

## Supplementary Materials (SM) for:

### Langevin and Fokker-Planck analyses of inhibited molecular passing processes controlling transport and reactivity in nanoporous materials

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### Fokker-Planck Equation (FPE) formulation of inhibited passing in narrow pores

Strongly-damped Langevin dynamics of the two molecules within the pore can be described by the equivalent Fokker-Planck equation (FPE), which for our systems with purely steric blocking just corresponds to a diffusion equation in high dimensions [22]. For convenience, we label the two molecules by  $i=1,2$  (rather than by  $\alpha, \beta$  as in the main text). It is convenient to introduce coordinates in the space-fixed frame for the molecules  $\underline{Q}_i = (\underline{q}_i, z_i)$  where  $z_i$  is the center-of-mass  $z$ -coordinate along the pore axis, and  $\underline{q}_i$  is the collection of center-of-mass lateral coordinates orthogonal to the pore axis, and also any angular coordinates. We let  $\delta z = z_1 - z_2$  denote center-of-mass  $z$ -coordinate separation of the two molecules. Also, the accessible phase-space volume in the coordinates  $\underline{q}_1$  and  $\underline{q}_2$  for a specified fixed  $\delta z = z_1 - z_2$  is given by

$$V(\delta z) = \int d\underline{q}_1 d\underline{q}_2 \Big|_{z_1 - z_2 = \delta z}, \quad (1)$$

integrating over the allowed non-overlap region. Finally, we let  $r_1$  and  $r_2$  denote the radii of the two particles if they are circular or spherical, or the radii of the circumscribing spheres for other shapes, and set  $d_{12} = r_1 + r_2 = d$ .

The most comprehensive time-dependent FPE formulation of passing considers the probability distribution  $f(\underline{Q}_1, \underline{Q}_2; t)$  for finding two molecules confined inside the pore in an allowed non-overlapping configuration. Given the translational invariance of the system in the  $z$ -direction, it is natural to consider the reduced distribution

$$f(\underline{q}_1, \underline{q}_2, \delta z; t) = \int dz_1 \int dz_2 \delta(z_1 - z_2 - \delta z) f(\underline{Q}_1, \underline{Q}_2; t), \quad (2)$$

for the probability of finding two molecules with  $z$ -coordinate separation  $\delta z$ . In our analysis of passing propensity,  $P$ , adjacent molecules start with separation  $\delta z = z_1 - z_2 = d$ , the minimum distance where no overlap or interference between the molecules occurs. Then, the normalized initial conditions correspond to

$$f(\underline{q}_1, \underline{q}_2, \delta z; t=0) = V(d)^{-1} \delta(\delta z - d), \quad (3)$$

where the accessible phase-space volume,  $V(d)$ , at  $\delta z = d$  gives the normalization constant. For the full probability distribution, one could assign any (normalized) probability distribution,  $f_{10}(z_1)$ , for the  $z$ -coordinate of particle 1, say, e.g.,  $f_{10}(z_1 = \delta(z_1))$  initially fixing particle 1 at the origin. The evolution of  $f(\underline{q}_1, \underline{q}_2, \delta z; t)$  will not depend on the

choice of  $f_{10}$ . In the Langevin simulations, we follow evolution either until the molecules separate (defined as reaching  $\delta z = 2d$ ) or pass (defined as reaching  $\delta z = -d$ ). This corresponds to imposing adsorbing Dirichlet boundary conditions (BC's)  $f=0$  for  $\delta z = -d$  and  $\delta z = +2d$ . We also impose zero-flux Neumann BCs at the boundary of the physically accessible region for other coordinates.

To provide a simpler concrete example of this FPE, we consider the case of two circular molecules in 2D, or two spherical molecules in 3D, with possibly different radii and translational diffusion coefficients,  $D_i$ . Then, the  $\underline{q}_i$  correspond to the translational coordinates orthogonal to the pore axis, and

$$\partial/\partial t f(\underline{Q}_1, \underline{Q}_2; t) = L_{\text{FPE}} f(\underline{Q}_1, \underline{Q}_2; t) \text{ with } L_{\text{FPE}} = D_1 \partial^2/\partial \underline{Q}_1^2 + D_2 \partial^2/\partial \underline{Q}_2^2. \quad (4)$$

