Diffusion in an array of cavities in two dimensions

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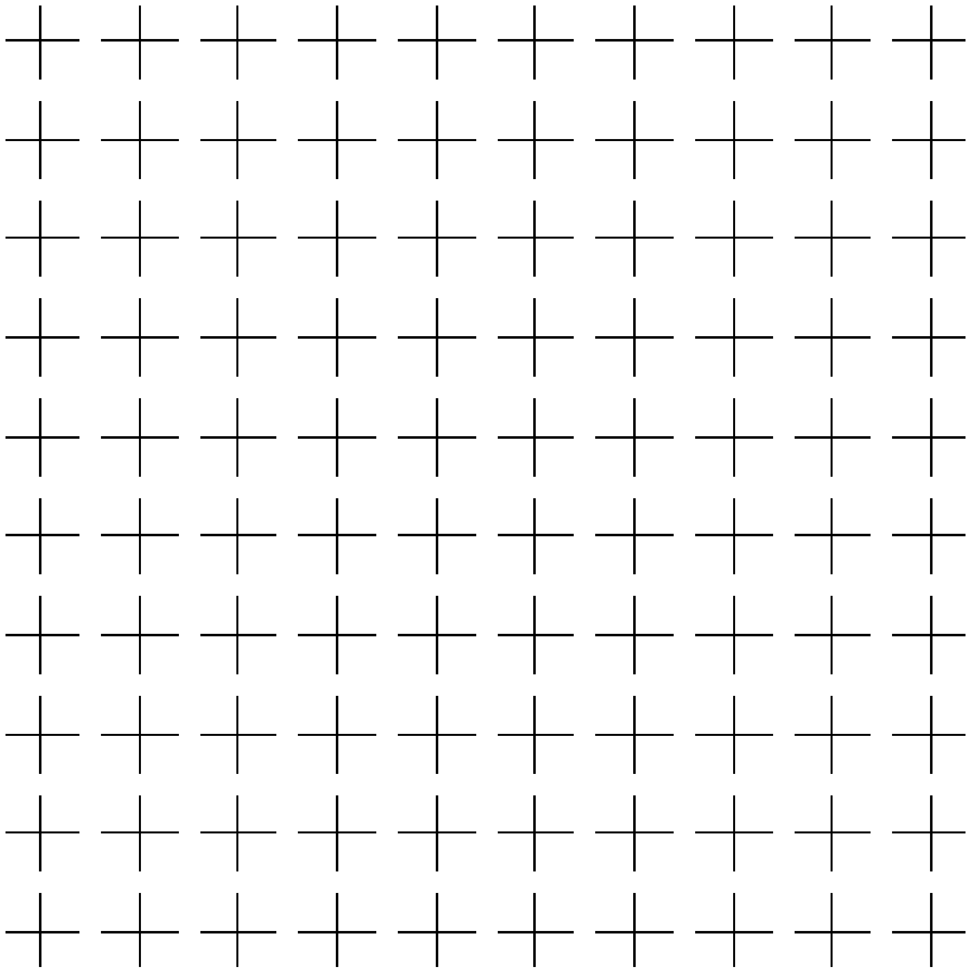
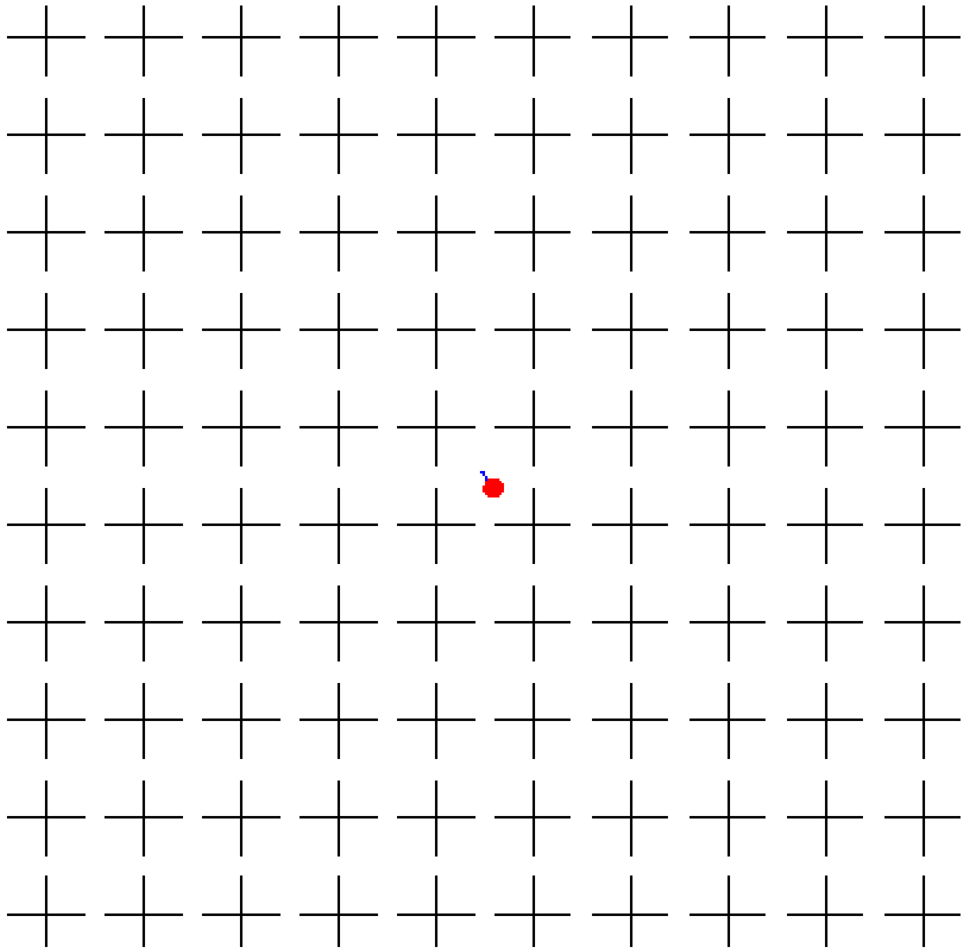
Diffusion of small particles in periodic arrays of cavities connected by holes

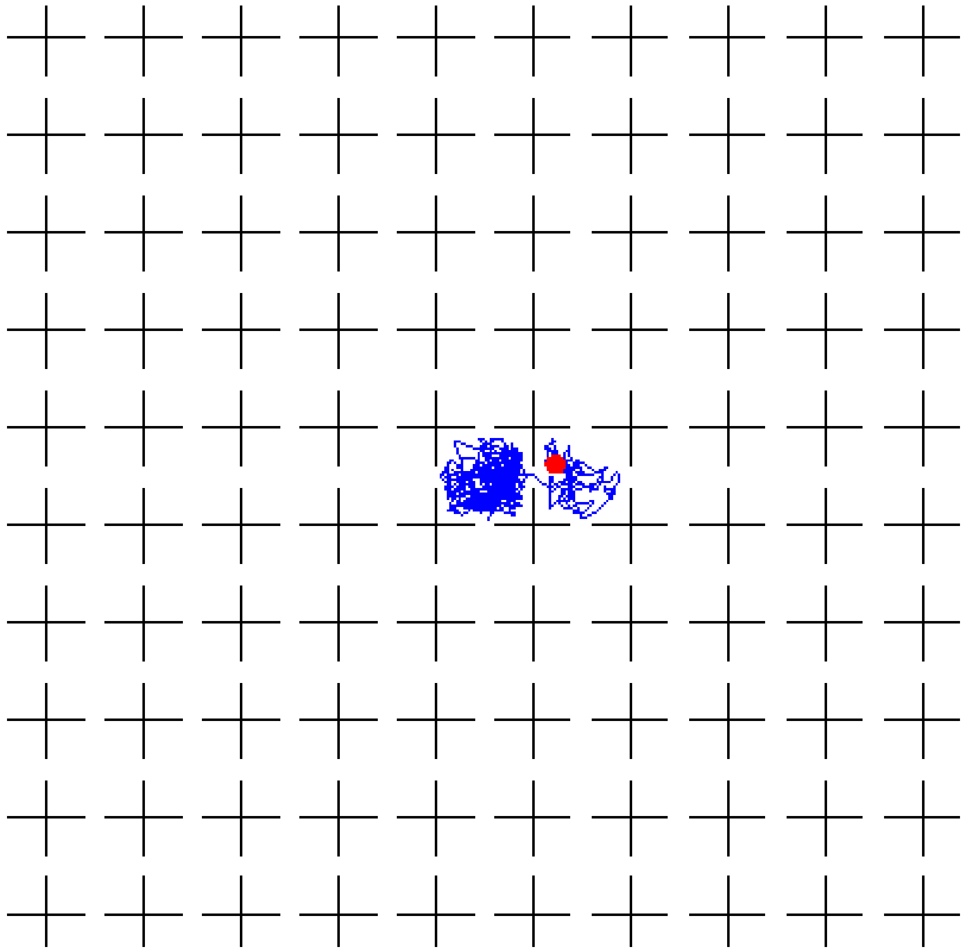


Diffusion of small particles in periodic arrays of cavities connected by holes



Cavity walls are impenetrable obstacles, but particles can pass through holes

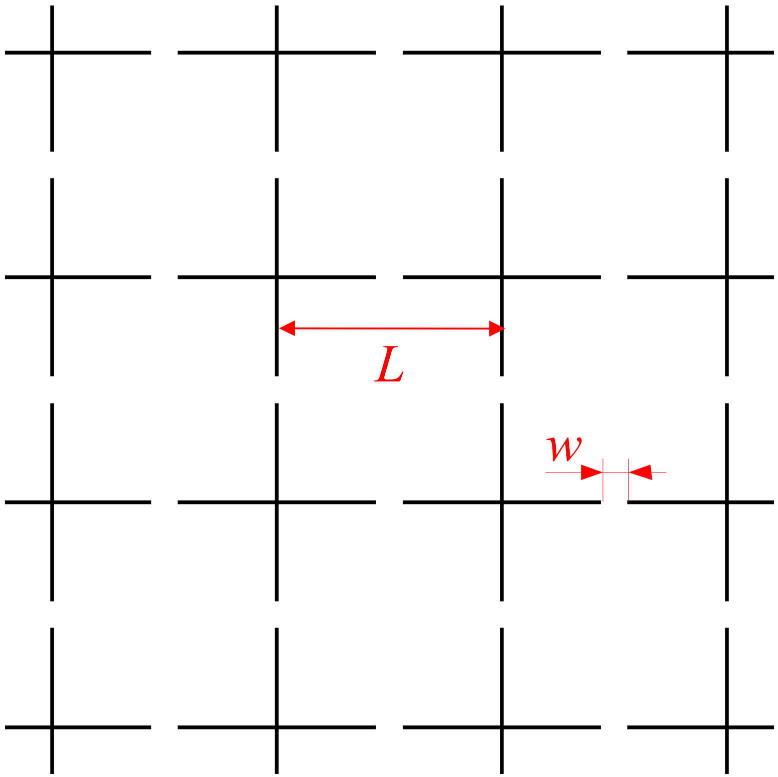
Diffusion of small particles in periodic arrays of cavities connected by holes



