}{\lambda(x)} y^2 \,, \tag{F.2}$$

where the integration constant $C_1(x)$ is arbitrary, and $C_2(x)$ is determined by the requirement $\Pi w = 0$. That is, $C_2(x)$ is found to be

$$C_2(x) = -\frac{\sigma^2}{4} \frac{\lambda'(x)}{\lambda(x)^3} \,.$$

Intriguingly the solvability condition does not rely on $C_1(x)$ at all. For this reason we may fix $C_1 \equiv 0$ without any loss of generality. In fact, the computed coefficients do not depend on $C_1(x)$ anyway. By this we obtain the diffusion coefficient in (6.9),

$$A(x) = -\int f(x, y) w(x, y) \mu_x(dy) = \frac{\sigma^4}{4} \left(\frac{\lambda'(x)}{\lambda(x)^2} \right)^2 . \tag{F.3}$$

Remark F.1. *Consider again the problem of inverting $\mathcal{A}_1$. Clearly the result of this operation is defined only up to functions that vanish under the action of $\mathcal{A}_1$,*

$$v_1 = \mathcal{A}_1^{-1} \mathcal{A}_2 v_0 + \zeta \quad \textit{with} \quad \zeta \in \ker \mathcal{A}_1 \,,$$

where the additional function ζ accounts for the indeterminacy of inverting $\mathcal{A}_1$. Gladly this does not change the diffusive limit equation as long as the solvability condition

$\Pi\mathcal{A}_2\Pi = 0$ *is met, for then also* $\Pi\mathcal{A}_2\zeta = 0$*, and so the indeterminacy disappears from the effective equation. See also [85].*

However we have to be very careful in relaxing the centering condition (6.11). To see what can happen consider the cell problem, and do not assume that $\mathcal{A}_2 v_0$ *be orthogonal to the kernel of* $\mathcal{A}_1$*; but then projecting equation (E.4) to the nullspace of* $\mathcal{A}_1$ *yields a contradiction, for* $\Pi\mathcal{A}_1 = \mathcal{A}_1\Pi$ *and therefore*

$$0 = \Pi\mathcal{A}_1 v_1 = \Pi\mathcal{A}_2 v_0 \neq 0\,.$$

Of course the solvability condition $\Pi\mathcal{A}_2\Pi = 0$ *is somehow weaker than the centering condition (6.11). Nevertheless the last equation clearly shows that the perturbation series breaks down, if the right hand side of equation (E.4) has a component in the nullspace of* $\mathcal{A}_1$*. In fact* $\Pi\mathcal{A}_2\Pi = 0$ *can be considered a* consistency condition *for the whole ansatz to make sense.*