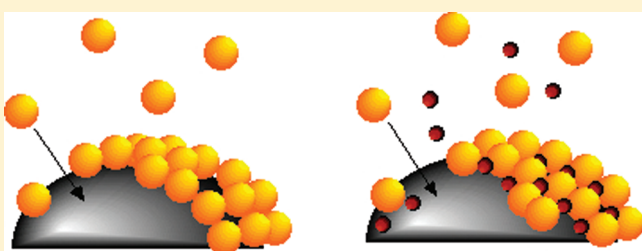


Effect of Colloidal Particle Size on Adsorbed Monodisperse and Bidisperse Monolayers

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ABSTRACT: Coating hydrogel films or microspheres by an adsorbed colloidal shell is one synthesis method for forming colloidosomes. The colloidal shell allows control of the release rate of encapsulated materials, as well as selective transport. Previous studies found that the packing density of self-assembled, adsorbed colloidal monolayers is independent of the colloidal particle size. In this paper we develop an equilibrium model that correlates the packing density of charged colloidal particles in an adsorbed shell to the particle dimensions in monodisperse and bidisperse systems. In systems where the molar concentration in solution is fixed, the increase in adsorption energy with increasing particle size leads to a monotonic increase in the monolayer packing density with particle radius. However, in systems where the mass fraction of the particles in the adsorbing solutions is fixed, increasing particle size also reduces the molar concentration of particles in solution, thereby reducing the probability of adsorption. The result is a nonmonotonic dependence of the packing density in the adsorbed layer on the particle radius. In bidisperse monolayers composed of two particle sizes, the packing density in the layer increases significantly with size asymmetry. These results may be utilized to design the properties of colloidal shells and coatings to achieve specific properties such as transport rate and selectivity.



INTRODUCTION

The ability to control the transport rate of diffusants into or out of an aqueous or hydrogel volume is of considerable interest for applications ranging from pharmaceuticals to cosmetics.^{1–8} Coating microcapsules by a shell of colloidal particles, thereby forming ‘colloidosomes’,^{9–16} enables control of porosity and permeability.^{9–16} Initially, the colloidal shells were formed around a hollow core (air or water) by adsorption of particles onto the interface, which were then fused to provide mechanical stability.⁹

The harsh conditions required for colloidal fusion are frequently incompatible with the needs of biorelated systems.^{9,10} The step can be eliminated, however, if the core of the colloidosome has some underlying structure that can provide stability. Therefore, the methodology first developed by Dinsmore et al.⁹ may be modified by using a hydrogel core,^{11,14–16} where the colloidal particles adsorb irreversibly onto the hydrogel surface through electrostatic interactions (see Figure 1) and the resulting layer properties are set by thermodynamic equilibrium. The hydrogel provides support, thereby eliminating the need for colloidal fusion.

The utilization of self-assembly to form adsorbed colloidal monolayers on hydrogel surfaces promises a simple and scalable synthesis method for the formation of biocompatible colloidosomes. To examine the properties and utility of colloidal shells formed by self-assembly, we have recently studied such colloidal shells, composed of polystyrene particles adsorbed on oppositely charged, alginate hydrogels.^{14–16} Quite surprisingly, we found that the transport of diffusants (model drugs such as caffeine)

through the shell was largely independent of the particle size for particles ranging from 20 nm to 3.3 μm .¹⁴ To understand why the transport of diffusants through the self-assembled colloidal shells does not depend on particle size, we developed a diffusion model for the system.¹⁵

The model demonstrates that for shells where the diffusant is a small molecule (namely, there is no size exclusion due to the finite size of the pores between adjacent colloidal particles), transport is set by one parameter: The packing density of colloidal particles in the shell.^{15,16} (Note that, due to the dimensions of the colloidal particles, the colloidal monolayer is not two-dimensional but is three-dimensional. Therefore, it is appropriate to use the packing density or the volume fraction of the particles in the layer, rather than surface coverage).¹⁵

While the diffusion model fit the experimental data well,^{15,16} it gave rise to a new question, namely, why is the packing density in the self-assembled colloidal monolayer independent of the particle size for particles ranging over 2 orders of magnitude? It may be argued that the value is set by the finite, close packing limit for colloidal particles. However, the volume fraction of the particles in the layers was found to be on the order of 1/3,^{14–16} much lower than the close-packing limit. Furthermore, for various applications where transport is to be significantly hindered, it is of interest to determine if the packing density can be increased in such self-assembled systems.

