



## Diffusion through colloidosome shells

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### ABSTRACT

Colloidosomes are aqueous cores surrounded by a shell composed of packed colloidal particles. Recent studies suggest that these colloidal shells reduce, or even inhibit, the transport of molecular species (diffusants). However, the effect of the colloidal shell on transport is unclear: In some cases, the reduction in transport of diffusants through the shell was found to be independent of the size of the colloidal particles composing the shell. Other studies find, however, that shells composed of small colloidal particles of order 100 nm or less hindered transport of diffusants more than those composed of micro-scale colloidal particles. In this paper we present a simple diffusion model that accounts for three processes that reduce diffusant transport through the shell: (i) a reduction in the penetrable volume available for transport, which also increases the tortuosity of the diffusional path, (ii) narrow pore size which may hinder transport for larger diffusants through size exclusion, and (iii) a reduction in interfacial area due to 'blocking' of the surface by the adsorbed particles. We find that the colloidal particle size does not affect the reduction in transport through the colloidal shell when the shell is a monolayer. However, in closely packed, thick layers where the thickness of the multi-layer shell is fixed, the rate of transport decreases significantly with colloidal particle dimensions. These results are in excellent agreement with previously published experimental results.

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### 1. Introduction

Controlling the rate of transport of an encapsulated species into or out of an aqueous or hydrogel volume is of considerable interest for various industries such as pharmaceuticals or cosmetics [1–8]. Colloidosomes are microcapsules that consist of a hollow or polymer hydrogel core coated by a shell composed of self-assembled colloidal particles. The colloidal particles adhere to the core surface through forces such as electrostatic interactions or interfacial interactions [1–14]. In recent years, the trademark of colloidosomes as a delivery device has been the ability to control porosity, and thus, permeability, through choice of the colloidal particle size, which can range from nanometers to microns [9–14]. Lee and Weitz [13] find that a small-molecule diffusants can freely pass through shells composed of colloidal particles that are 10–20 nm, while a larger drug cannot, presumably due to size exclusion. In a more detailed study, Kim et al. [11] found that the permeability of a small-molecule diffusant through buckled, multi-layered colloidosome shells decreases with the size of the colloidal particles composing the shell. In contrast, we have recently shown that although a monolayer of colloidal particles hinders the transport of small hydrophilic diffusants (caffeine and aspirin) when

compared to uncoated gels, the flux is independent of the colloidal particle size [14].

Here we develop a simple diffusion model to describe the transport of diffusants through colloidosome shells. The model accounts for three mechanisms that can hinder transport: The 'composite' nature of the colloidal shell where the reduced volume of the penetrable phase and increases path tortuosity hinder transport, size exclusion due to narrow pore size, and the reduction in interfacial area between the aqueous core and the colloidal shell.

The model is applied to two types of colloidosome shells: Monolayers, where the thickness of the shell is equal to the diameter of the colloidal particles, and thick multi-layered shells where the shell thickness is independent of particle size. We find that colloidal monolayers hinder transport when compared to uncoated systems. However, the reduction in diffusion is independent of the particle size, in agreement with our recent experimental results [14]. However, in the case of thick layers, the model predicts that decreasing the colloidal particle size should cause a significant reduction in the rate of transport, as indeed observed by Kim et al. [11].

### 2. Model

A colloidosome shell is composed of two phases: Impenetrable colloidal particles, interspaced by a penetrable phase (aqueous solution or a polymer gel, depending on the core type and

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synthesis process). As a result, transport through the shell is hindered by two contributions: First is the reduced volume for transport, namely, the ‘porous media’ effect, which is also associated with increased diffusional pathway due to tortuosity (see Fig. 1A). Second is the characteristic shell pore dimension, which could reduce or suppress transport of diffusants whose dimensions are similar or larger than the pore width (Fig. 1B). In addition, the adsorption of colloids at the interface with the core reduces the area available for transport (Fig. 1C). This latter contribution, which is due to the interfacial area available for transport, is not accounted for in the ‘porous media’ effect which is volume based (see more detailed discussion below).

