An annealed model of diffusion in semi-permeable domains

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Reading progress

- *Conformal Field Theory* (CFT) - Chpt. 5
    - Goal: Complete reading Chpt. 1-7, 10, 12, 13-15 before end of term
- *Critical Dynamics* (CD) - Chpt. 4
    - Goal: Complete reading Chpt. 1-9 before end of term
- *Quantum Field Theory and the Standard Model* (QFT) - Chpt. 18
    - Goal: Complete reading Chpt. 14-23 before end of term
- *Field Theory of Non-Equilibrium Systems* (FTNE) - DNS
    - Goal: Complete reading Chpt. 1-2, 6, 9-12 before end of term
- Working on finishing typesetting for CFT Chpt. 4 & CD Chpt. 3

The model

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- Reflected Brownian motion (RBM) occurs, governed by the Skorokhod equation[1]

$$dX_t^{(1)} = \sqrt{2D_1}\, dW_t + n(x)\, d\ell_t^{(1)}, \qquad (1)$$

until the boundary local time,

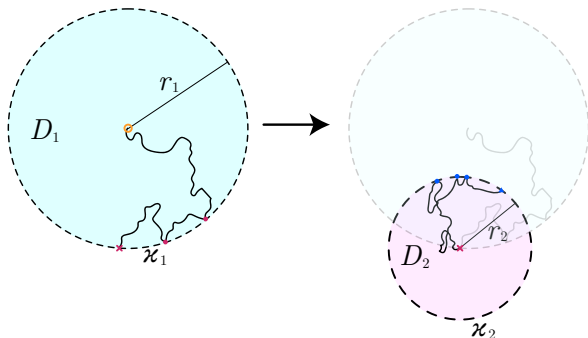$$\ell_t^{(1)} := 2Dn \int_{\partial \mathcal{B}_1} d^{n-1}x \int_0^t \delta(X_s - x)\, ds \qquad (2)$$

exceeds a random variable $\hat{\ell}^{(1)}$, whose probability law obeys $\mathbb{P}\{\hat{\ell}^{(1)} > \ell\} = e^{-q_1 \ell}$, for $q_1 = \kappa_1 / D_1$

The model

- Once the (boundary) *reaction time* $\mathcal{T}_1 = \inf\left\{t > 0 : \ell_t^{(1)} > \hat{\ell}^{(1)}\right\}$ for the domain has been reached, an new RBM initiates at the centre of another sphere $\mathcal{B}_2$ with sampled parameters (D_2, r_2, κ_2)
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- $\mathbb{P}_{x_0}\{\ell_t > \ell\} \iff \mathbb{P}_{x_0}\{t > \mathcal{T}_\ell\}$ and so

$$U(\ell, t \mid x_0) = \frac{\partial \mathbb{P}_{x_0}\{t > \mathcal{T}_\ell\}}{\partial t} = \int_\ell^\infty d\ell' \frac{\partial \rho(\ell', t \mid x_0)}{\partial t}, \tag{4}$$

where ρ is the PDF of the boundary local time[1]

The exit time density

- After taking a temporal Laplace transform ($t \xrightarrow{\mathcal{L}} \alpha$), it can be shown that U permits a spectral representation in terms of the eigenfunctions of the Dirichlet-to-Neumann (DtN) operator[1],

$$\tilde{U}(\ell, \alpha \mid x_0) = \sum_n e^{-\mu_n^\alpha \ell} [V_n^{(\alpha)}(x_0)]^* \int_{\partial\Omega} d^{n-1}s \, V_n^{(\alpha)}(s) \qquad (5)$$

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  - Let w be a solution to the Helmholtz equation $(\alpha - D\Delta)w = 0$ with Dirichlet BC $w|_{\partial\Omega} = f$. The DtN operator $\mathcal{M}_\alpha$ is defined by $[\mathcal{M}_\alpha f](x) = \partial_n w|_{x \in \partial\Omega}$

Spectral representation

- In general we can write the eigenequation as

$$\mathcal{M}_\alpha v_n^{(\alpha)}(x) = \mu_n^{(\alpha)} v_n^{(\alpha)}(x) \tag{6}$$

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- We allow for arbitrary boundary data $f(\theta)$. Let $u(r, \phi) = Q_n(r)e^{in\phi}$ with $\lambda = \sqrt{\alpha/D}$. The modified Helmholtz equation reads

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- Solutions are modified Bessel functions. Enforcing regularity,

$$u(r, \phi, \alpha) = \sum_{n=-\infty}^{\infty} a_n I_{|n|}(\lambda r) e^{in\phi} \qquad (8)$$

