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Random walk to freedom: The time of effusion

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Abstract

The problem of effusion is studied using Monte Carlo simulations and scaling analysis. Particles confined to the interior of a container undergo a random walk with step size δ. If a hole is opened in one of the container walls, an outgoing diffusive current of particles will exit through it. Effusion is exponentially fast with the characteristic time dependent on δ, the container volume, and the size of the pore. It is found that if the effusion time is properly scaled, all the data can be collapsed onto one universal curve independent of the geometry of container and the pore.

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The problem of determining the effusion time of solute through a pore of a vesicle [1,2] is of great practical interest in a number of different contexts ranging from the design of efficient drug delivery systems [3,4] to understanding the generation of post-synaptic currents at chemical synapses [5,6].

Formulated in terms of a diffusion equation the problem is particularly difficult, since the boundary conditions required to tackle it are of mixed type—a combination

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of Neumann and Dirichlet. An exact analytical solution is, therefore, unlikely and one is forced to use either numerical methods or direct Monte Carlo simulations of the effusion process. In this paper we shall take the second route. We simulate particles, undergoing a random walk with step size δ and step time τ_m, confined to the interior of a vesicle.

The geometries that we are interested in are shown in Figs. 1 and 3. We start with N particles randomly distributed inside the vesicle. At time $t = 0$ a pore represented by an absorbing surface is nucleated. At each Monte Carlo step every particle attempts to make a random move to a new position. There are three possible outcomes: (1) the particle hits the wall, in which case the move is rejected, (2) the move is successful and a new particle position is recorded, (3) the particle is removed from the vesicle as it passes through the pore. The number of particles inside the vesicle decreases exponentially [7–9] as

$$N(t) \sim e^{-t/\tau} , \tag{1}$$

where τ is the characteristic effusion time.

Purely on dimensional grounds, the time of effusion must have the form

$$\tau = \frac{\tau_m R^2}{\delta^2} f\left(\frac{\delta}{a}, \frac{R}{a}\right) , \tag{2}$$

where $f(x, y)$ is a scaling function of two variables. For $\delta \ll a$ the particle density $\rho(\mathbf{r}, t)$ satisfies the diffusion equation

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho , \tag{3}$$

with

$$D = \frac{\delta^2}{6\tau_m} \tag{4}$$

and reflecting boundary conditions on the surface of the vesicle and absorbing boundary condition at the pore.

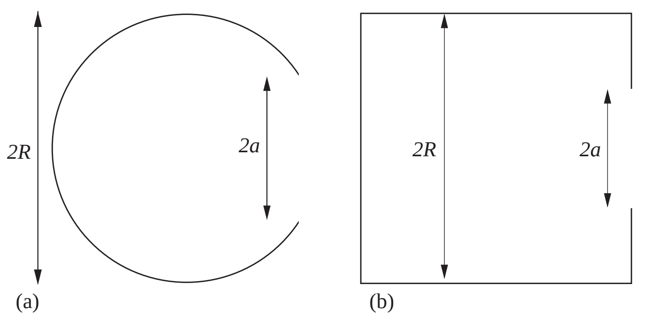

Fig. 1. Two dimensional sections of $3d$ figures. Figure (a) shows a vesicle with a circular pore of radius a on its surface. In figure (b), a square hole of dimension $2a \times 2a$ is located symmetrically at the center of one of the cube's faces.

Using a heuristic argument, based on results for the steady state flux of particles passing through a small hole in a planar wall [10,11], it is possible to argue that in the limit $a \ll R$ and $\delta \to 0$ the effusion time should be [12,13]

$$\tau = \left(\frac{\pi^2}{32AP}\right)^{1/3} \frac{V}{D} , \tag{5}$$

where A and P are the area and the perimeter of the pore and V is the volume of the vesicle. Thus, for a circular pore the effusion time diverges as $1/a$. The scaling function is then,

$$f(0,y) \sim y \quad \text{for } y \gg 1 . \tag{6}$$

When the step size is larger than the pore size, $R \gg \delta > a$, we expect the time of effusion to diverge with the diminishing area of the pore. Indeed, in this limit, the simulations find