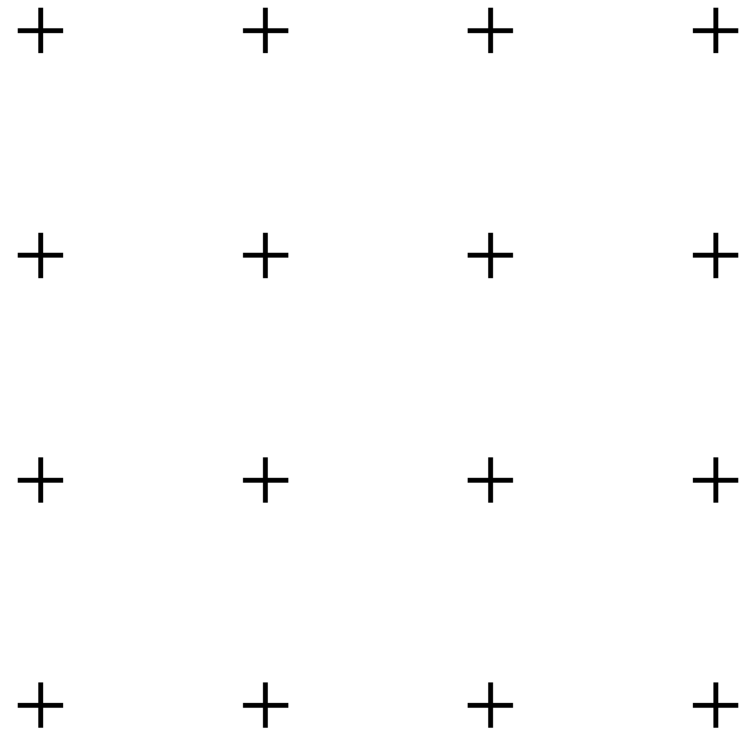
Cavity walls are impenetrable obstacles, but particles can pass through holes

A toy model of various porous media (gels, microfabricated arrays, etc.) Both 2D and 3D variants are of interest.

Square cavities in 2D



Small holes

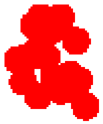


Large holes (= small obstacles)

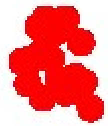
Parameter $a = w/L$ (changes between 0 and 1)

In this model, can go from no diffusion to free diffusion.

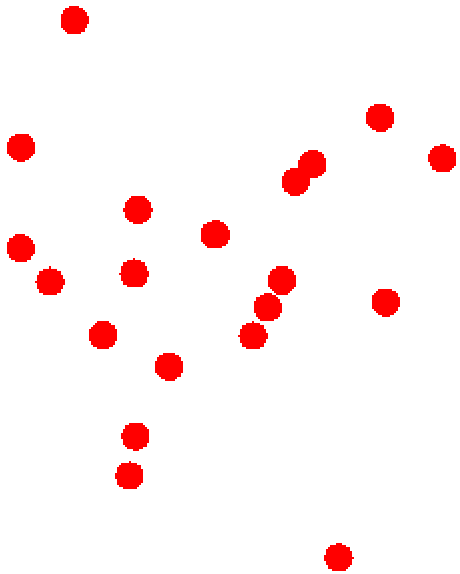
Diffusion in free space



Diffusion in free space



Diffusion in free space

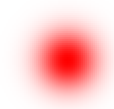


Diffusion coefficient D_0:

$$\langle r^2 \rangle = 2dD_0 t$$

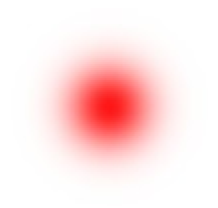
(here dimensionality $d = 2$)