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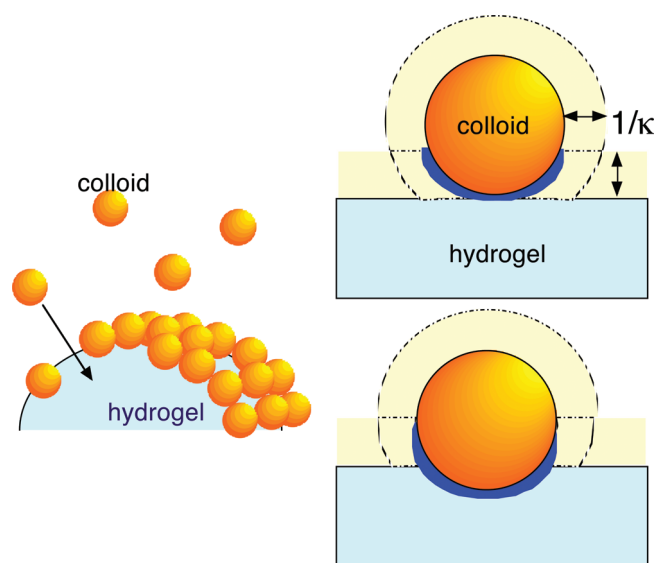


Figure 1. The system studied. Left: Colloidal particles self-assembled on a hydrogel particle. The particles adsorb, driven by electrostatic interactions, onto the surface of a hydrogel particle. The hydrogel provides structure to the assembly, so no fusion step is required. As a result, the density of the particles on the surface is driven by adsorption thermodynamics. Right: A colloidal particle adsorbed on an oppositely charged surface. The range of electrostatic interactions is set by $1/\kappa$, the Debye screening length. Therefore, the area of the particle participating in the adsorption interaction (as depicted by the red region) is equal to $2\pi R/\kappa$.

The formation of adsorbed monolayers, such as colloidal particles on hydrogel surfaces, is controlled by a balance between the particle entropy in solution (a function of the molar concentration) and the adsorption energy.^{17,18} For a given type of particle, increasing the concentration of particles in solution reduces the entropy loss, thus increasing the probability of adsorption and the density of particles in the adsorbed layer.^{17,18} In charged systems, electrostatic repulsion between the adsorbed particles reduces the maximal packing density. As a result, the volume fraction of the particles in the adsorbed layer increases with increasing ionic strength, as defined by a decrease in the Debye screening length $1/\kappa$.^{19–22}

The effect of particle size on adsorbed monolayers is less studied. Serizawa et al.²³ found that the maximal colloidal packing density increased with increasing particle size (when the molar concentration was held constant). For 84 nm particles, the packing density was 0.2, while for 780 nm particles it increased to 0.8.²³ Other studies examined the effect of particle size polydispersity.^{24–28} They found that the distribution of particles on the surface may differ significantly from the solution composition.²⁴ The maximal packing density increases with increasing size asymmetry in both two dimensions²⁷ and three dimensions,^{28,29} although the effect in two dimensions is weaker. However, to the best of our knowledge, there is no theoretical analysis to date that can explain the (lack of) dependence of the colloidal packing density in the adsorbed monolayer on the particle size.

In this paper we develop a model for the adsorption of charged colloidal particles on an oppositely charged surface, focusing on the effect of particle radius. The model accounts for the correlation between the particle radius and the strength of adsorption energy (the larger the contact surface between the particle and

the surface, the stronger the adsorption energy per particle), and the electrostatic repulsion between the adsorbed particles on the surface, which reduces the maximal density. We examine two cases: Monodisperse, where all particles are similar, and bidisperse, where the suspension contains two types of particles.