The ‘composite’ nature of the shell reduces the volume available for transport, and increases the ‘path length’ that a diffusant must traverse within the shell (Fig. 1A). Bell and Crank [15] have calculated the reduction factor for transport in a composite medium,  $\alpha_c$ . In loosely packed systems where the volume fraction of particles is of order  $1/2$  or lower

$$\alpha_c = \frac{1}{1 + \phi^{1/3}} \quad (1a)$$

while in dense, highly packed layers

$$\alpha_c = \frac{1}{1 + \phi} \quad (1b)$$

where  $\phi$  is the volume fraction of the impenetrable phase (in our case, the colloidal particles),  $b$  is the radius of the colloids, and  $\zeta$  is a measure of the particle spacing (see Fig. 1). Thus, if the volume fraction of the particles  $\phi$  is zero, there is no reduction in transport and  $\alpha_c = 1$ . As  $\phi$  increases,  $\alpha_c$  decreases. Note, however, that the maximal value of  $\phi$  for spherical particles is 0.65–0.67, so that the minimal value of  $\alpha_c$  is of order 0.6.

The Bell and Crank [15] analysis for composite media assumes that the diffusants are point-particles. However, diffusants may be large, especially in biological systems where these may be proteins, biopolymers or even cells. In systems where the diffusant size is of the same order of magnitude as the characteristic pore size (Fig. 1B), transport of such diffusants may be hindered or suppressed completely. Beck and Shultz [16] have shown that the reduction factor,  $\alpha_p$  for the flux due to pore dimensions can be given by

$$\alpha_p \approx \left(1 - \frac{R_D}{R_p}\right)^4 \quad (2)$$

where  $R_D$  is the radius of the diffusant, and  $R_p$  that of the pore. Note that this expression is valid only for  $R_D \leq R_p$ . To relate  $\alpha_p$  to the shell of a colloidosome,  $R_p$  must be expressed in terms of the colloidal particle size and the packing density of colloids in the shell. In systems where the shell is loosely packed, so that the volume

fraction of the particles  $\phi$  is lower than  $\sim 0.5$ , the radius of the pore may be expressed, using geometrical considerations as  $b(0.8/\phi^{1/3} - 1)$ , as shown in Fig. 1B.

In highly packed systems where the particles are above the overlap limit (namely,  $0.55 < \phi < 0.65$ ). The simulations of Rintoul and Torquato [17] shows that  $R_p$  is of order 5–10% of the colloidal dimensions: [17] For a shell with a packing density of  $\phi$  0.6 composed of 1  $\mu\text{m}$  particles, the characteristic pore size is of order 70 nm, while one composed of particles of order 20 nm will have pores of order 1.4 nm. Fitting their simulations results yielded the linear correlation [17]  $R_p \approx b\{(\pi 6\phi)^{1/3} - 1\}$ .

The composite medium model is appropriate for description of the transport through the colloidal shell of a colloidosome. However, it does not account for the interface between the core and the shell, where the ‘blocking’ of the interface area by adsorbed colloids would further reduce transport. Naively, this blocking effect should be proportional to the fraction of interface area unavailable for transport. However, Berg [18] has shown that the size of the ‘blockers’ plays a role as well (see Fig. 1C). Indeed, they show that it is linear with the radius of the surface ‘blocker’, rather than scale as the area [18]. Defining the fraction of the surface area occupied by the impenetrable disks as  $\phi_s$ , the radius of the disk-like regions as  $b$ , and the thickness of the film containing the diffusant as  $a$  yields [18]

$$\alpha_s \approx \frac{1}{1 + \frac{a\phi_s}{\pi b(1-\phi_s)}} = \frac{\pi b(1-\phi_s)}{\pi b(1-\phi_s) + a\phi_s} \quad (3)$$

When the fraction of the impenetrable phase on the surface,  $\phi_s$ , is zero (or the radius of the disks  $b = 0$ ), there is no interfacial reduction in transport and  $\alpha_s = 1$ . If the impenetrable phase occupies the entire interface,  $\alpha_s = 0$ .