It is natural to change variables from  $z_1$  and  $z_2$  to  $\delta z = z_1 - z_2$  and  $Z = (D_2/D_1)^{1/2} z_1 + (D_1/D_2)^{1/2} z_2$  which yields

$$L_{\text{FPE}} = D_1 \partial^2/\partial \underline{q}_1^2 + D_2 \partial^2/\partial \underline{q}_2^2 + (D_1 + D_2) [\partial^2/\partial (\delta z)^2 + \partial^2/\partial Z^2]. \quad (5)$$

Thus, it follows that  $f(\underline{Q}_1, \underline{Q}_2; t) = f(\underline{q}_1, \underline{q}_2, \delta z; t) f(Z, t)$ , where the  $f(Z, t)$  satisfies a standard diffusion equation with diffusion coefficient  $D_1 + D_2$  (cf. Ref.[25]). The form and evolution of  $f(Z, t)$  does not impact the quantities of interest, and specifically the passing propensity,  $P$ . Of more relevance and significance,  $f(\underline{q}_1, \underline{q}_2, \delta z; t)$  satisfies the FPE

$$\partial/\partial t f(\underline{q}_1, \underline{q}_2, \delta z; t) = L_{\text{FPE}} f(\underline{q}_1, \underline{q}_2, \delta z; t) \text{ with } L_{\text{FPE}} = D_1 \partial^2/\partial \underline{q}_1^2 + D_2 \partial^2/\partial \underline{q}_2^2 + (D_1 + D_2) \partial^2/\partial (\delta z)^2, \quad (6)$$

where, for convenience, we use the same notation for the FPE operator in (6) as in the full FPE (4). It is appropriate to note that all these FPE operators (and those for more complex molecular shapes) have the self-adjoint form,  $L_{\text{FPE}} = \nabla \underline{\underline{D}} \nabla$ , where  $\nabla$  denotes the gradient operator in the spatial variables, and  $\underline{\underline{D}}$  is a symmetric diffusion tensor with components reflecting the amplitude of the noise terms in the Langevin equation.

From  $f(\underline{q}_1, \underline{q}_2, \delta z; t)$ , one accumulates over time the probability flux reaching  $\delta z = -d$  and  $+2d$ , and thereby determines the probability of passing,  $P = P_{\text{pass}}$ , or separation,  $P_{\text{sep}} = 1 - P_{\text{pass}}$ , as

$$P_{\text{pass(sep)}} = \pm \int_{0 < t < \infty} \iint d\underline{q}_1 d\underline{q}_2 \underline{e}_{\delta z} \cdot \underline{\underline{D}} \nabla f(\underline{q}_1, \underline{q}_2, \delta z; t) |_{\delta z = 2d, -d}, \quad (7)$$

for unit vector  $\underline{e}_{\delta z}$  in  $\delta z$ -direction. A schematic of this approach appears in Fig.2(c) just showing the further-reduced probability distribution,  $f(\delta z, t) = \iint d\underline{q}_1 d\underline{q}_2 f(\underline{q}_1, \underline{q}_2, \delta z; t)$ .

Numerical analysis of this FPE initial value problem for two circular molecules in a 2D rectangular channel, and two spherical molecules in a 3D cylindrical channel, was performed using a uniform hypercubic mesh in  $(\underline{q}_1, \underline{q}_2, \delta z)$ -space. Time evolution was implemented with an Euler method. In the cases analyzed, the molecules had equal size with radius,  $r$ , and equal diffusion coefficients. A detailed assessment of accuracy was performed for the 2D problem (3 variable FPE) by varying the mesh spacing from  $r$  to  $r/16$ . A limited analysis was performed in 3D (5 variable FPE) with mesh spacing

down to  $r/8$ . We find good agreement with Langevin results wider pores with large “gap sizes” (see the text), but accuracy is limited for smaller gaps due to finite mesh size.

