ARTICLE

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SUPPLEMENTARY INFORMATION:
Exact integrated equations to describe diffusion kinetics

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The functions used to generate Fig 2 and 3 in the main text are based on the integrals of Crank's solutions [1] for tracer diffusion through a planar sheet. In the Supplementary Information we provide the code for these Matlab functions. All these functions and an example of their use, specifically their use to generate Figure 2 of the main text, can also be downloaded from:
Swapnil-dx/Integrated-diffusion-equations-for-polymers: Diffusion kinetics equations (Matlab) (v1.1.1). Zenodo. https://doi.org/10.5281/zenodo.17832809.

1. List of Matlab functions

To make the - admittedly confusing - equations somewhat more accessible we provide the key equations using Matlab code. All equations listed below are given as Matlab functions to which experimental data may be fit. They are illustrated in the right columns of Figure 2 and Figure 3. The average concentrations are calculated either by integrating over a small sliver of the film (red lines) or over the entire film (blue lines). The former is relevant, for example, for evanescent field or plasmonic interaction measurements (index "ev"). The latter pertains to gravimetric, optical absorption or bulk refractive index measurements of concentration (index: "film").
Here, we provide the Matlab functions listed below to generate the concentration gradients. We also provide examples for the use of some of these functions. The equation numbers refer to the main text.

Film mounted on an impermeable substrate:
Concentration gradient across impermeable membrane during absorption

Imp_Abs_conc Figure 2A

$$X(y,t) = X_1\left[1-\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{(-1)^m}{2m+1}\exp\left(-D(2m+1)^2\frac{\pi^2 t}{4d^2}\right)\times\cos\left((2m+1)\frac{\pi y}{2d}\right)\right] \tag{10}$$

```
function f=Imp_Abs_conc(X1,D,d,t,y,num_terms)
   i=0;
   Terms(num_terms:length(y))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=(-1)^j/(2*j+1)*cos((2*j+1)*pi*y/(2*d))*exp(-D.*(2*j+1)^2*pi^2*t/(4*d^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(1-4/pi*SumofTerms);
end
```

Concentration gradient across impermeable membrane during desorption

Imp_Des_conc Figure 2C

$$X(y,t) = X_\infty\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{(-1)^m}{2m+1}\exp\left(-D(2m+1)^2\frac{\pi^2 t}{4d^2}\right)\times\cos\left((2m+1)\frac{\pi y}{2d}\right) \tag{12}$$

```
function f=Imp_Des_conc(X1,D,d,t,y, num_terms)
   i=0;
   Terms(num_terms:length(y))=zeros;
      for j=0:num_terms
       i=i+1;
         Terms(i,:)=(-1)^j/(2*j+1)*cos((2*j+1)*pi*y/(2*d))*exp(-D.*(2*j+1)^2*pi^2*t/(4*d^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(4/pi*SumofTerms);
```

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```
end
```

Absorption process through evanescent wave

Imp_Abs_ev Figure 2B blue line

$$\bar{X}(t) = X_\infty\left[1-\frac{8d}{\pi^2\delta y}\sum_{m=0}^{\infty}\frac{(-1)^m}{(2m+1)^2}\exp\left(-\frac{D\pi^2(2m+1)^2 t}{4d^2}\right)\times\ \sin\left((2m+1)\frac{\pi\delta y}{2d}\right)\right] \tag{16}$$

```
function f=Imp_Abs_ev(X1,D,d,t,dy, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
      Terms(i,:)= (-1)^j/(2*j+1)^2*sin((2*j+1)*pi*dy/(2*d))*exp(-D.*(2*j+1)^2*pi^2*t/(4*d.^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(1-8*d/(pi^2*dy)*SumofTerms);
end
```

Desorption process through evanescent wave

Imp_Des_ev Figure 2D blue line

$$\bar{X}(t) = X_\infty\left[\frac{8d}{\pi^2\delta y}\sum_{m=0}^{\infty}\frac{(-1)^m}{(2m+1)^2}\exp\left(-\frac{D\pi^2(2m+1)^2 t}{4d^2}\right)\times\ \sin\left((2m+1)\frac{\pi\delta y}{2d}\right)\right] \tag{18}$$