We find that in the monodisperse system, the increase in adsorption energy associated with larger particles increases the density of particles in the adsorbed layer when the molar concentration is fixed, as may be expected. However, if the mass fraction of particles is held constant, the molar concentration of particles decreases with the particle volume. The result is a region where the density of particles in the monolayer changes non-monotonically with the particle dimensions, thereby giving rise to a range of particle sizes where the packing density is relatively constant. In the case of bidisperse monolayers, the packing density increases significantly with increasing size asymmetry between the particles, since the smaller particles can pack more effectively. These results can now be used to tailor the properties of a colloidosome shell, thereby enabling control of the transport rate.

Adsorption Model. The Langmuir isotherm is, arguably, the most common way to describe monolayer formation.^{17,18} In this approach, the fractional packing density of particles in the monolayer θ is given by

$$\theta = \frac{\phi}{\phi_{\max}} = \frac{cKe^{-\varepsilon/kT}}{1 + cKe^{-\varepsilon/kT}} \quad (1)$$

where c is the molar concentration of adsorbing species, K is a system constant, and ε/kT is the (dimensionless) adsorption energy per particle. ϕ_{\max} denotes the maximal packing density possible for the system. Note that a positive ε value indicates that adsorption is unfavorable, while a negative value of ε corresponds to an attraction between the adsorbing species and the surface.

The adsorption of colloidal particles onto a hydrogel surface is driven by electrostatic interactions between surface charges on the colloid and oppositely charged ones in the hydrogel. Therefore, the number of electrostatic bonds formed is related to the number of the colloid surface charges that are within the electrostatic Debye screening length $1/\kappa$ from the surface. If the colloidal surface charge density is fixed, the number of bonds formed, and thus the effective adsorption energy per particle, is proportional to the surface area of the particle that is within $1/\kappa$ from the surface (see Figure 1). From simple geometry, the surface area of the colloid that is within this distance from the hydrogel is equal to $2\pi R/\kappa$.

Our goal is to examine the effect of the colloidal particle size on the packing density, assuming that all other properties, including charge density, are similar. Therefore, we define $\varepsilon/kT = \alpha R$, where α is independent of the particle size but accounts for such parameters as the charge density and the bond energy per charge.

In systems of uncharged hard spheres, the maximal monolayer volume fraction is independent of the particle dimensions. Random adsorption leads to values of ϕ_{\max} that range between 0.5 and 0.65 (see, for example, refs 30 and 31). However, in a system of charged particles the range of the electrostatic repulsion between the similarly charged particles affects the packing density.^{19–22} ϕ_{\max} is taken to be proportional to $(R/R_{\text{eff}})^2$, where R_{eff} is the effective radius of the particle which includes the effects of electrostatics. Thus, if electrostatics are negligible and $R_{\text{eff}} \approx R$, we recover the uncharged hard sphere limit. On the other hand, when the range of electrostatic interactions is large compared to

the particle size so that $R_{\text{eff}} \gg R$, the packing density is low since particles cannot adsorb in the effective 'repulsion zone' surrounding particles already on the surface. Here we use for R_{eff} an analytical expression,³²

$$R_{\text{eff}} = \frac{1}{2\kappa} \ln \left[\frac{A}{\ln A} \right] \quad (2a)$$

where

$$A \approx \frac{2.8\kappa R^2(4\kappa R + 6)^2 e^{2\kappa R}}{l_B(\kappa R + 1)^2} \quad (2b)$$

and l_B is the Bjerrum length.¹⁸

The maximal packing density of randomly adsorbed, charged, monodisperse hard spheres, such as the colloids discussed here, is affected by electrostatic effects. This yields for a particle packing density, or volume fraction, in a monolayer composed of monodisperse particles

$$\phi = 0.547 \left(\frac{R}{R_{\text{eff}}} \right)^2 \frac{cK e^{-\alpha R}}{1 + cK e^{-\alpha R}} \quad (3)$$

For a monolayer composed of a bidisperse mixture, of small and large particles, the Langmuir isotherm expression must be modified to include adsorption of both species:¹⁸

$$\phi = \phi_{\text{max}}^{\text{bi}} \frac{Kc_L e^{-\alpha R_L} + Kc_S e^{-\alpha R_S}}{1 + Kc_L e^{-\alpha R_L} + Kc_S e^{-\alpha R_S}} \quad (4)$$

where the subscripts L (S) refers to the large (small) particles. Since both types of particles are similar in their composition and properties and differ only in their radius, K and α are the same.