Diffusion in free space



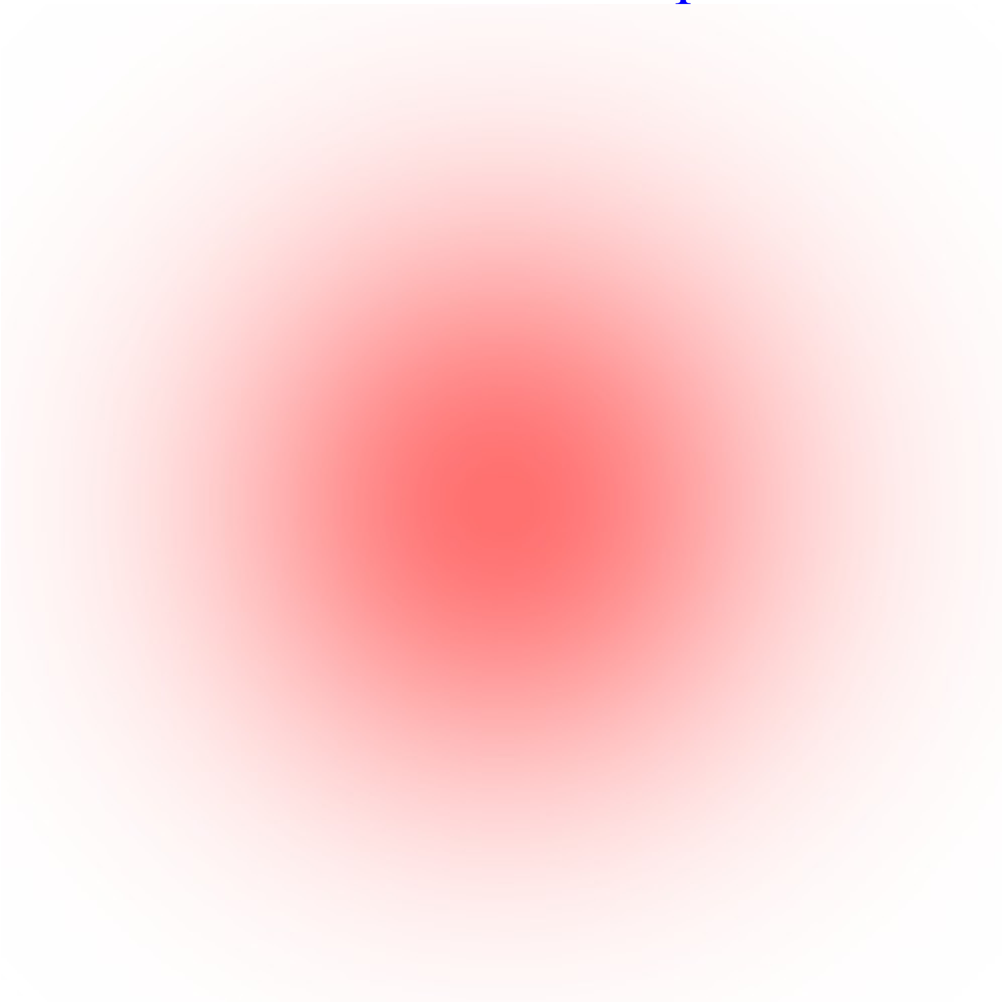
Concentration c

Diffusion in free space



Concentration c

Diffusion in free space

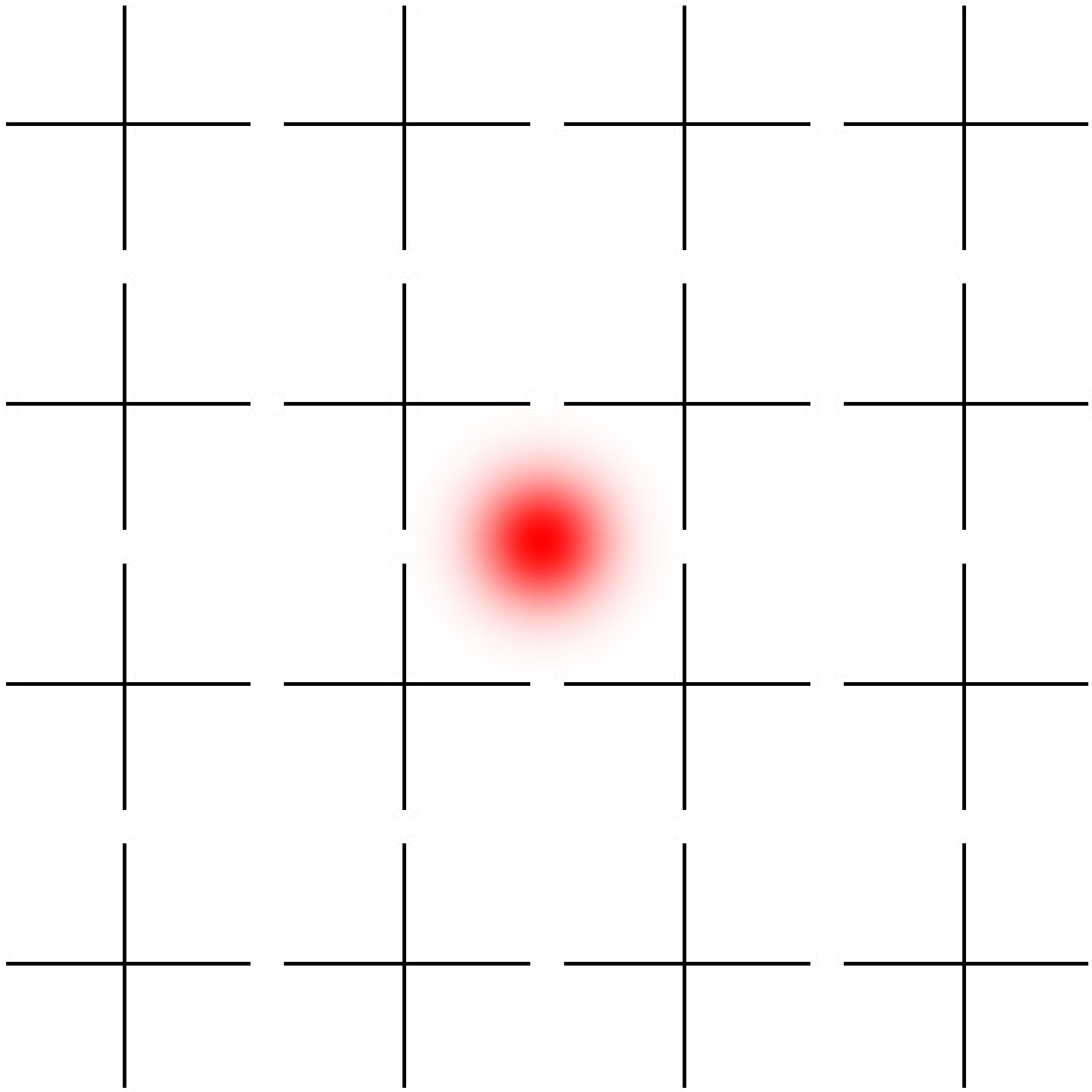


Concentration c

$$\frac{\partial c}{\partial t} = D_0 \nabla^2 c$$

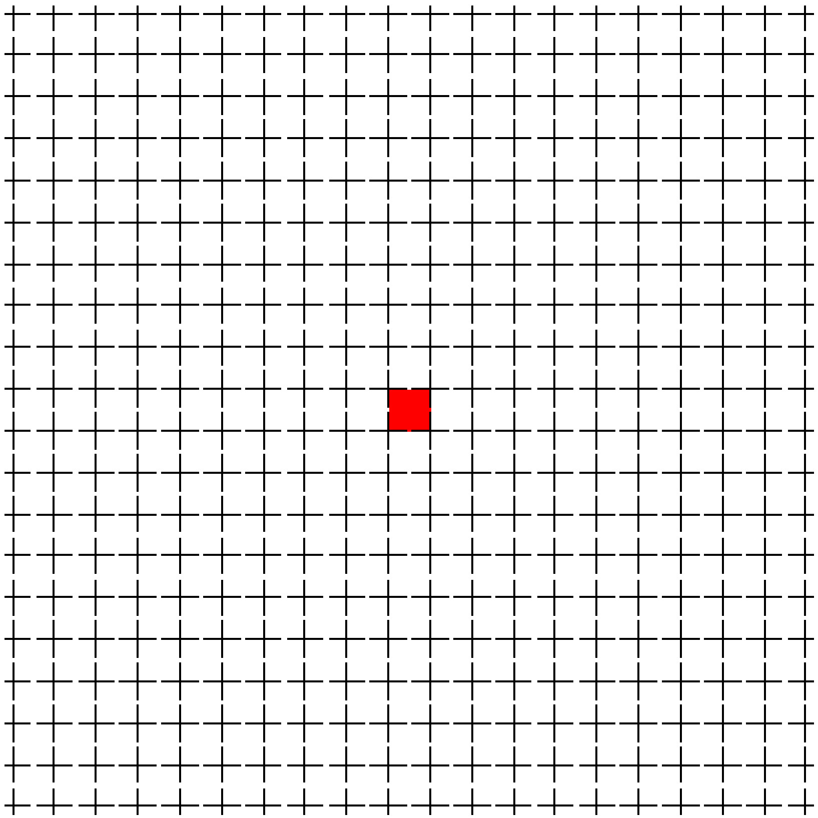
D_0 determines how fast the distribution spreads

Diffusion in an array of cavities



At short times, very different picture

Diffusion in an array of cavities



But over longer time scales and larger length scales, qualitatively similar

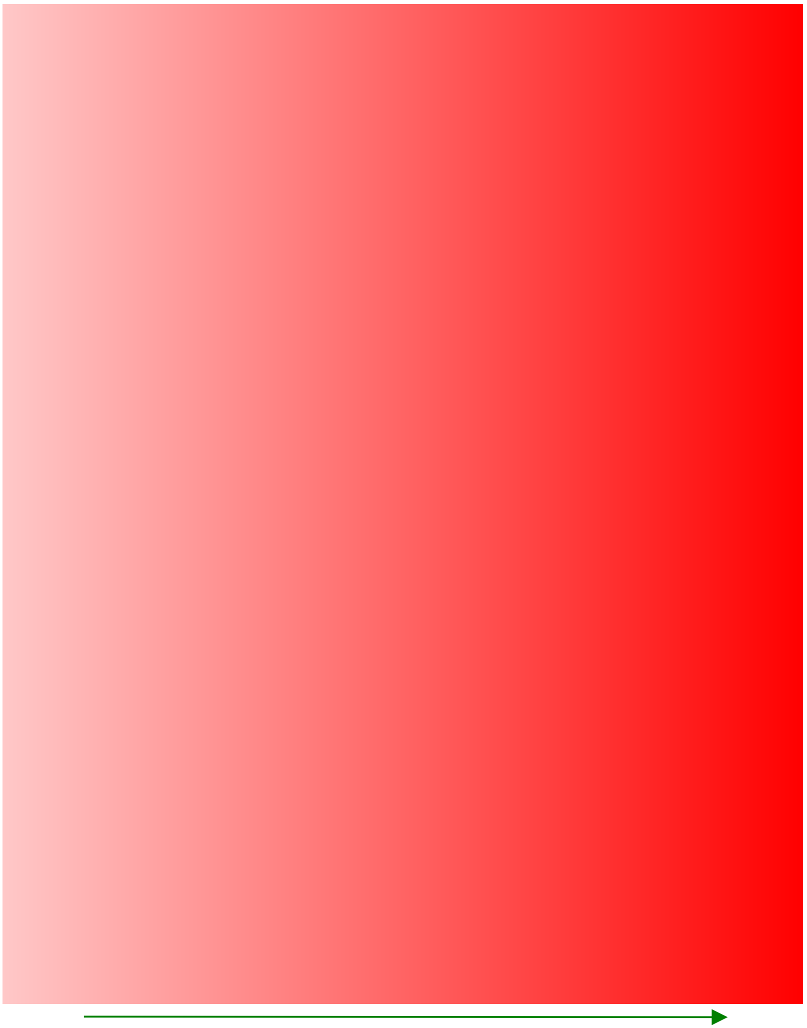
Can define effective diffusion coefficient D_{eff}:

$$\langle r^2 \rangle = 2dD_{\mathrm{eff}}\, t \ , \ \boldsymbol{t \to \infty}$$

Scaled diffusion coefficient $D^* = D_{\mathrm{eff}}/D_0$

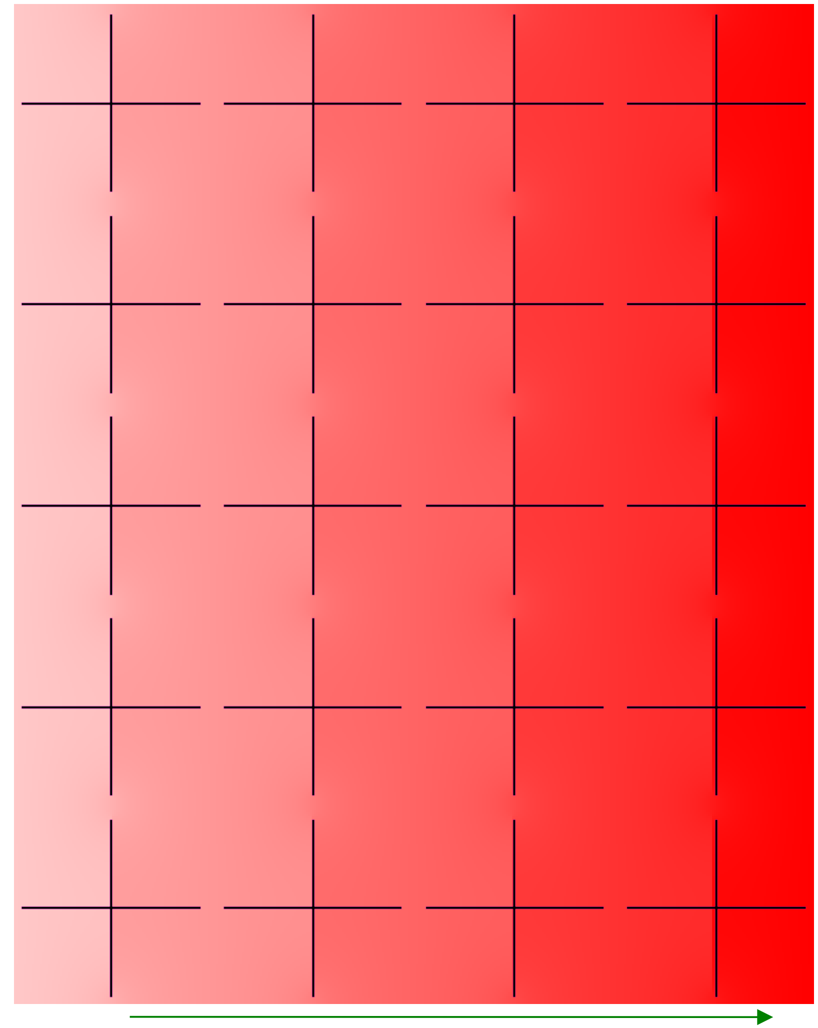
Calculating D_{eff}

Stationary solutions ($\nabla^2 c = 0$)