Combining the three mechanisms allows the calculation of the reduced diffusion coefficient  $\alpha_T = \alpha_c \alpha_p \alpha_s$  for a diffusant through a colloidosome shell, as a function of the packing density and particles size. For a loosely packed layer:

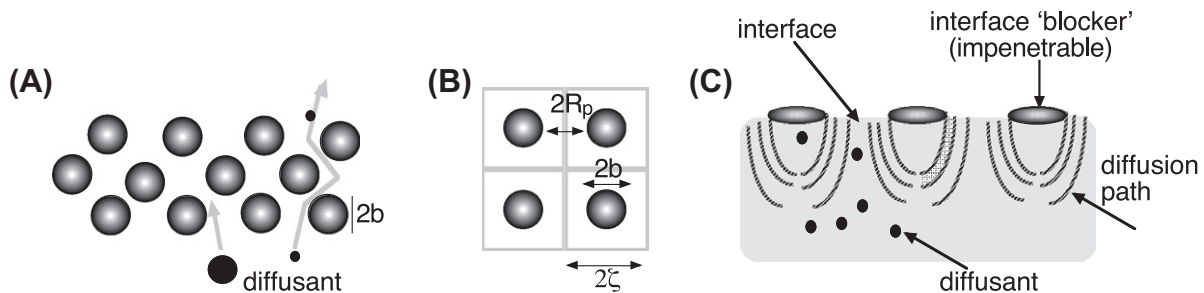
$$\alpha_T = \frac{\left(1 - \frac{R_D}{b(\pi/6\phi)^{1/3} - 1}\right)^4}{(1 + \phi^{2/3}(\pi/6)^{1/3}) \left(1 + \frac{a\phi_s}{\pi b(1-\phi_s)}\right)} \quad (4a)$$

and for a highly packed, dense layer:

$$\alpha_T = \frac{\left(1 - \frac{R_D}{b(11/50 - \phi/4)}\right)^4}{(1 + \phi) \left(1 + \frac{a\phi_s}{\pi b(1-\phi_s)}\right)} \quad (4b)$$

The effective diffusion coefficient of the diffusant through a colloidal shell is therefore reduced by a factor of  $\alpha_T$ .

Eq. (4) provides the main derivation of this paper, namely, the effect of the colloidal particle size ( $b$ ) and packing density in the



**Fig. 1.** (A) A schematic of a colloidosome shell. The radius of the colloidal particle is  $b$ . The packing of the colloidal particles in the shell reduces volume available for transport and increases the tortuosity of the diffusion path, thereby reducing the diffusion rate for all diffusants. In addition, the diameter of some diffusants may be similar or larger than the characteristic pore size, so that their transport is reduced or suppressed. (B) Pore dimension in loosely packed colloidal shells. The volume fraction of particles,  $\phi$ , is given by  $(4\pi b^3/3)/8\zeta^3$ . Thus,  $\zeta/b \sim (\pi 6\phi)^{1/3}$ . The pore radius, which is of order  $\zeta - b$ , is therefore approximated by  $b(\pi 6\phi)^{1/3} - 1$  which is of order  $b(0.8/\phi^{1/3} - 1)$ . (C) Disk-like blockers of interfacial transport lead to the formation of ‘stagnant’ regions where transport is slower, thereby reducing flux through the interface.

shell ( $\phi$ ,  $\phi_s$ ) on the reduction in flux through colloidosome shells. However, to evaluate the flux, we need to incorporate  $\alpha_T$  in a diffusion model. The diffusion of a component through a two-layered spherical system, as shown in Fig. 2A, has been previously calculated [19]. Assuming that the solution surrounding the sphere is a perfect sink (namely, the concentration of the diffusant is zero, at all times), the time dependent concentration profile of the diffusant in the core region is given by [19]

$$c(r, t) = c_0 \frac{2La}{r} \sum_{n=1}^{\infty} \frac{\sin \beta_n r / a}{\sin \beta_n (\beta_n^2 + L^2 - L)} e^{-D\beta_n^2 t / a^2} \quad (5)$$

where the initial concentration is defined by  $c_0$ ,  $D$  is the diffusion coefficient in the core region,  $a$  is the sphere radius,  $r$  is the radius, and  $t$  is time.  $L$  is a dimensionless parameter that defines the properties of the shell [19]:

$$L = \frac{aD_s}{hD} \quad (6)$$

where  $h$  is the shell thickness and  $D_s$  the diffusion coefficient in the shell.  $S$  is a parameter defining the fraction of surface area available for transport [18].  $L$  defines the effective reduction in transport due to the presence of a shell, accounting for both the thickness of the shell and the (potentially different) transport rate through the shell, when compared to the core. Thus, complete suppression of transport, where  $L = 0$  occurs either when the shell is impenetrable ( $D_s = 0$ ) or when the shell is infinitely thick ( $h \rightarrow \infty$ ). When the shell does not offer any resistance to transport (e.g. if there is no shell and  $h = 0$ )  $L \rightarrow \infty$ .