$$\frac{\tau\delta^2}{R^2} \sim \frac{\tau_m \delta R}{a^2} , \tag{7}$$

which means that the scaling function is

$$f(x,y) \sim xy \quad \text{for } x \gg 1;\ y \gg 1 . \tag{8}$$

The fact that for $R/a \gg 1, f(x,y)$ is proportional to y for both large and small values of x suggests that it can be written as

$$f(x,y) \approx g(x)y \quad \text{for } y \gg 1 , \tag{9}$$

where for $x \gg 1$, $g(x) \sim x$. The form of $g(x)$ can, in principle, depend on the vesicle and the pore geometries.

Eq. (9) implies that for a given geometry, if one plots the scaled effusion time

$$\tau^* \equiv \frac{\tau\delta^2 a}{\tau_m R^3} \tag{10}$$

versus δ/a, the effusion times for all the different combinations of δ, R and a should collapse onto one single curve $g(x)$, as long as $R/a \gg 1$. This is indeed what is found in Fig. 2.

To further check the robustness of the scaling theory presented above we now apply it to calculate the effusion time from a cylindrical vesicle of length L and radius R through a circular pore of radius a located symmetrically on one of the sides of the cylinder, Fig. 3. On dimensional grounds the effusion time must now be of the form

$$\tau = \frac{\tau_m L^2}{\delta^2} f\left(\frac{\delta}{a}, \frac{R}{a}, \frac{R}{L}\right) . \tag{11}$$

Motivated by Eq. (9), we make an ansatz of separability of the scaling function in the limit $L, R \gg a$,

$$f(x,y,z) \approx g_c(x) y p_c(z) . \tag{12}$$

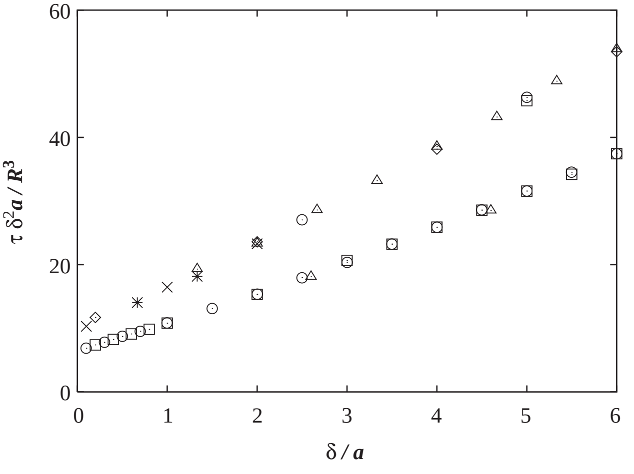

Fig. 2. The scaled effusion time as a function of δ/a for various combinations of δ, a, and R, such that $a/R<0.1$. The curves from top to bottom are: for cubes with square pores and spheres with circular pores. A perfect collapse of the data is obtained.

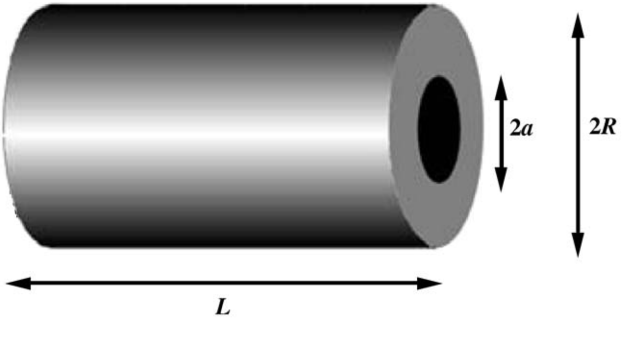

Fig. 3. Cylindrical vesicle of length L and radius R with a circular pore of radius a on one side.