const gradient

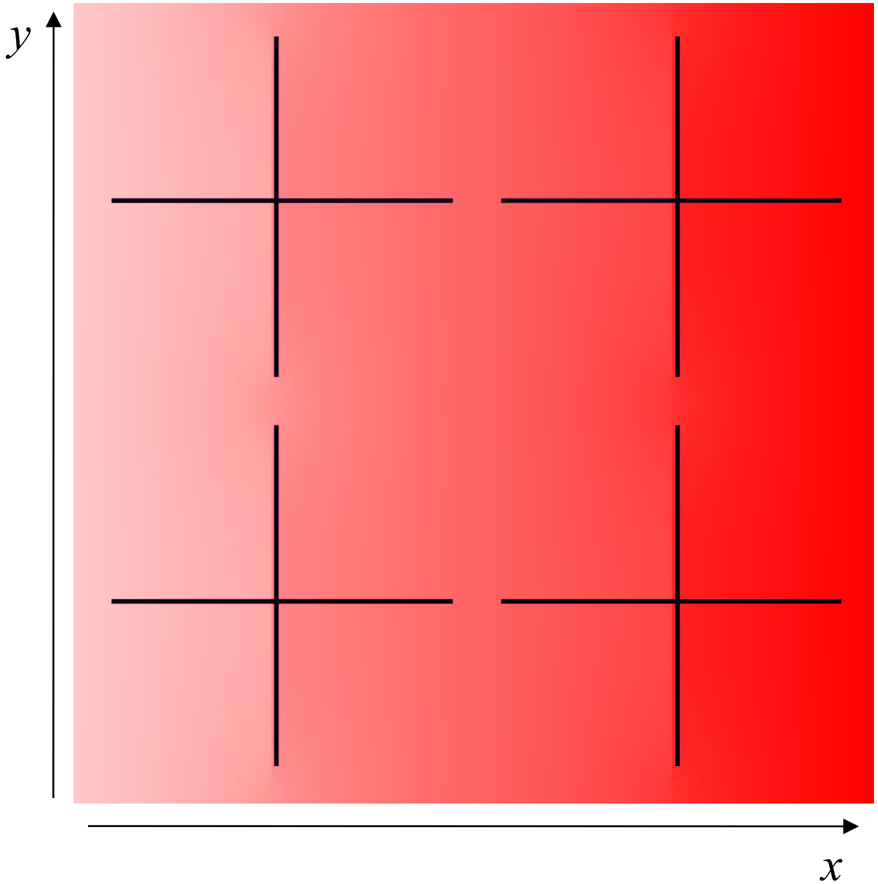
$$D_0 = -\frac{\text{current}}{\text{gradient}}$$



const gradient **on average**

$$D_{\text{eff}} = -\frac{\langle \text{current} \rangle}{\langle \text{gradient} \rangle}$$

Calculating D_{eff}



$$\nabla^2 c = 0$$

$$\frac{\partial c}{\partial \vec{n}} = 0 \qquad \text{at obstacle surfaces}$$

$$c(x+L,y) - c(x,y) = C = \text{const}$$

$$c(x,y+L) - c(x,y) = 0$$

Then

$$D_{eff} = -\frac{D_0 \int \frac{\partial n}{\partial x} dV}{C / L}$$

Same equation and boundary conditions as for mobility (average particle velocity under external force) and effective conductance.

Can be solved analytically in limiting cases (small or large holes), otherwise numerically (much more efficient and accurate than simulating Brownian motion of particles).

Small hole limit

$$D^* = \frac{D_{eff}}{D_0} = \frac{\pi/2}{\ln(\gamma/a)} \qquad (a \ll 1)$$

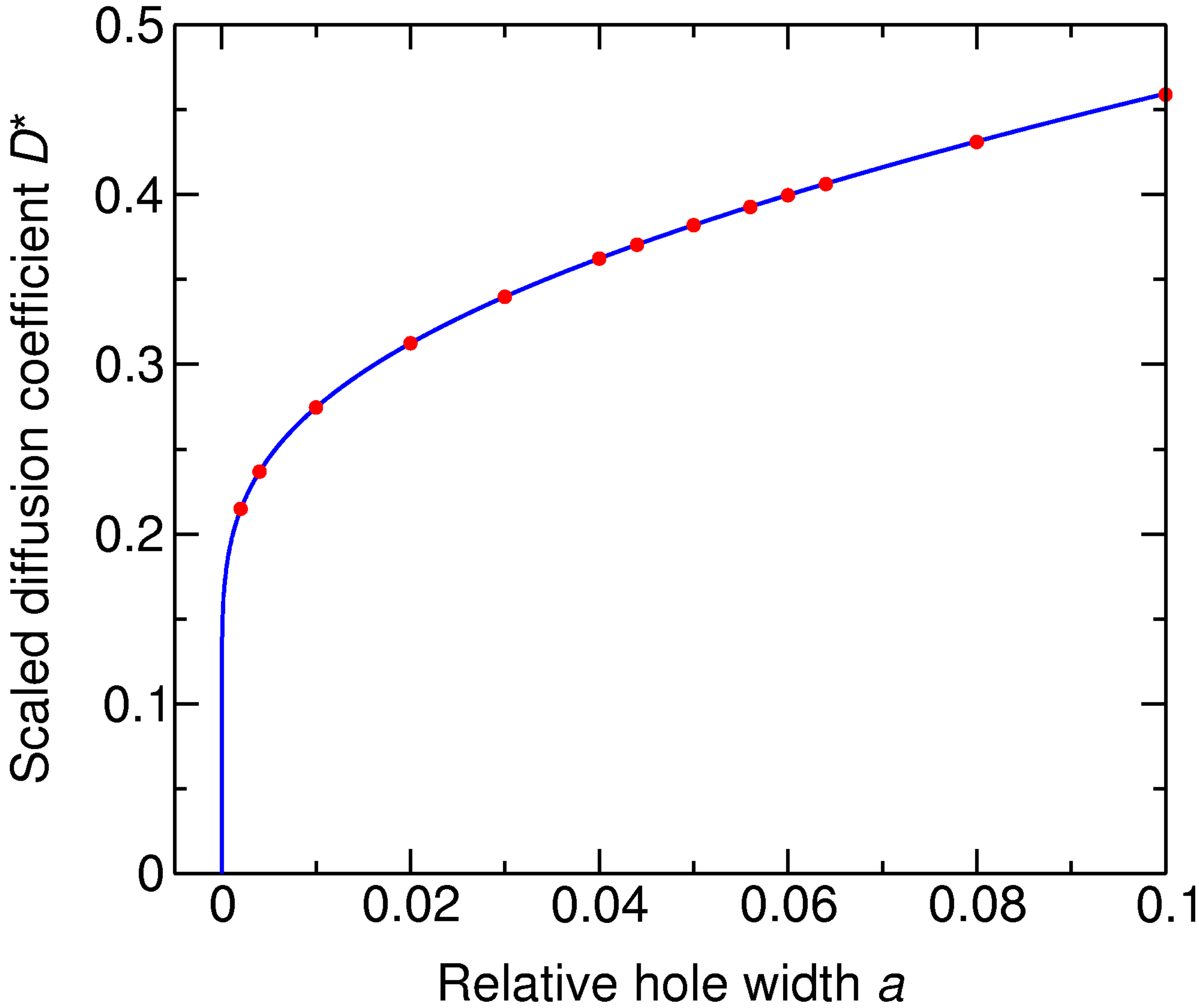
$$a = \frac{\text{hole width}}{\text{cavity size}}$$

$$\gamma = 4\exp\left\{\sum_{n=1}^{\infty}\ln\left(1+\frac{1}{n^2}\right) - \frac{\pi}{2} - \sum_{n=1}^{\infty}\frac{\exp(-2\pi n)[1-\exp(-2\pi n)]}{n[1+\exp(-2\pi n)]}\right\} = 3.051039$$

It is known [D. Holcman *et al.*, J.Stat.Phys. **117** (2004) 975] that the mean escape time from a 2D cavity through a small hole is logarithmic in the hole size. So the inverse logarithmic dependence of D^* is expected, but, e.g., it would be impossible to find γ in this way