The bidisperse monolayer composition also affects the maximal packing density, or volume fraction; as may be expected, a mixture of large and small particles may pack more closely than a monodisperse one.^{27–29} Here we apply the classic analysis of Yerazunis et al.³³ to calculate the combined packing density of both types of particles in the monolayer

$$\phi_{\text{max}}^{\text{bi}} \approx \frac{\phi_{\text{max}}^S}{1 - y \left(1 - \phi_{\text{max}}^S - 0.315 \left\{ \frac{R_S}{R_L} \right\}^{0.706} \right)} \quad (5)$$

where ϕ_{max}^S is the maximal volume fraction for the monodisperse, smaller particles as given by eq 2, and y is the volume fraction of the large particles in the system. The volume fraction of the larger particles in the adsorbed layer, y , can be calculated self-consistently from the adsorption isotherm (eq 4):

$$y = \frac{Kc_L e^{-\alpha R_L}}{Kc_L e^{-\alpha R_L} + Kc_S e^{-\alpha R_S}} \quad (6)$$

RESULTS AND DISCUSSION

In Figure 2 we plot the volume fraction in a monolayer of monodisperse particles, ϕ , as a function of the reduced particle radius κR . We compare the case where the molar concentration of the particles in the suspension is held constant (so that the mass fraction of the particles increases with particle volume, namely R^3), to one where the mass fraction of the particles in solution is held constant, so that the molar concentration c decreases as $1/R^3$.

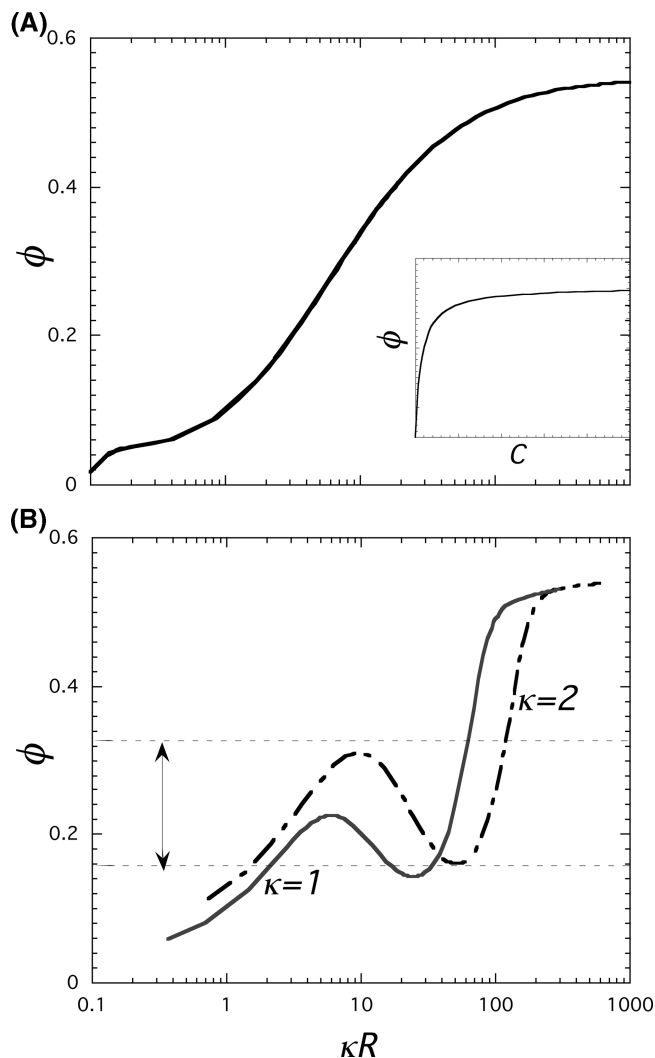


Figure 2. The volume fraction of particles in a monolayer composed of monodisperse particles, ϕ , as a function of the reduced particle radius κR . (A) The molar concentration of the particles, c is held constant, and ϕ is given by eq 3. The values of the parameters are $\kappa = 1$, $\alpha = 0.15$, and $cK = 1000$. The inset shows the monolayer volume fraction as a function of molar concentration, c , for $\kappa R = 100$. (B) The mass fraction of the particles is held constant, so that $cK = K'/R^3$. κ and α are as the same as for panel A. The dotted lines represent the range of packing densities found from fitting the release profile of monodisperse layers for particles in the range of 20 nm to 3.3 μm .^{15,16} $K' = 500$. $\kappa = 1$ and $\kappa = 2$ as noted.