The diffusion equation for this system is solved using separation of variables [19]. The eigenvalues  $\beta_n$  are given by the roots of the expression [19]

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (7)$$

Integrating the flux from the sphere enables calculating the overall mass transferred,  $M(t)$ , and the fraction of mass transferred,  $f(t)$  [19]:

$$f(t) = \frac{M(t)}{M_{\infty}} = 1 - \frac{\sum_{n=1}^{\infty} \frac{e^{-D\beta_n^2 t / a^2}}{\beta_n^2 (\beta_n^2 + L^2 - L)}}{\sum_{n=1}^{\infty} \frac{1}{\beta_n^2 (\beta_n^2 + L^2 - L)}} \quad (8)$$

where  $M_{\infty}$  is the initial amount of diffusant in the sphere core.

Crank's equations for diffusion in a two-layered sphere [19] as given in equations (5)–(8) directly applies to colloidosomes, as depicted in Fig. 2B, where  $D_s = \alpha_T D$ .

### 3. Results

In the following, we consider transport through two types of colloidosome shells: monolayers, formed by particle adsorption onto the core interface, where the thickness of the layer  $h$  is equal to the colloid dimension  $2b$ , and densely packed shells formed through surface collapse where the thickness of the shell is independent of the colloid particle diameter [11].

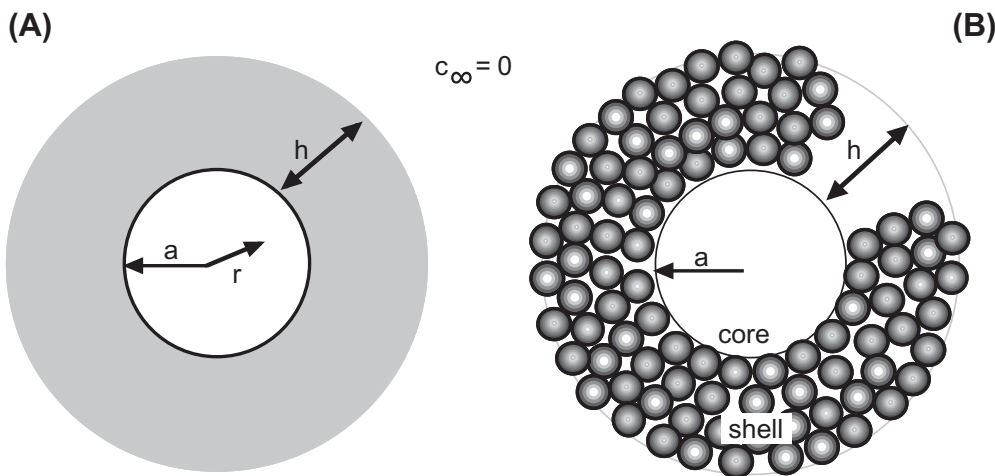
#### 3.1. Case 1: monolayer shells

The colloidosomes considered in this case are formed by adsorption of a colloidal monolayer onto the surface of a core. As a result, the shell thickness is equal to the colloidal particle diameter and  $h = 2b$ . The volume fraction of particles in the shell,  $\phi$  is set only by the processing method (namely, independent of the particle size), and is equal to the fraction of the interfacial area occupied by the particles,  $\phi_s$ . The diffusion coefficient in the shell is  $D_s = D\alpha_T$  (4a), and the dimensionless transport parameter  $L$  is then given by