Given the computational challenges for small gap size, we consider an equivalent time-independent (stationary) FPE formulation of the passing problem. In this formulation, one considers the steady-state probability,  $f^{ss}(\underline{q}_1, \underline{q}_2, \delta z)$ , for a scenario where probability is continually fed into the system at  $\delta z = d$ , and one retains absorbing BC's  $f^{ss} = 0$  for  $\delta z = -d$  and  $\delta z = +2d$ , and zero-flux Neumann BCs at other boundaries. Thus, (6) is replaced by the time-independent equation

$$0 = L_{FPE} f^{ss}(\underline{q}_1, \underline{q}_2, \delta z) + V(d)^{-1} \delta(\delta z - d). \quad (8)$$

Now the probability of passing  $P=P_{pass}$  or separation  $P_{sep}$  are obtained from the steady-state fluxes

$$P_{pass(sep)} = \iint d\underline{q}_1 d\underline{q}_2 \underline{n} \cdot \underline{D} \nabla f^{ss}(\underline{q}_1, \underline{q}_2, \delta z) |_{\delta z = 2d, -d}. \quad (9)$$

A schematic of this approach appears in Fig.3(d) just showing the further-reduced probability distribution  $f^{ss}(\delta z) = \iint d\underline{q}_1 d\underline{q}_2 f^{ss}(\underline{q}_1, \underline{q}_2, \delta z)$ . Proof of the equivalence of this formulation with the original time-dependent one follows from an eigenfunction expansion of their solutions in terms of the orthonormal eigenfunctions of the self-adjoint operator,  $L_{FPE}$ . See the Appendix.

Actually, this reformulated stationary FPE problem is similar in complexity to the original time-dependent problem with regard to numerical analysis. However, a key advantage of the stationary FPE formulation is that it is amenable to a natural simplification in the regime of small gap size, as described in the text:  $f^{ss}(\underline{q}_1, \underline{q}_2, \delta z)$  is roughly constant for  $\delta z < d$  while  $V(\delta z)$  remains substantial, only decreasing dramatically once  $V(\delta z)$  decreases; it decrease linearly in  $\delta z$  for  $\delta z > d$  to zero at  $\delta z = 2d$ . See Fig.2(d) for a schematic of this behavior. Thus, in this regime,  $f^{ss}$  can be determined from the simpler conventional mixed boundary value problem (BVP),

$$0 = L_{FPE} f^{ss}(\underline{q}_1, \underline{q}_2, \delta z) \text{ for } -d < \delta z < d, \text{ with } f^{ss} = 0 \text{ (constant) at } \delta z = -d \text{ (} \delta z = +d), \quad (10)$$

and where again we impose zero flux BCs at the other boundaries. The flux at  $\delta z = -d$  is determined non-trivially from this solution, and the flux at  $\delta z = +2d$  is immediately determined given the linear profile in  $\delta z$  of  $f^{ss}$  for  $+d < \delta z < +2d$ .

With regard to numerical analysis, the great advantage of reformulating the problem (for small gap sizes) as a conventional mixed BVP is that now analysis is possible with standard (and precise) adaptive-mesh finite-element methods (FEM) techniques and software [27]. Specifically, for narrow gaps, necessary accuracy is achieved by concentrating a finer mesh around the point of greatest constriction in the high-dimensional constricted channel which corresponds to the spatial domain for the BVP for this stationary FPE. For the passing problem involving two circular molecules in a rectangular pore, this BVP involves a 3-variable FPE and can thus be analyzed numerically with available FEM software [27]. However, other problems correspond to a FPE with more than 3-variables, e.g., passing of two spherical molecules inside a

cylindrical pore corresponds to a 5-variable FPE. For such higher-dimensional problems, FEM software is not readily available. This motivates consideration of an approximate reduced-dimensional version of the passing problem.

The basic idea in our reduced-dimensional FPE formulation is to replace all the variables  $\underline{q}_1$  and  $\underline{q}_2$  appearing in  $f(\underline{q}_1, \underline{q}_2, \delta z; t)$  and  $f^{ss}(\underline{q}_1, \underline{q}_2, \delta z)$  with a single effective variable,  $q_{eff}$ . Thus, we consider an effective 2-variable FPE problem for either  $f(q_{eff}, \delta z; t)$  and  $f^{ss}(q_{eff}, \delta z)$ . Naturally, the range of  $q_{eff}$  should reflect the available phase-space volume, so we specify the range  $-\frac{1}{2}V(\delta z) < q_{eff} < +\frac{1}{2}V(\delta z)$ . The FPE is solved with boundary conditions and/or initial values analogous to the higher-dimensional problem, and the passing propensity is calculated in an analogous fashion. Once again, the simplified approximate mixed BVP for the stationary FPE (which gives an accurate assessment of passing for small gap sizes) can be analyzed precisely using adaptive-mesh FEM methods.