We see that in both cases, in the limit of very large particles ($R \rightarrow \infty$), the monolayer volume fraction approaches the maximal limit for randomly adsorbing hard spheres. This is due to the fact that in this limit the adsorption energy αR is high, dominating over entropy effects so that the particles are driven to the surface. Moreover, the difference between R_{eff} and R is negligible in this limit, so that electrostatic repulsion between the particles does not affect the volume fraction in the layer.

In the opposite limit where R is extremely small, we find that $\phi \rightarrow 0$. The adsorption energy per particle in this case is small when compared to the entropic energy in solution, so that the driving force for adsorption is weak. Moreover, R_{eff} may be much larger than R , indicating a relatively long-ranged repulsion between particles on the surface, thereby reducing the packing density further.

In the intermediate particle radii, values where κR is on the order of 10, we see significant differences between the two cases shown in Figure 2. In the first case (c constant) we see a smooth increase in ϕ with R (Figure 2A). This is because the molar concentration of the particles in solution is fixed, so that an increasing particle radius means both an increase in the adsorption energy (and thus driving force to the surface) and a reduction in the effective range of electrostatic repulsion, namely, R_{eff}/R .

When the mass fraction is fixed (i.e., c/R^3), increasing the particle radius also decreases the number of particles in solution, thereby opposing adsorption. The result (Figure 2B) is an unusual, nonmonotonic adsorption isotherm where the magnitude of the nonlinearity increases with increasing strength of adsorption (as defined through K or α). Moreover, the value of κ affects the dependence of ϕ on R , since R_{eff} varies with κR .

In the case of bidisperse monolayers, the adsorption isotherm depends on an additional parameter, namely the size ratio between the two particles. In Figure (3A) we examine the case where the molar concentrations of the two particles are identical and fixed (namely, $c_S = c_L$). Also fixed is the size of the smaller particle, R_S , while the ratio of the particle sizes R_L/R_S is varied. We find that as the ratio increases, so does the volume fraction in the layer with the biggest increase (slope) in the region where R_L/R_S of order 10. In the limit where $R_L/R_S \gg 1$, the volume fraction in the adsorbed monolayer is nearly 100%. The increase in the packing density in the monolayer may be attributed to two factors; first, as R_L increases, so does the adsorption energy of the larger particles. Second, the potential density of packing increases with size disparity, so that the maximal density in the layer increases.

Next we examine (Figure 3B) the case where the molar concentrations of the particles are equal, and the ratio R_L/R_S is fixed. In an uncharged system, the volume fraction should be independent of R_S when the size ratio of the particles is fixed, since there are only two length scales in the system: R_S and R_L . However, in the case of adsorption driven by electrostatics there is an additional length scale, namely $1/\kappa$. Therefore, we find that in a system where the ratio between the two particle sizes is moderate, increasing R_S significantly increases the packing density. This is because electrostatic repulsion significantly reduces the adsorption of both types of particles when R_S is on the same order of magnitude as $1/\kappa$. However, when the size ratio is large, electrostatics do not affect the adsorption of the large particles, so that the packing density is much less sensitive to R_S .

The last bidisperse case we examine (Figure 3C) is where the mass concentration of both particles is equal and constant (namely $c_S/R_S^3 = c_L/R_L^3$). We see that, as in the cases where the molar concentration is fixed, the volume fraction in the adsorbed layer increases with increasing particle size ratio R_L/R_S , and with the size of the smaller particle. In the limit where R_L/R_S is large, the increase is monotonic. However, when the size asymmetry is more moderate, we find a plateau where the packing density is insensitive to R_S . In this region, the increase in particle size, which corresponds to an increase in adsorption energy and to a reduction in the effects of electrostatic repulsion, are offset by the associated reduction in the molar concentration of particles.