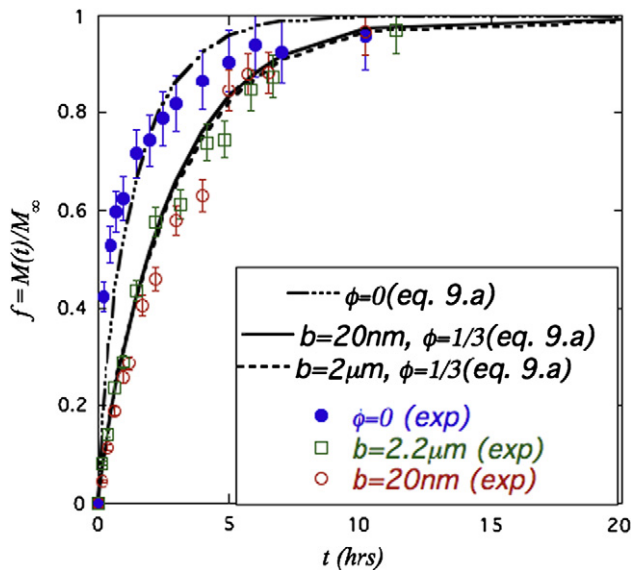
$$L = \frac{aD_s}{hD} = \frac{a \left( 1 - \frac{R_p}{b(\pi/6\phi)^{1/3} - 1} \right)^4}{2b\alpha_c \left( 1 + \frac{a\phi}{\pi b(1-\phi)} \right)} \quad (9)$$

Note that  $L$  accounts for both the reduction in transport through the colloidal shell, as well as the thickness of the shell itself. Thus, the rate of diffusion through shells with similar resistance to transport will decrease with increasing shell thickness (namely, colloidal particle size).

In Fig. 3 we plot the fraction of diffusant released, as a function of time (Eq. (8)) for three systems: Uncoated cores (namely, where  $\phi = 0$ ), shells composed of relatively small colloidal particles where  $2b = 20$  nm, and shells composed of larger particles where  $2b = 2$   $\mu$ m. The volume fraction in the two latter cases shells is taken to be 1/3, which corresponds to the value estimated in previous experiments [14]. It should be noted that due to the self-assembled nature of the colloidal shell in these systems, the



**Fig. 2.** (A) A schematic of a two-layered sphere. The core radius is defined by  $a$ , and the shell thickness is given by  $h$ . The concentration of the diffusant in the surrounding solution,  $c_{\infty}$ , is taken to be zero at all times. (B) A schematic of a colloidosome. The core, whose radius is  $a$ , may be composed of either an aqueous solution or a crosslinked hydrogel sphere. The shell is composed of adsorbed colloidal particles. The thickness of the shell,  $h$ , depends on the method of colloidosome synthesis. In simple-adsorption schemes [14] the shell is formed by a colloidal monolayer and  $h$  is therefore equal to the colloidal particle diameter. In more sophisticated methods [11] the shell may be composed of colloidal multi-layers.



**Fig. 3.** The fractional mass transferred,  $f = M(t)/M_\infty$  (Eq. (8)) as a function of time. The lines denote the theoretical calculation (substituting Eq. (9) into Eqs. (6)–(8)) for uncoated spheres where  $\phi = 0$ , to colloidosomes coated by a loosely packed monolayer. The diffusant parameters used are appropriate for a small, hydrophilic molecules such as aspirin or caffeine in water:  $D \approx 5 \times 10^{-6} \text{ cm}^2/\text{s}$  [20] and  $R_D \approx 0.5 \text{ nm}$  [21,22]  $\phi = 1/3$  and  $a = 5000 \mu\text{m}$ . The symbols denote our experimental data measured for caffeine release from colloidosomes, as published in [14].

packing density is typically low and does not approach the close-packed limit.

We find that the presence of the colloidal monolayer shell reduces transport when compared to the uncoated case. However, somewhat unexpectedly, particle size  $b$  does not affect the transport profile. This is in agreement with our recent experiments [14], where we found that the size of the colloidal particles in the shell did not affect the transport of caffeine and aspirin through a loosely packed colloidal monolayer for particles ranging from 20 nm to 2.2  $\mu\text{m}$ .