Finally, we comment on the additional features present for elongated molecules with cylindrical symmetry in 3D (or reflection symmetry about their long axis in 2D). Here it is convenient to return to the original formulation involving  $f(\underline{Q}_1, \underline{Q}_2; t)$  with  $\underline{Q}_i = (q_i, z_i)$ . To describe the translational diffusion of an elongated molecule with diffusion coefficients  $D_{||}$  and  $D_{\perp}$  as described in the text, it is convenient to first consider the translational diffusion tensor  $\underline{D}(\text{trans|bf})$  in the body-fixed frame. This tensor is diagonal with entries  $D_{||}$  and  $D_{\perp}$  (the latter appearing twice in 3D problems). The desired translational diffusion tensor in the space-fixed frame is given by  $\underline{D}(\text{trans}) = \underline{R} \underline{D}(\text{trans|bf}) \underline{R}^{-1}$ , where  $\underline{R}$  is the unitary rotation tensor for a rotation which aligns the long axis of the molecule with the z-axis of the pore. Unitarity of  $\underline{R}$  ensures that  $\underline{D}(\text{trans})$  is symmetric. Thus, the space-fixed translational diffusion depended on molecular orientation, but rotational diffusion is independent of translational diffusion. Of course, our reduction to a 2-variable effective FPE cannot incorporate the details of diffusional anisotropy and rotational diffusion for elongated molecules.

We have proposed that the passing propensity should not depend strongly on the specific values of various diffusion coefficients for elongated molecules provided that these are similar in magnitude. This claim can be rationalized as follows. Starting with the stationary FPE, one can change variables suitably rescaling by the square root of the relevant diffusion coefficients. This yields an equivalent problem with equal diffusion coefficients, but in a rescaled geometry. However, the rescaled geometry is just dilated or contracted from the original, so the shape of the construction is the same. Thus, one does not expect large changes in the passing probability, which we have shown are induced by quantitative changes in shape (e.g., from quartic to quadratic to V-shaped).

## **APPENDIX: Equivalence of the time-dependent and stationary FPE approaches**

Consider the FPE-type problems (6) or (8) with adsorbing Dirichlet boundary conditions (BCs) for  $\delta z = -d$  and  $+2d$ , and zero-flux Neumann BCs at the other boundaries. Then, for these BC's, the associated eigenvalue problem for the self-adjoint FPE operator,  $L_{FPE} = \nabla \underline{D} \nabla$ , with symmetric diffusion tensor  $\underline{D}$ , has the form

$$L_{FPE} u_n(\underline{q}_1, \underline{q}_2, \delta z) = -\lambda_n u_n(\underline{q}_1, \underline{q}_2, \delta z) \text{ where } \iiint d\underline{q}_1 d\underline{q}_2 d(\delta z) u_n^* u_m = \delta_{n,m}.$$

An eigenfunction expansion of the solution for the time-dependent initial value problem for the FPE described above yields

$$f(\underline{q}_1, \underline{q}_2, \delta z; t) = \sum_n c_n \exp(-\lambda_n t) u_n(\underline{q}_1, \underline{q}_2, \delta z) \text{ with } c_n = V(d)^{-1} \iint d\underline{q}_1 d\underline{q}_2 u_n^*(\underline{q}_1, \underline{q}_2, \delta z=d).$$

The coefficients  $c_n$  are selected to recover the initial conditions. An eigenfunction expansion of the solution for the time-independent formulation of the passing problem yields

$$f^{ss}(\underline{q}_1, \underline{q}_2, \delta z) = \sum_n b_n u_n(\underline{q}_1, \underline{q}_2, \delta z) \text{ with } b_n = V(d)^{-1} \iint d\underline{q}_1 d\underline{q}_2 u_n^*(\underline{q}_1, \underline{q}_2, \delta z=d)/\lambda_n.$$

Determination of the probabilities for separation and passing from either of these problems yields the same result, e.g.,

$$P_{\text{pass}} = V(d)^{-1} \sum_n \iint d\underline{q}_1' d\underline{q}_2' u_n^*(\underline{q}_1', \underline{q}_2', \delta z=d) \iint d\underline{q}_1 d\underline{q}_2 \underline{n} \cdot \underline{D} \nabla u_n(\underline{q}_1, \underline{q}_2, \delta z=-d)/\lambda_n.$$