Small hole limit

Comparison with numerical data



$$D^* = \frac{\pi/2}{\ln(\gamma/a)}$$

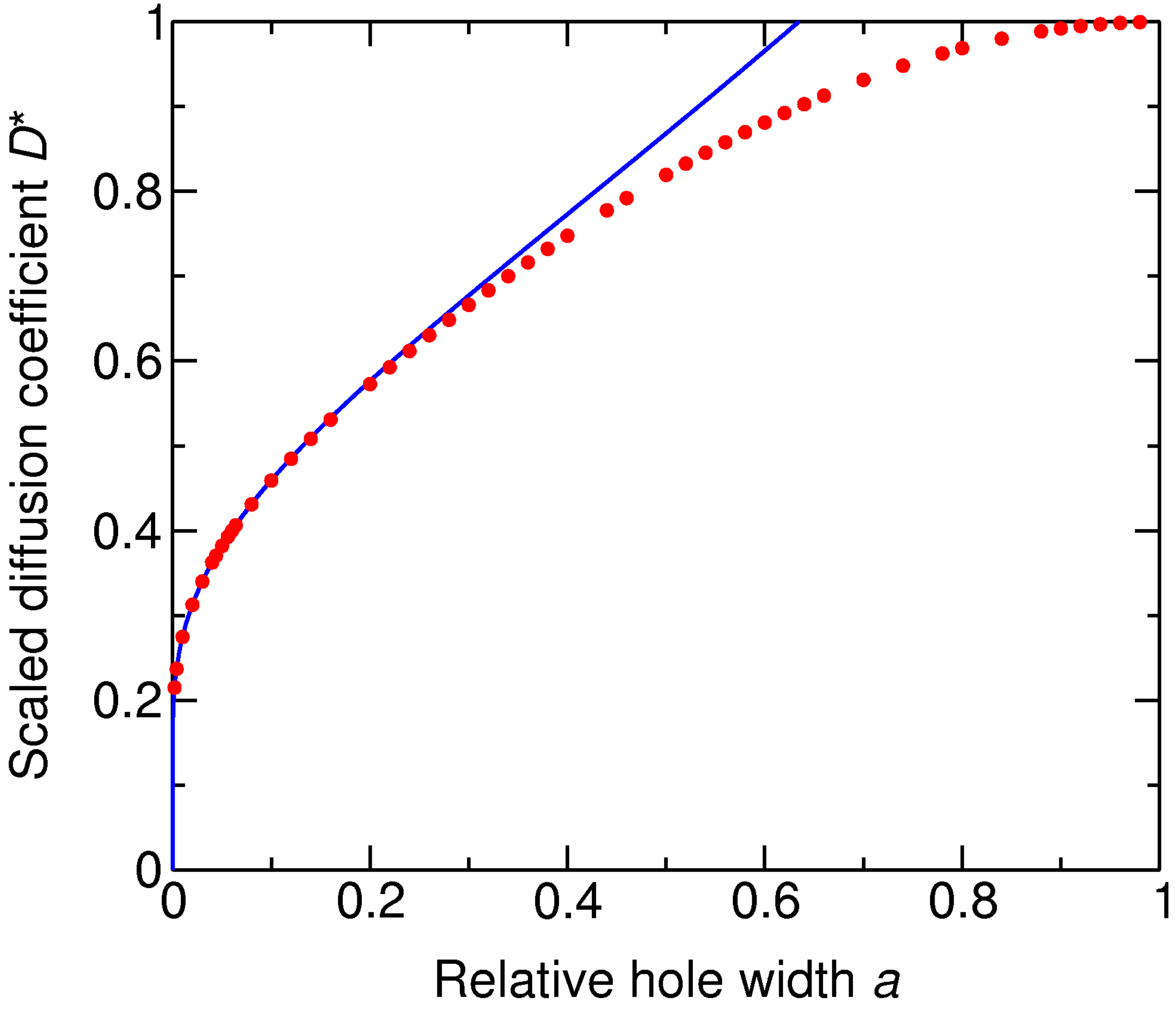
Theoretical:
$\gamma = 3.051039$

From fit to data:
$\gamma = 3.056$

Strikingly sharp initial rise:

at $a = 10^{-6}$, $D^* = 0.105$ (> 10% of free diffusion coefficient!)

Full range of hole widths



An analytical formula valid for all x

1) It can be shown that

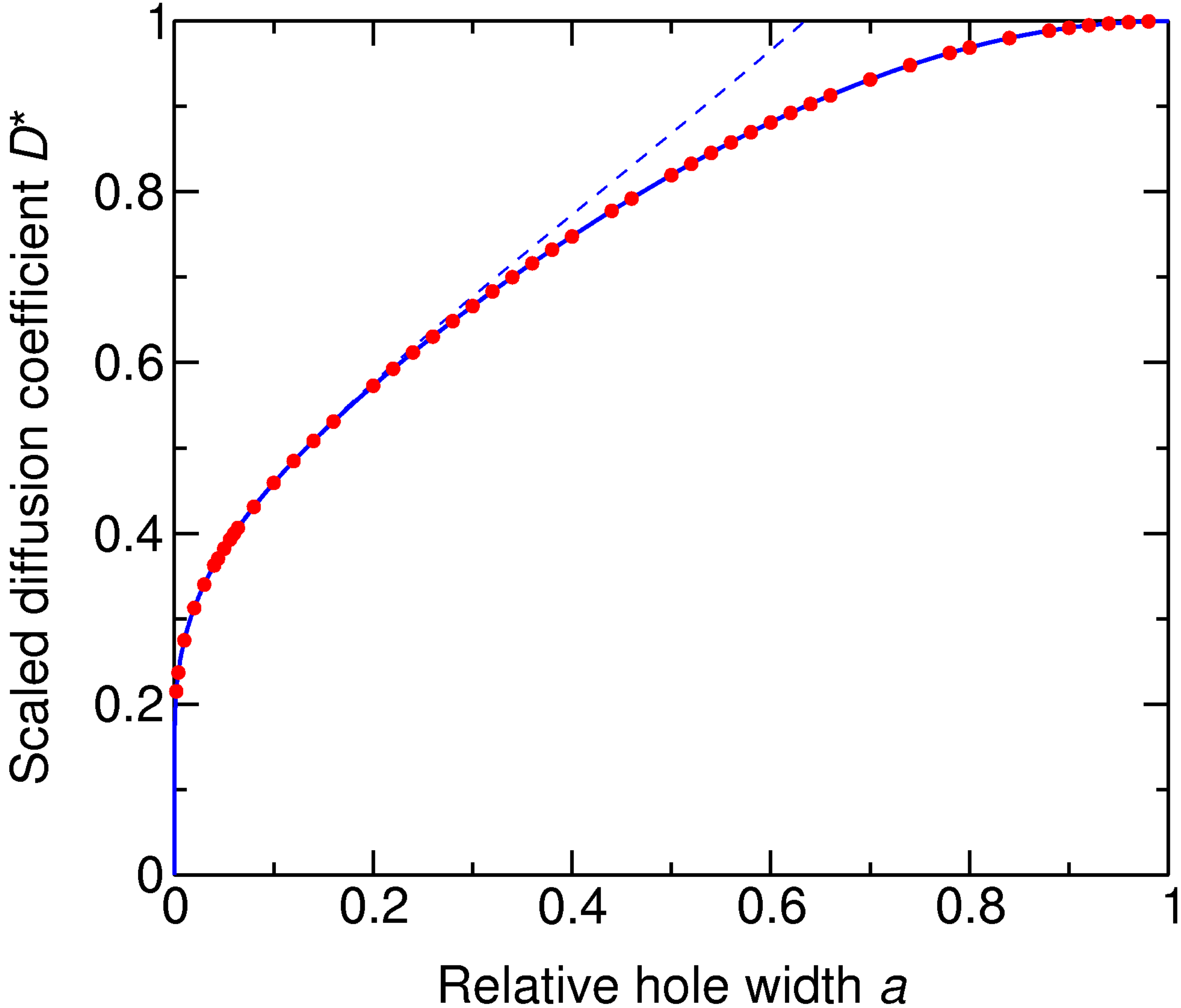
$$D^* = \frac{\pi/2}{\ln(\gamma/a) + C_1 a^2 + C_2 a^4 + C_3 a^6 + C_4 a^8 + \ldots} \qquad (1)$$

2) The behavior in the limit $a \to 1$ (large holes) is known [M.F. Thorpe, 1992]:

$$D^* = 1 - (\pi/4)(1-a)^2 + O[(1-a)^4] \qquad (2)$$

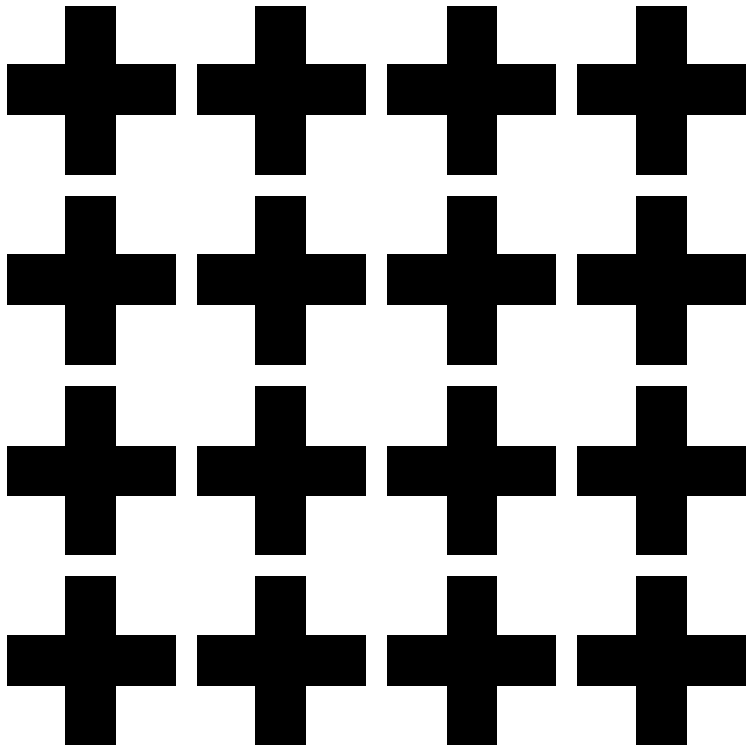
3) Choose $C_1,\ldots,C_4$ so $D^*(1)$ and the first 3 derivatives match in (1) and (2)

No fitting, no adjustable parameters, just straightforward interpolation between two theoretical limits.