To understand why the colloidal particle size does not affect transport in these systems, let us consider each of the contributions to mass transfer in the shell: In the cases discussed here, size exclusion does not play a role (unless the diffusant is macromolecular) since the relatively low packing volume fraction in the shell corresponds to pores that are much larger than small-molecule diffusants. As noted earlier, the reduction due to the composite nature of the shell depends only on the packing volume fraction (since it accounts for point-like diffusants). On the other hand, the reduction factor due to the obstruction of the release from the surface,  $\alpha_s$ , is linearly proportional to the size of the particles on the surface (i.e. the particle size  $b$ ) in systems where  $b \ll a$  and  $\phi_s$  is of order. This is due to the fact that as the particle size increases, so does the size of the region on the surface available for mass transfer (even though the overall fraction of surface available for transport is fixed), and thus the effect of surface blocking is reduced. Thus, the combined reduction factor  $\alpha_T$  is proportional to the colloidal particle size. However, this reduction factor must be multiplied by the thickness of the shell which in this case is equal to the colloidal particle diameter (see the definition of  $L$ ). Thus, the result is an overall reduction in transport that is independent of the colloidal particle size, a function of the particle volume fraction only.

### 3.2. Case 2: dense colloidosome shells of fixed thickness

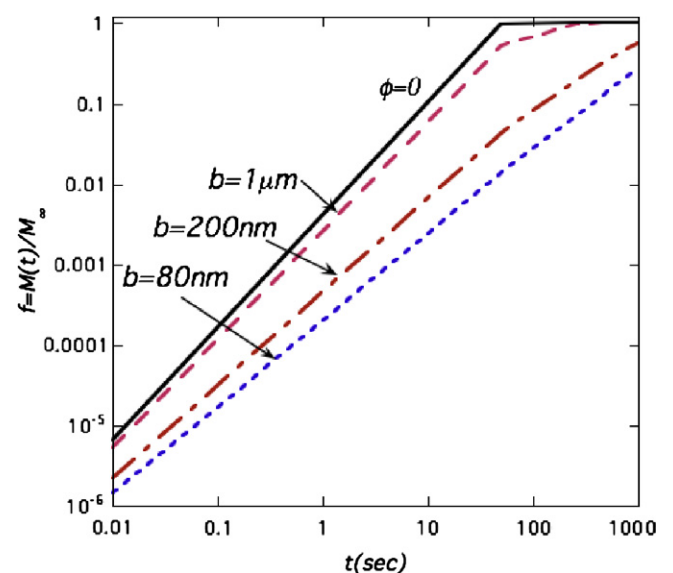
One of the methodologies for forming colloidosomes is by utilizing environmentally sensitive gels (which respond to temperature,

pH, or electric fields) to induce collapse to decrease the surface area available for transport. As the gel decreases in size, the distance between the colloidal particles attached to the surface also decreases as well, forming a more densely packed monolayer. However, if the volume of the gels decreases even further, the colloidal layer buckles. This produces a high-density, multi-layered colloidal shell whose thickness  $h$  has been found to be independent of the colloidal particle size [11].

In Fig. 4, we plot the fraction of mass released,  $f$  (Eq. (8)) for such a system, using for the reduced diffusion coefficient the expression given in Eq. (4b). Comparing transport for an uncoated sphere to colloidosomes coated by shells of identical thickness and density, but composed of different particle sizes, namely,  $b$  values, we find that the transport rate decreases (as given by an increase in time required for release of a given  $f$ ) with decreasing colloidal particle size. The fastest release is obtained, as expected, for the uncoated system, where the time required for release of the diffusant is (Fig. 4) of order 50 s. Coatings composed of 1  $\mu\text{m}$  particles hinder transport slightly, so increasing the time required for release to order 250 s. However, coatings composed of 80 nm particles require more than order of magnitude longer, of order 3500 s, despite the fact that the particle volume fraction is the same in all shells. Moreover, the reduced transport in the shells composed on smaller particles cannot be attributed to obstruction due to narrow pores; the diffusant size used in the calculation ( $R_D = 0.5 \text{ nm}$ ) is much smaller than the pore size in the 80 nm case, which is approximately 5.5 nm [17].

These results differ significantly from those found for the loosely packed shell, where the particle size does not affect the release. However, they are in good agreement with the observations of Kim et al. [11] who measured absorption of fluorescein by colloidosomes coated by a dense multi-layered shell. Measuring the intensity (as a measure of the amount of fluorescein absorbed), they find that the flux decreases with decreasing colloidal particle size.