Spectral representation

- But now we note that $e^{in\phi}$ is not altered by the normal derivative. As such, we may identify the eigenfunctions $v_n(\phi) = e^{in\phi}$ as the Fourier modes and compute

$$[\mathcal{M}_\alpha v_n](\phi) = \partial_r u_n(R, \phi) = \lambda \frac{I'_{|n|}(\lambda R)}{I_{|n|}(\lambda R)} e^{in\phi}, \qquad (9)$$

so we can identify the eigenvalues

$$\mu_n^{(\alpha)} = \lambda \frac{I'_{|n|}(\lambda R)}{I_{|n|}(\lambda R)} = \lambda \frac{d}{dz} \log I_{|n|}(\lambda R), \qquad \lambda = \sqrt{\alpha/D} \quad (10)$$

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- We can approximate these eigenvalues at long times, $\lambda R \ll 1$ as

$$\mu_n^{(\alpha)} \sim \frac{n}{R} + \frac{\lambda^2 R}{2(n+1)} - \frac{\lambda^4 R^3}{8(n+1)^2(n+2)} + \mathcal{O}(\lambda R^5) \quad (11)$$

References

[1] D. S. Grebenkov, Phys. Rev. Lett. **125**, 078102 (2020).

[2] P. Massignan, C. Manzo, J. A. Torreno-Pina, M. F. García-Parajo, M. Lewenstein, and G. J. Lapeyre, Phys. Rev. Lett. **112**, 150603 (2014).

[3] D. S. Grebenkov, J. Chem. Phys. **151** (2019), 10.1063/1.5115030.

Details of spectral representation

Probabilistically, we can understand diffusion within a domain Ω with semi-permeable boundary of permissivity $\kappa(x)$ as the BVP[3]

$$\frac{\partial G(x, t \mid x_0)}{\partial t} - D\Delta G(x, t, \mid x_0) = 0, \quad x \in \Omega \qquad (12a)$$

$$G(x, t = 0 \mid x_0) = \delta(x - x_0) \qquad (12b)$$

$$\left(D\frac{\partial}{\partial n_x} + \kappa(x)\right) G(x, t \mid x_0) = 0, \quad x \in \partial\Omega. \qquad (12c)$$

If we are to take the Laplace transform with respect to time,

$$\tilde{G}(x, \alpha \mid x_0) = \int_0^\infty e^{-\alpha t} G(x, t \mid x_0) \, dt, \qquad (13)$$

this reduces Eq. (12a) to the inhomogeneous Helmholtz problem:

$$(\alpha - D\Delta)\tilde{G}(x, \alpha \mid x_0) = \delta(x - x_0). \qquad (14)$$

Details of spectral representation

Since the problem is linear, we are free to take

$$\tilde{G}(x, \alpha \mid x_0) = \tilde{G}_0(x, \alpha \mid x_0) + \tilde{g}(x, \alpha \mid x_0), \tag{15}$$

where $\tilde{G}_\infty$ is the propagator with absorbing boundary conditions,

$$(\alpha - D\Delta)\tilde{G}_\infty(x, \alpha \mid x_0) = \delta(x - x_0), \quad x \in \Omega \tag{16a}$$

$$\tilde{G}_\infty(x, \alpha \mid x_0) = 0, \quad x \in \partial\Omega. \tag{16b}$$

Thus the unknown contribution which reacts with the boundary satisfies

$$(\alpha - D\Delta)\tilde{g}(x, \alpha \mid x_0) = 0, \quad x \in \Omega \tag{17a}$$

$$\left(D\frac{\partial}{\partial n_x} + \kappa(x) \right) \tilde{g}(x, \alpha \mid x_0) = \tilde{j}_\infty(x, \alpha \mid x_0), \quad x \in \partial\Omega, \tag{17b}$$

where $\tilde{j}_0$ is the Laplace transform of the diffusive flux density at time t on a point of the perfectly reactive surface.

Details of spectral representation

Consider the Dirichlet BVP

$$(\alpha - D\Delta)u(x, \alpha) = 0, \quad x \in \Omega \tag{18a}$$

$$u(x, \alpha) = f(x, \alpha), \quad x \in \partial\Omega. \tag{18b}$$

We define the Dirichlet-to-Neumann (DtN) $\mathcal{M}_\alpha$ as

$$[\mathcal{M}_\alpha f](x) = \left(\frac{\partial u}{\partial n}\right)_{x \in \partial\Omega}, \tag{19}$$

which determines the flux produced at the boundary by u (Neumann BC) given boundary value f. To this end, on the boundary, we may write the boundary conditions for the unknown contribution to the propagator Eq. (17a) as (with $\mathcal{Q} = \kappa(y)/D$)

$$(\mathcal{M}_\alpha + \mathcal{Q}) \, \tilde{g}(y, \alpha \mid x_0) = \frac{1}{D}\tilde{j}_\infty(y, \alpha \mid x_0), \quad y \in \partial\Omega. \tag{20}$$

Details of spectral representation

Formally, we may invert Eq. (20),

$$\tilde{g}(y, \alpha \mid x_0) = (\mathcal{M}_\alpha + \mathcal{Q})^{-1} \frac{\tilde{\jmath}_\infty(y, \alpha \mid x_0)}{D}. \tag{21}$$