Accuracy better than 0.02%

So far, assumed that cavity walls are infinitely thin.



Cavities connected by tubes.

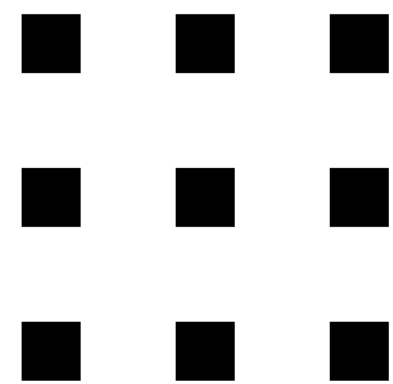
Two parameters:

$$a = \frac{\text{hole width}}{\text{cavity size}} \quad \text{as before}$$

$$(0 \le a \le 1)$$

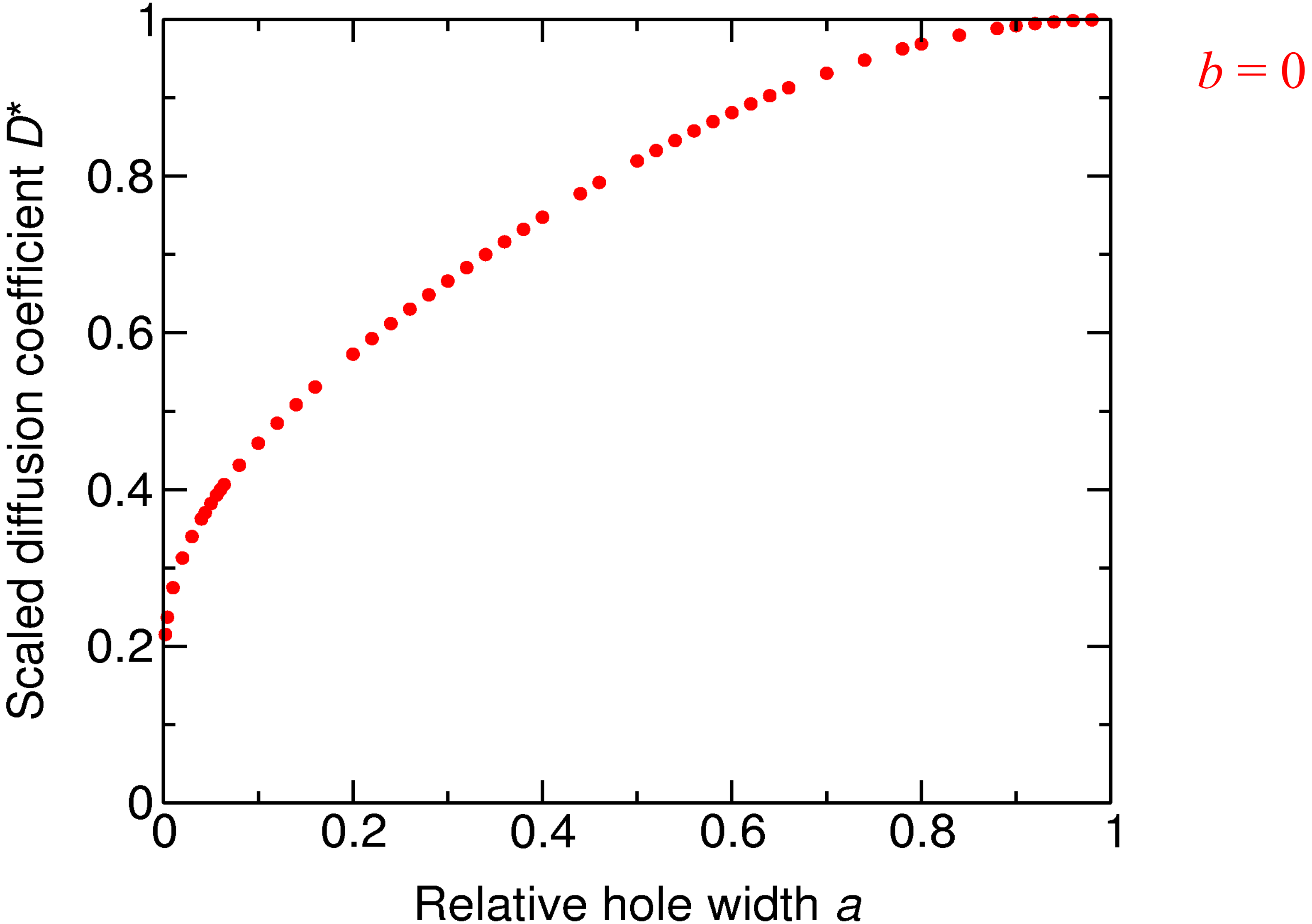
$$b = \frac{\text{tube length}}{\text{cavity size}} \quad (0 \le b < \infty)$$

When $a = 1$, $b \neq 0$, array of square obstacles

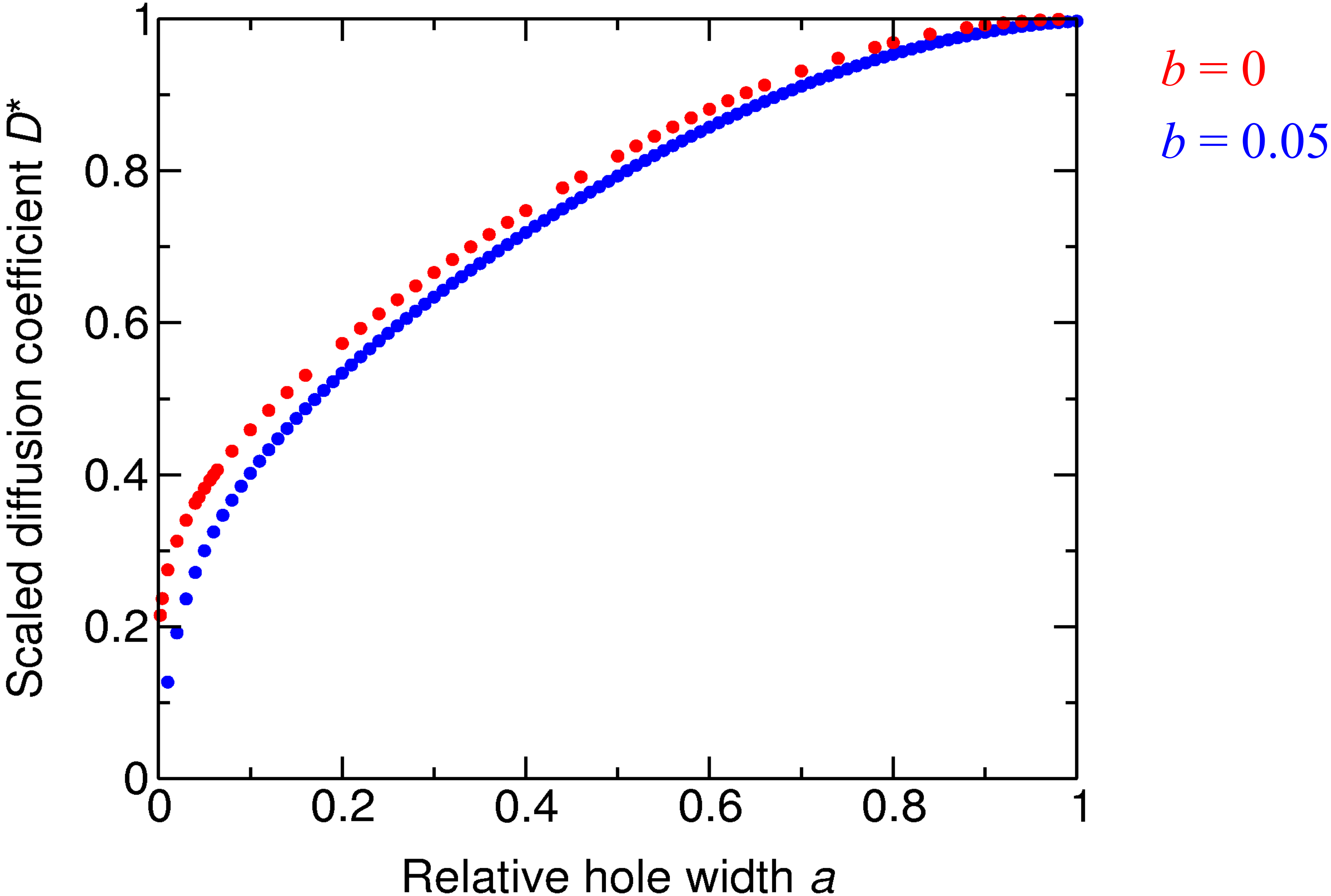


This consideration is also relevant for particles of a finite size.