Unlike the case of loosely packed monolayers (case 1), in the closely packed buckled layers the pore size may decrease sufficiently to provide an effect of size exclusion. Based on the correlations obtained by Rintoul and Torquato [17] and assuming that the



**Fig. 4.** The fraction of mass released from a colloidosome composed of a thick, multi-layered dense shell. We compare an uncoated sphere of radius 100  $\mu\text{m}$  to colloidosomes coated by a shell with  $\phi = 0.6$  and thickness  $h = 4 \mu\text{m}$ . Shells are composed of different particle sizes: 80 nm, 200 nm and 1  $\mu\text{m}$ . The diffusant is taken to be a small molecule with  $R_D = 0.5 \text{ nm}$  and  $D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$  [20]. The parameters used correspond to the experiments of Kim et al. [11].



volume fraction in such shells is close to the maximal packing density ( $\phi \approx 0.64$ ) [19] yields a cutoff size that scales as  $0.06b$ , namely, 6% of the colloidal particle size. Therefore, transport of diffusants larger than this limit would be entirely suppressed, while smaller diffusants would follow the correlations outlined above.

#### 4. Discussion and conclusions

The ability to selectively control transport of diffusants in and out of enclosed volumes is of considerable interest to applications ranging from cosmetics to cell implantation [1–8]. Recent studies suggest that a shell composed of colloidal particles can reduce or inhibit transport of diffusants [9–14]. However, the experimental results seem contradictory: When the colloidal shell is multi-layered and dense [11], the rate of release decreases significantly with decreasing colloidal particle size. In contrast, in systems where the colloidal shell is monolayer-thick and loosely packed, the shell reduces release when compared to uncoated cores, but the rate is independent of colloidal particle size [14].

Our simple diffusion model examines the effect of a colloidal shell on diffusant transport. The model accounts for three components reducing diffusant diffusion in the shell: first is the reduction in the penetrable volume available for transport in the shell, which also increases the tortuosity of the diffusional path. Second is the narrow pore size, which may hinder transport for larger diffusants, thereby causing 'size exclusion'. Last is the reduction in interfacial area due to 'blocking' of the surface by the adsorbed particles.

We find that the cutoff for size exclusion is linear with the particle size in both loosely packed and highly dense layers. However, in the case of highly packed layers the pore size, which sets the cutoff diffusant size, may be much smaller than the colloidal particle radius [11]. Due to the 4th power given in Eq. (2), the transport of diffusants is either practically unhindered (if  $R_D < R_p$ ), or completely suppressed (if  $R_D \geq R_p$ ).

In the case of diffusants that are smaller than the pore size, we find that the effect of the colloidal particle size on transport depends on the type of shell. In the case of loosely packed monolayers, the diffusion rate is independent of particle size – a function of the packing density only. On the other hand, in buckled multi-layered shells, the diffusant transport rate decreases significantly with the colloidal particle size.

To understand these seemingly contradictory results, we need to examine the two remaining contributions to transport reduction. The reduction in transport due to the composite nature of the shell is independent of the particle size, a function of the

impenetrable phase volume fraction only. However, transport through the surface increases linearly (if  $b \ll a$ ) with the size of the regions available for transport, which is proportional to the size of the colloidal particles. Thus, the combined effect is an increase in the transport rate (or a reduction in the inhibition) that is proportional to the particle size. However, the thickness of the shell affects the transport rate as well: the thicker the shell, the more pronounced the reduction in transport. In systems where the colloidosome shell is a monolayer, the shell thickness is equal to the particle diameter, and the result is a transport rate that is independent of the colloidal particle size. In multi-layered colloidosomes where the shell thickness is fixed, the reduced parameter  $L$  increases with the particle size  $b$  and, therefore, the transport rate increases with increasing particle size. It should be noted, however, that the flux is not linearly proportional to  $L$ , and thus does not increase linearly with the particle size.

In conclusion, we present here a simple diffusion model for transport through colloidosome shells. The model accounts for the different mechanisms hindering transport in the colloidal shell, thereby explaining seemingly contradictory experimental data.

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