As noted in the Introduction, previous studies have investigated the effect of particle size on the properties of colloidal shells adsorbed onto hydrogel surfaces.^{14–16} The shells were formed by

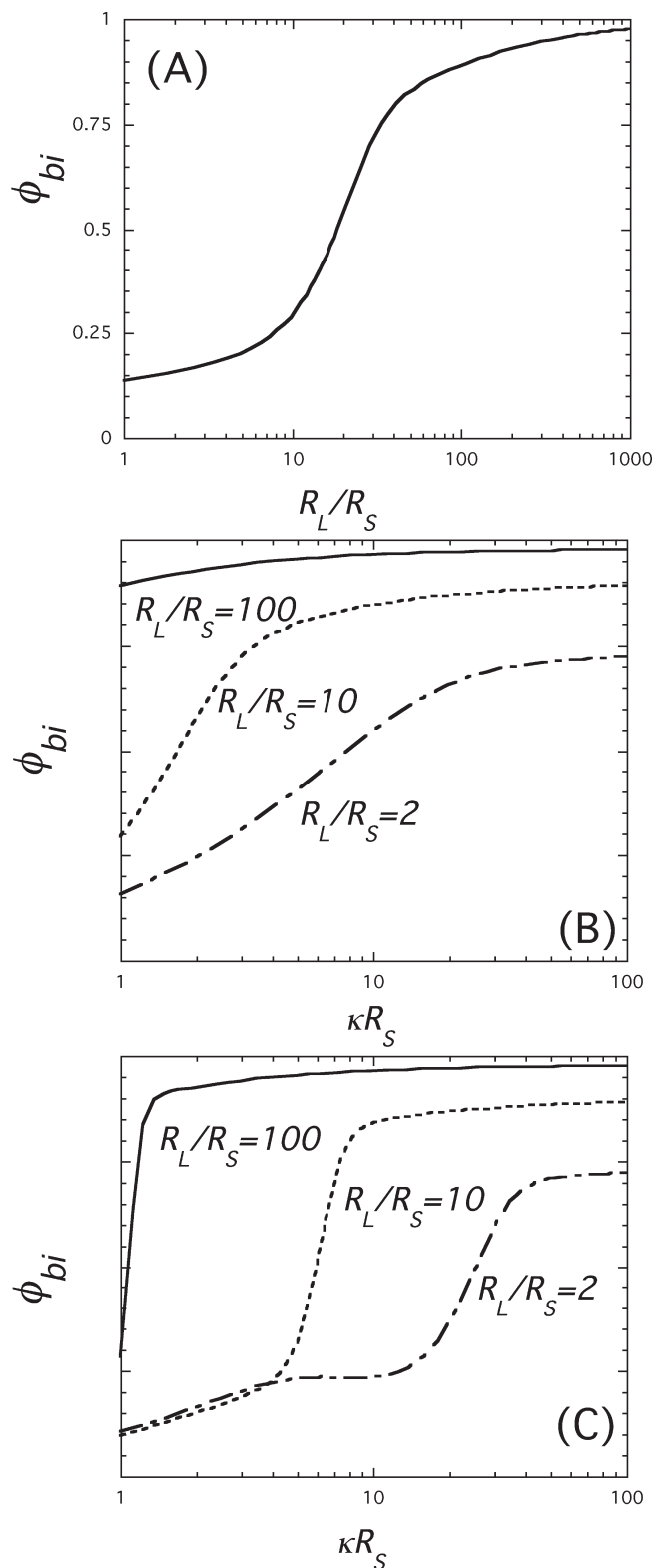


Figure 3. The volume fraction in an adsorbed bidisperse monolayer. All values are as in Figure 2, unless otherwise noted. (A) The molar concentration of both small and large particles is equal and fixed, and $\kappa R_S = 1$. (B) The molar concentration of both particles is equal and fixed. For each curve, the ratio of particles is fixed at the value noted. (C) The mass fraction of the two types of particles is equal and fixed. For each curve, the ratio of particles is fixed at the value noted.