This is now the form of a Dirichlet problem, allowing us to write the bulk solution

$$\tilde{g}(x, \alpha \mid x_0) = \int_{\partial\Omega} d^{n-1}y \, \tilde{\jmath}_\infty(y, \alpha \mid x) \tilde{g}(y, \alpha \mid x_0), \quad x \in \Omega. \tag{22}$$

If we let the surface propagation operator be written $\mathcal{O} = (\mathcal{M}_\alpha + \mathcal{Q})^{-1}$,

$$\tilde{G}(x, \alpha \mid x_0) = \tilde{G}_\infty(x, \alpha \mid x_0) + \int_{\partial\Omega} d^{n-1}y \, \tilde{\jmath}_\infty(y, \alpha \mid x) \frac{\mathcal{O}}{D} \tilde{\jmath}_\infty(y, \alpha \mid x_0). \tag{23}$$

Details of spectral representation

The identity $\tilde{j}_\infty(y, \alpha \mid y_0) = \delta(y - y_0)$ for $y, y_0 \in \partial\Omega$ implies that the propagator between two surface points

$$D(\mathcal{M}_\alpha + \mathcal{Q})\tilde{G}(y, \alpha \mid y_0) = \delta(y - y_0). \tag{24}$$

Now we may express the bulk propagator as

$$\tilde{G}(x, \alpha \mid x_0) = \tilde{G}_\infty(x, \alpha \mid x_0) +$$
$$\int_{\partial\Omega} dy_1 \, dy_2 \, \tilde{j}_\infty(y_2, \alpha \mid x) \frac{\tilde{G}(y_2, \alpha \mid y_1)}{D} \tilde{j}_\infty(y_1, \alpha \mid x_0). \tag{25}$$

In braket notation, eigenvalues of the DtN operator satisfy the eigenequation

$$\mathcal{M}_\alpha \left| v_n^\alpha(x) \right\rangle = \mu_n^\alpha \left| v_n^\alpha(x) \right\rangle. \tag{26}$$

Details of spectral representation

Provided $\partial\Omega$ is bounded, the eigenvalues are non-negative and the eigenfunctions form a complete, orthonormal basis on the boundary. We may hence resolve the identity and insert it into Eq. (25):

$$
\tilde{G}(x, \alpha \mid x_0) = \tilde{G}_\infty(x, \alpha \mid x_0)
$$
$$
+ \frac{1}{D} \sum_{n,m} \int_{\partial\Omega} dy_1 \, dy_2 \, \tilde{j}_\infty \left| v_n^{(\alpha)}(s) \right\rangle \left\langle v_n^{(\alpha)}(s) \middle| \mathcal{O} \middle| v_m^{(\alpha)}(s') \right\rangle \left\langle v_m^{(\alpha)}(s') \middle| \tilde{j}_\infty \right.
$$
$$
\tag{27}
$$

If the permissivity is taken to be constant, the matrix is diagonal

$$
\left\langle v_n^{(\alpha)}(s) \middle| (\mathcal{M}_\alpha + q)^{-1} \middle| v_m^{(\alpha)}(s') \right\rangle = \left(\mu_n^{(\alpha)} + q \right)^{-1} \delta_{n,m}. \tag{28}
$$

Details of the spectral representation

Inserting the element into the propagator,

$$\tilde{G}(x, \alpha \mid x_0) = \tilde{G}_{\infty}(x, \alpha \mid x_0) + \frac{1}{D} \sum_n \frac{[V_n^{(\alpha)}(x_0)]^* V_n^{(\alpha)}(x)}{\mu_n^{(\alpha)} + q}, \quad (29)$$

where we have defined the projections

$$V_n^{(\alpha)}(x) = \int_{\partial\Omega} d^{n-1}y \, v_n^{(\alpha)}(y) \tilde{j}_{\infty}(y, \alpha \mid x). \quad (30)$$

Bessel ratio asymptotic form

We begin with the standard power series

$$
I_n(z) = \sum_{k=0}^{\infty} \frac{1}{k!\Gamma(n+k+1)} \left(\frac{z}{2}\right)^{n+2k}
$$
$$
= \frac{1}{n!} \left(\frac{z}{2}\right)^n \left[1 + \frac{z^2}{4(n+1)} + \frac{z^4}{32(n+1)(n+2)} + \mathcal{O}(z^6)\right].
$$

Taking the logarithm, performing an expansion
$\log\left(1+x\right) \sim x - \frac{x^2}{2} + \frac{x^3}{3} + \mathcal{O}(x^4)$, and differentiating,

$$
\frac{I_n'(z)}{I_n(z)} = \frac{n}{z} + \frac{z}{2(n+1)} - \frac{z^3}{8(n+1)^2(n+2)} + \mathcal{O}(z^5) \qquad (31)
$$