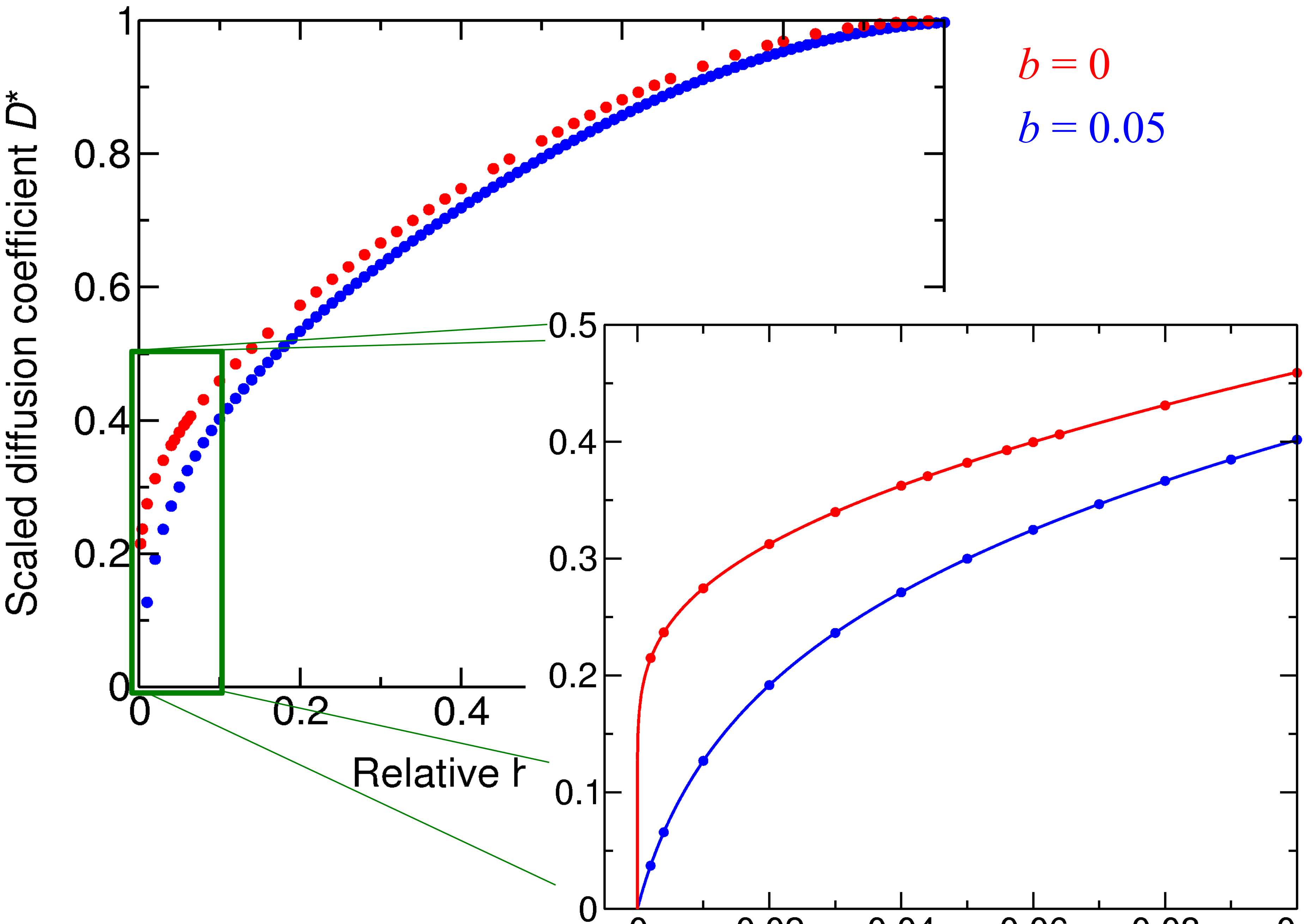
Similar problem in 3D considered by Berezhkovskii *et al.* [JCP **119** (2003) 6991]



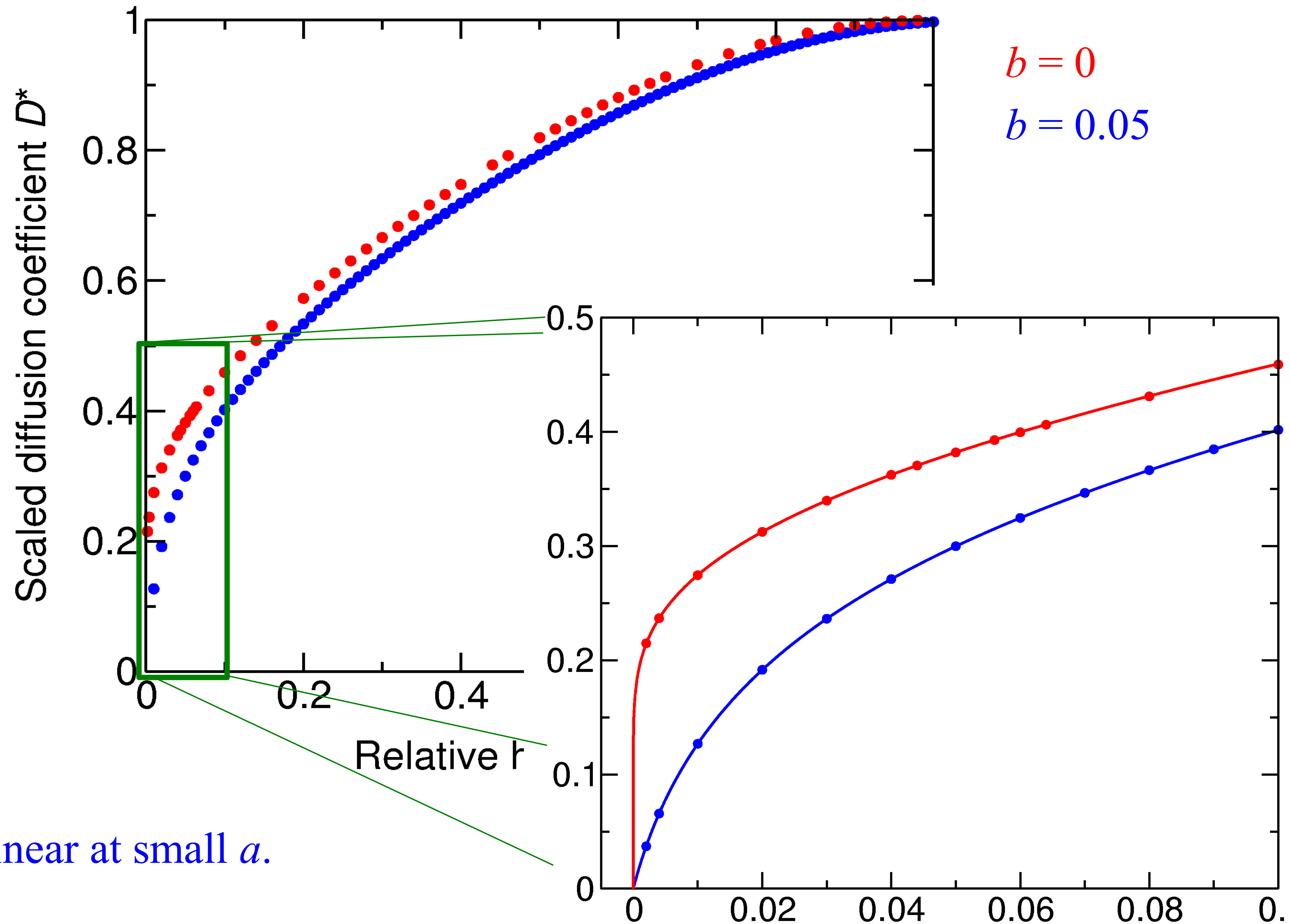
b = 0
Scaled diffusion coefficient D*
Relative hole width a
0
0.2
0.4
0.6
0.8
1



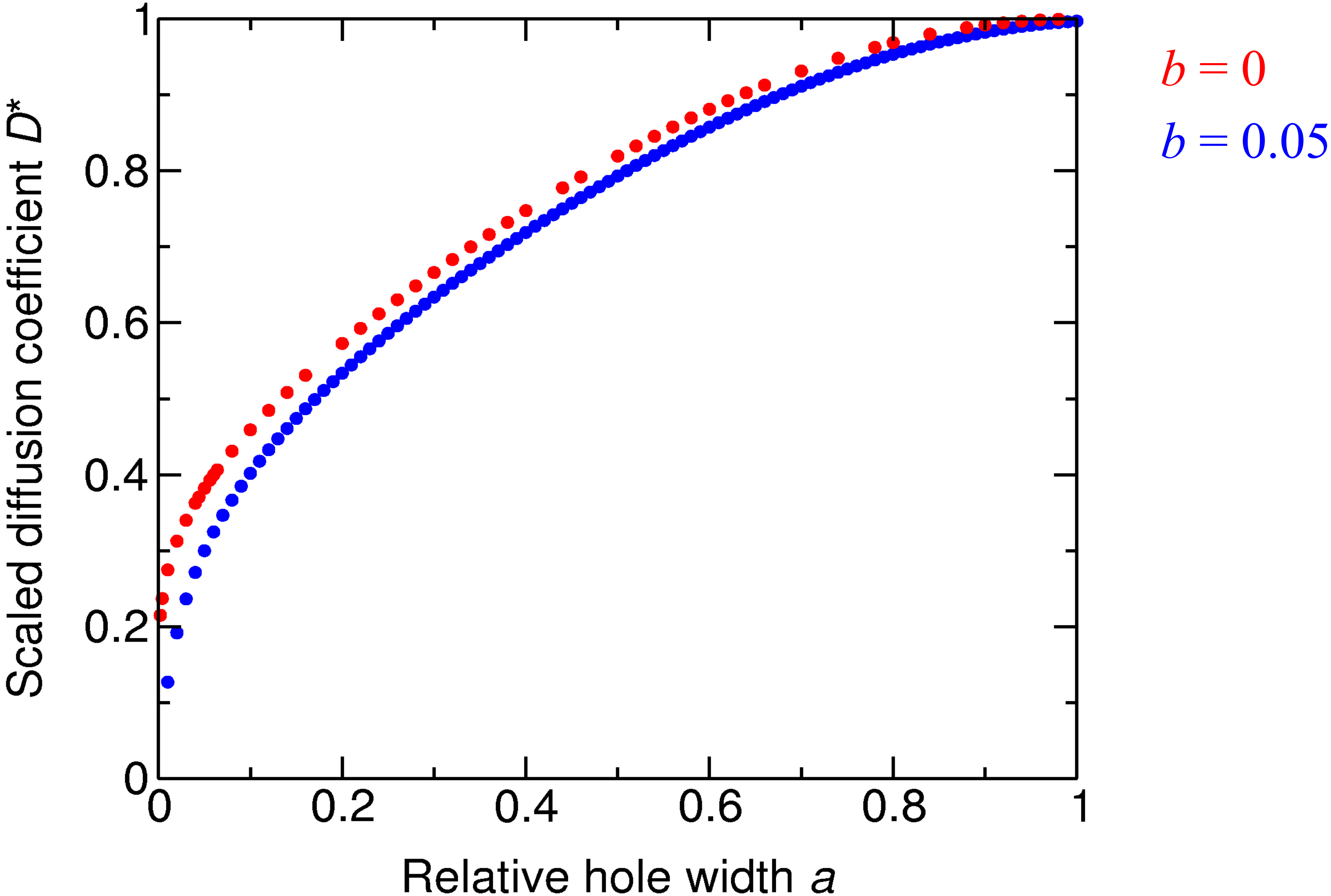
Scaled diffusion coefficient D*
Relative hole width a
b = 0
b = 0.05
0
0.2
0.4
0.6
0.8
1