```
function f=Imp_Des_ev(X1,D,d,t,dy, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
      Terms(i,:)= (-1)^j/(2*j+1)^2*sin((2*j+1)*pi*dy/(2*d))*exp(-D.*(2*j+1)^2*pi^2*t/(4*d.^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(8*d/(pi^2*dy)*SumofTerms);
end
```

Absorption process integrated over film

Imp_Abs_film Figure 2B red line;

$$\bar{X}(t)=X_\infty\left[1-\frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-D(2m+1)^2\frac{\pi^2 t}{4d^2}\right)\right] \tag{21}$$

```
function f=Imp_Abs_film(X1,D,d,t, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)= 1/(2*j+1)^2*exp(-D.*(2*j+1)^2*pi^2*t/(4*d.^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(1-8/pi^2*SumofTerms);
end
```

Desorption process integrated over film

Imp_Des_film Figure 2D red line;

$$\bar{X}(t)=X_\infty\frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-D(2m+1)^2\frac{\pi^2 t}{4d^2}\right) \tag{22}$$

```
function f=Imp_Des_film(X1,D,d,t, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)= 1/(2*j+1)^2*exp(-D.*(2*j+1)^2*pi^2*t/(4*d.^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(8/pi^2*SumofTerms);
end
```

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Free-standing film (mounted on a permeable substrate)

Concentration gradient across permeable membrane during absorption

Per_Abs_conc Figure 3A

$$X(y,t)=X_1\left[\frac{y}{d}+\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi y}{d}\exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right)\right] \quad (25)$$

```
function f=Per_Abs_conc(X1,D,d,t,y, num_terms)
   i=0;
   Terms(num_terms:length(y))=zeros;
      for j=1:num_terms
      i=i+1;
         Terms(i,:)=(-1)^j/j*sin(j*pi*y/d)*exp(-D.*j^2*pi^2*t/(d^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(y/100+2/pi*SumofTerms);
end
```

Concentration gradient across permeable membrane during desorption assuming linear concentration gradient

Per_Des_conc_grad Figure 3C

$$X(y,t)=\frac{2X_1}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi y}{d}\exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right) \quad (27)$$

```
function f=Per_Des_conc_grad(X1,D,d,t,y, num_terms)
   i=0;
   Terms(num_terms:length(y))=zeros;
      for j=1:num_terms
      i=i+1;
         Terms(i,:)=(-1)^j/(j)*sin(j*pi*y/d)*exp(-D.*j^2*pi^2*t/(d^2));
      end
   SumofTerms=sum(Terms);
   f=-X1*(2/pi*SumofTerms);
end
```

Concentration gradient across permeable membrane during desorption assuming constant initial concentration

Per_Des_conc_const Figure 3E

$$X(y,t)=\frac{4X_0}{\pi}\left[\sum_{m=0}^{\infty}\frac{1}{2m+1}\exp\left(-\frac{D(2m+1)^2\pi^2 t}{d^2}\right)\times\sin\frac{(2m+1)\pi y}{d}\right] \quad (28)$$

```
function f=Per_Des_conc_const(X1,D,d,t,y, num_terms)
   i=0;
   Terms(num_terms:length(y))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=1/(2*j+1)*sin((2*j+1)*pi*y/d)*exp(-D.*(2*j+1)^2*pi^2*t/(d^2));
      end
   SumofTerms=sum(Terms);
   f=X1*(4/pi*SumofTerms);
End
```

Absorption process through evanescent wave

Per_Abs_ev Figure 3B blue line

$$\bar{X}(\delta y,t)=X_1\left[\frac{\delta y}{2d}+\frac{2d}{\delta y\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\left(1-\cos\frac{n\pi\delta y}{d}\right)\exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right)\right] \quad (39)$$