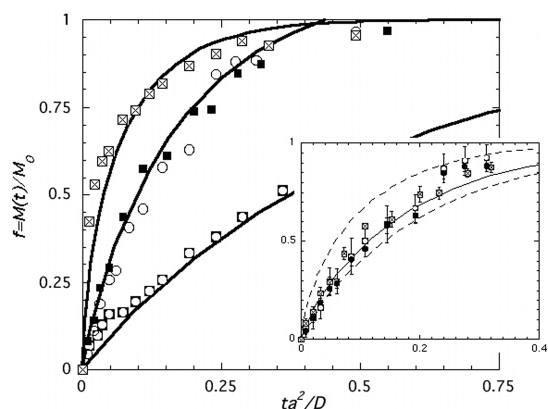


Figure 4. Release data of model drug (caffeine) from alginate hydrogels coated by an adsorbed monolayer of polystyrene particles.¹⁴ f denotes the fraction of encapsulated drug released by time t . a here is the thickness of the hydrogel film, and D is the diffusion coefficient of caffeine in the hydrogel. Crossed squares, uncoated hydrogel, filled squares, 20 nm particle coating, circles, 3.3 μm particle coating, open squares, mixed 20 nm, and 3.3 μm particle layer. The lines denote fitting to a diffusion model,¹⁵ with values of ϕ that are 0 for the uncoated layer, 0.25 for the monodisperse layers, and 0.75 for the mixed layer. The inset shows the release from alginate hydrogels coated by monodisperse layers of 20 nm, 1 μm , 2.2 μm , and 3.3 μm . The solid line is the fit for the release for $\phi = 0.25$. The dashed lines are fits for $\phi = 0.16$ and $\phi = 0.33$.

simple adsorption of the particles, so that the thermodynamic equilibrium model developed here holds. The particle sizes ranged from 20 nm to 3.3 μm , but the mass fraction was the same for all monolayers.

Due to the low packing density in the layers, it was not possible to estimate the packing density directly using microscopy. However, measurements of the release of model drugs showed that the release profile was similar for all shells, namely, independent of the particle size, despite 2 orders of magnitude differences in R (see Figure 4).^{14,15} Since parameters such as the drug loading were identical, this indicates that the packing density in all cases was similar.^{14–16} Using a classical transport model, the release data could be fitted and a value for the packing density in the layer extracted,¹⁵ yielding values of $0.16 \leq \phi \leq 0.33$ where the variance is due to factors such as the range of concentration measurements and the accuracy of the fit. Examining the model for the relevant case (see Figure 2B), we find that, indeed, it is possible to obtain packing densities in the range observed for particles with radii ranging over 2 orders of magnitude, from $\kappa R \sim 1$ to $\kappa R \sim 200$.

The release of drug from a hydrogel covered by a bidisperse monolayer composed of a mixture of 20 nm and 3.3 μm , adsorbed from a solution containing equal mass fraction is much slower than that from a monodisperse monolayer (Figure 4). The volume fraction in the mixed layer, fit to the release model¹⁵ is on the order of 0.75. The model predictions for the mixed layer (Figure 3C) are in good qualitative agreement with this experimental observation, where for the experimental ratio of particle sizes $R_L/R_S = 3.3 \mu\text{m}/20 \text{ nm} = 165$, ϕ should be much higher than the maximal value for a monodisperse layer.

In conclusion, we present here a model for the dependence of the packing density, or the particle volume fraction in a monolayer of colloidal particles adsorbed on an oppositely charged hydrogel. We find that in the case of monodisperse layers composed of a single type of particles, the volume fraction increases

with the particle size since the strength of the adsorption energy increases linearly with particle dimensions. However, in systems where the mass fraction of the particles in the adsorbing solutions is held fixed, the increase in adsorption energy with R is countered by the associated reduction in the molar concentration, leading to a region where ϕ changes nonmonotonically with R . In the case of bidisperse layers, the volume fraction in the layer is higher than that of the equivalent monodisperse layer, since the size differences allow for more effective packing on the surface. The volume fraction increases with increasing size asymmetry. These results may be utilized to design the properties of colloidal shells and coatings, such as those in colloidosomes, thereby controlling the layer properties.

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