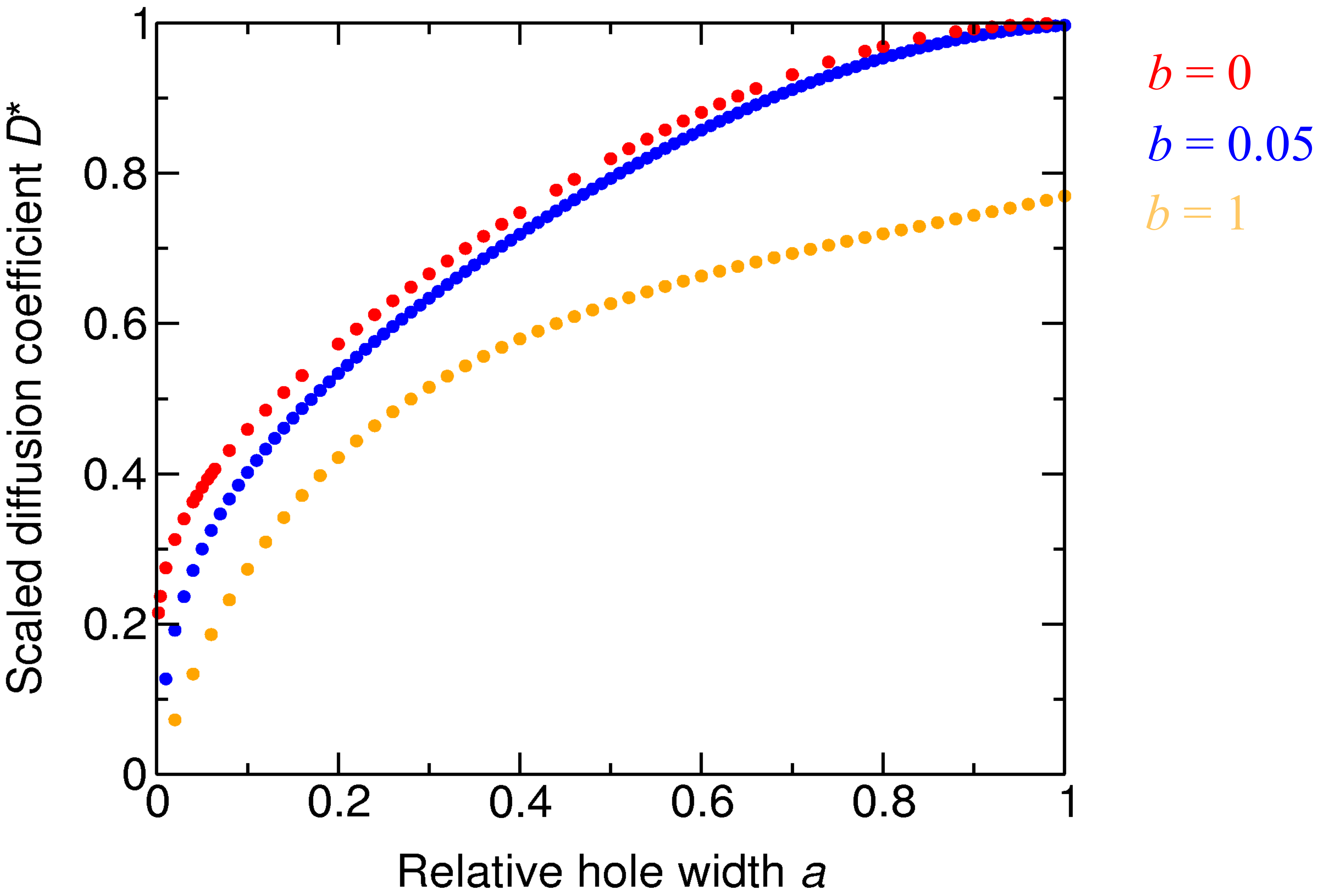
Scaled diffusion coefficient D^*
Relative h
$b = 0$
$b = 0.05$
0
0.2
0.4
0.6
0.8
1
0
0.1
0.2
0.3
0.4
0.5
0.02
0.04
0.06
0.08



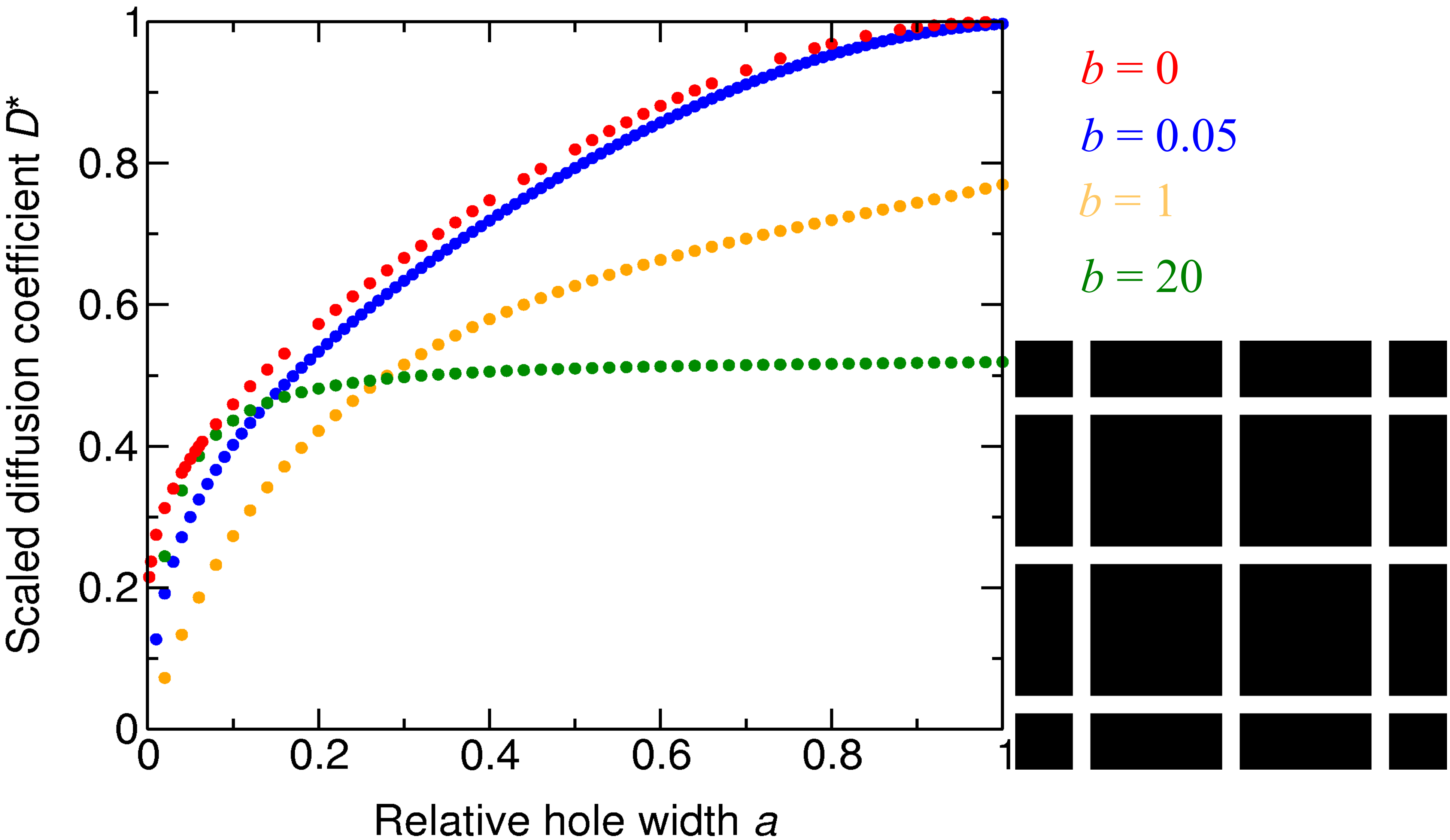
Linear at small a.



Linear at small a.



Linear at small a. Slope decreases with b



Linear at small a. Slope decreases with b, then increases.

At large b and not too small a, approaches 0.5 – free 1D diffusion alternating between x and y directions.

Summary

1. We have studied, both analytically and numerically, diffusion of small particles in arrays of square cavities with holes.

2. For small holes, an inverse logarithmic dependence of the effective diffusion coefficient on the hole width is observed, with an extremely sharp initial rise.

3. A remarkably accurate expression for the effective diffusion coefficient valid in the whole range of hole sizes (from no diffusion to free diffusion)can be obtained by interpolating between the known limiting expressions, without adjustable parameters.

4. When a finite wall thickness is taken into account, the inverse logarithmic dependence is replaced by a linear dependence.

5. In 3D, a similar inverse logarithmic dependence on the hole width is observed for elongated holes.