Furthermore, the presence of V in Eq. (5) implies that the effusion time should scale with the volume of the vesicle. This means that the scaling function $p_c(z)\sim z$. Therefore, as long as $L, R \gg a$, if one plots the scaled effusion time

$$\tau^* = \frac{\tau\delta^2 a}{\tau_m L R^2} \tag{13}$$

versus δ/a, the effusion times for all the different combinations of δ, R, L, and a should collapse onto one single curve $g_c(x)$. This is precisely what is found in Fig. 4.

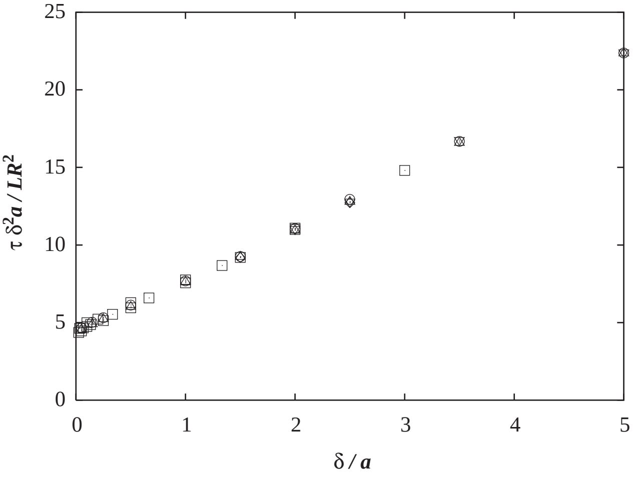

Fig. 4. Effusion time, scaled as in Eq. (13), for small pores with $a/R<0.1$, as a function of δ/a for various combinations of δ, a, L, and R, corresponding to the different symbols in the figure. A perfect collapse of the data is obtained.

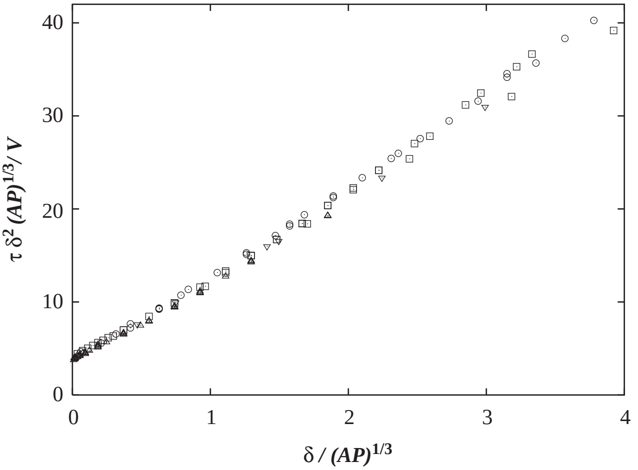

Fig. 5. The effusion time scaled as in Eq. (14) as a function of δ/l, for various sizes and shapes of the vesicles and the pores. A very good collapse of data is found over a wide range of δ's. Deviations appear only when the step size of the walkers becomes comparable to the size of the container. Under these conditions the dynamics loses the universality, and the effusion time becomes dependent on the detailed geometry.

It should be noted that the effusion time in all the cases discussed above is proportional to the volume of the container. Furthermore, the presence of the length scale $l=(AP)^{1/3}$, instead of just a, in Eq. (5) suggests that the natural scaling variables should be V and l. Rewriting our previous results in terms of these we arrive at

$$\tau^* \equiv \frac{\tau\delta^2(AP)^{1/3}}{\tau_m V} = h\left(\frac{\delta}{(AP)^{1/3}}\right), \tag{14}$$

$h(0) = 3(\pi/2)^{2/3}$. In Fig. 5, we show that when scaled as in Eq. (14), all the data of Figs. 2 and 3 collapses onto one universal curve. We have also checked that this scaling persists for pores of other geometrical shapes such as ellipses with different aspect ratios.

Our results confirm the form of the effusion time found in Refs. [12,13] in the limit $\delta \to 0$. Furthermore, we also obtain a universal scaling function for the effusion time of a random walk with an arbitrary step size δ.

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