```
function f=Per_Abs_ev(X1,D,d,t,dy, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=1:num_terms
      i=i+1;
         Terms(i,:)=(-1)^j/j^2*(cos(j*pi*dy/d)-1)*exp(-D.*j^2*pi^2*t/d^2);
      end
   SumofTerms=sum(Terms);
   f=X1*(dy/(d*2)-2*d/(dy*pi^2)*SumofTerms);
end
```


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Desorption process through evanescent wave with constant initial concentration

Per_Des_ev_const Figure 3D blue line

$$\bar{X}(t) = \bar{X}(\delta y, \infty)\frac{4d}{\delta y \pi^2} \times \left[\sum_{n=0}^{\infty} \frac{1}{(2m+1)^2}\left(1 - \cos\frac{(2m+1)\pi\delta y}{d}\right)\exp\left(-\frac{D(2m+1)^2\pi^2 t}{d^2}\right)\right] \quad (41)$$

```
function f=Per_Abs_ev(X1,D,d,t,dy, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=1/(2*j+1)^2*(1-cos((2*j+1)*pi*dy/d))*exp(-D.*(2*j+1)^2*pi^2*t/d^2);
      End
   SumofTerms=sum(Terms);
   f=X1*(4*d/(dy*pi^2)*SumofTerms);
end
```

Desorption process through evanescent wave assuming linear concentration gradient

Per_Des_ev_grad Figure 3F blue line

$$\bar{X}(t) = X_1\left[\frac{2d}{\delta y \pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\left(\cos\frac{n\pi\delta y}{d} - 1\right)\exp\left(-\frac{Dn^2\pi^2 t}{d^2}\right)\right] \quad (42)$$

```
function f=Per_Des_ev_grad(X1,D,d,t,dy, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=1:num_terms
      i=i+1;
         Terms(i,:)=(-1)^j/j^2*(cos(j*pi*dy/d)-1)*exp(-D.*j^2*pi^2*t/d^2);
      end
   SumofTerms=sum(Terms);
   f=X1*(2*d/(dy*pi^2)*SumofTerms);
end
```

Absorption process integrated over film

Per_Abs_film Figure 3B red line

$$\bar{X}(t) = X_1\left[\frac{1}{2} - \frac{4}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-\frac{D(2m+1)^2\pi^2 t}{d^2}\right)\right] \quad (44)$$

```
function f=Per_Abs_film(X1,D,d,t, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=1/(2*j+1)^2*exp(-D.*(2*j+1)^2*pi^2*t/d^2);
      end
   SumofTerms=sum(Terms);
   f=X1*(1/2-4/pi^2*SumofTerms);
end
```

Desorption process integrated over film with constant initial concentration

Per_Des_film_const Figure 3D red line

$$\frac{\bar{X}(t)}{\bar{X}(d,\infty)} = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-\frac{D(2m+1)^2\pi^2 t}{d^2}\right) \quad (45)$$

```
function f=Per_Des_film_const(X1,D,d,t, num_terms)
    i=0;
    Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=1/(2*j+1)^2*exp(-D.*(2*j+1)^2*pi^2*t/d^2);
      end
   SumofTerms=sum(Terms);
   f=X1*(8/(pi^2)*SumofTerms);
end
```

Desorption process integrated over film assuming linear concentration gradient

Per_Des_film_grad Figure3F red line;

$$\frac{\bar{X}(t)}{X_1} = \frac{4}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left(-\frac{D(2m+1)^2\pi^2 t}{d^2}\right) \quad (46)$$

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```
function f=Per_des_film_grad(X1,D,d,t, num_terms)
   i=0;
   Terms(num_terms:length(t))=zeros;
      for j=0:num_terms
      i=i+1;
         Terms(i,:)=1/(2*j+1)^2*exp(-D.*(2*j+1)^2*pi^2*t/d^2);
      end
   SumofTerms=sum(Terms);
   f=X1*(4/(pi^2)*SumofTerms);
end
```

References

1. Crank, J., *The Mathmatics of Diffusion*. First Edition ed. 1956, London, UK: Oxford University Press.

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