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Vesicles in contact with nanoparticles and colloids

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*Dedicated to Heinz Horner on the
occasion of his 60th birthday*

Abstract. – Flexible membranes which are in contact with dispersed nanoparticles or colloids are theoretically studied. For closed vesicles, the membrane/particle interactions change the “spontaneous” curvature of the membrane provided the surrounding solution contains more than one species of particles. If the membrane/particle interactions are repulsive, the membrane curves toward the larger particles. If the membrane/particle interactions are attractive, the membrane curves away from the adsorption layers of small particles but wraps itself around large particles which become completely encapsulated.

Several chemical procedures have been used in order to grow nanoparticles or colloids in vesicles and liposomes composed of lipid bilayers or other amphiphilic membranes, see, *e.g.*, [1-3]. The particles can grow inside or outside the vesicles or at the vesicle surfaces, and their size can vary from the subnano range up to many tens of nanometers. This has to be compared with the membrane thickness which is typically $\simeq 4$ nm and with the size of the vesicles which is often many micrometers [4]. Thus, the particles can be smaller or larger than the membrane thickness but they are usually much smaller than the vesicle size.

In this paper, we study the behavior of membranes and vesicles in contact with such dispersed particles from the theoretical point of view. In fact, our arguments apply to any “particle” which i) is *rigid* and ii) *cannot permeate* the membrane on the experimentally relevant time scales. Thus, the two surfaces of the membrane act as flexible but impenetrable walls for the dispersed particles. In addition, these surfaces may exert repulsive or attractive forces onto these particles.

It is shown below that, in addition to the usual osmotic effects, the dispersed particles induce a “spontaneous” curvature of the vesicle membrane provided the solution contains *more than one* species of particles. Furthermore, this “spontaneous” curvature depends on the particle size R_{pa} and thus can be controlled by varying R_{pa} . We will distinguish three cases: i) if all particles species are non-adhesive, the membrane curves toward the larger particles, see

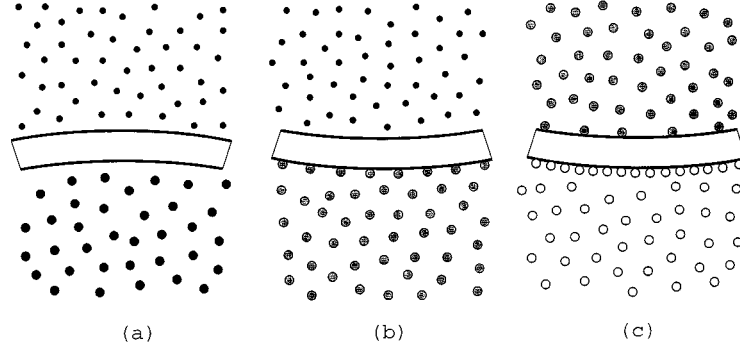


Fig. 1. – “Spontaneous” curvature of a membrane segment which is in contact with dispersed particles: (a) two non-adhesive particle species; (b) one adhesive and one non-adhesive species; and (c) two adhesive species.

fig. 1(a). In this case, the “spontaneous” curvature M_{sp} *increases* with increasing size R_{pa} of the particles; ii) if all particle species are adhesive and small compared to the membrane thickness l_{me} , the membrane curves away from the more strongly adsorbed particles, see fig. 1(c), and M_{sp} *decreases* with increasing R_{pa} ; and iii) finally, for adhesive particles which are large compared to l_{me} (but small compared to the vesicle size), the vesicle membrane typically encapsulates the particles completely.

A membrane curvature can also be induced by electrolytes [5-7] and by anchored polymers [8-10]. In all cases, the curvature effects are accessible to experimental studies of vesicles since one can deduce the “spontaneous” curvature of the vesicle membrane from observations of the vesicle shape via optical microscopy [11]. Recently, we have used this approach for vesicles in solutions of glucose and raffinose, as will be described elsewhere [12].

To proceed, consider a vesicle membrane which divides space into an interior (in) and an exterior (ex) compartment with volumes $\mathcal{V}^{\text{in}} \sim R_{\text{ve}}^3$ and \mathcal{V}^{ex} , respectively. Both compartments may contain different particle species labeled by j . For dilute solutions, the osmotic pressure ΔP across the membrane is given by $\Delta P = T(N^{\text{ex}} - N^{\text{in}})$ with $N^{\alpha} \equiv \sum_j N_j^{\alpha}$, where N_j^{α} is the number density of j -particles per unit volume with $\alpha = \text{in}, \text{ex}$. This osmotic-pressure difference is balanced by the bending rigidity κ of the bilayer membrane [13] which leads to $N^{\text{ex}}\mathcal{V}^{\text{in}} = (N^{\text{in}}\mathcal{V}^{\text{in}} + c_P\kappa/T)$. In principle, this is a nonlinear equation for \mathcal{V}^{in} since the dimensionless coefficient c_P depends on the shape and thus on \mathcal{V}^{in} . However, one usually has $N^{\text{in}}\mathcal{V}^{\text{in}} \gg \kappa/T$, which leads to

$$\sum_j \Delta N_j \equiv \sum_j (N_j^{\text{ex}} - N_j^{\text{in}}) \simeq 0, \quad (1)$$

where we have ignored terms of order $\kappa/T\mathcal{V}^{\text{in}} \sim \kappa/TR_{\text{ve}}^3$.

We now envisage the membrane as a thin film which is bounded by the ex- and in-surface in contact with the exterior and interior solution, respectively. These two surfaces exert attractive or repulsive forces onto the dispersed particles. The resulting adsorption or depletion layers contribute to the excess free energies or interfacial tensions σ^{ex} and σ^{in} . If these interfacial tensions are different, they will induce a “spontaneous” curvature of the membrane [14].

When the neutral surface of the curved membrane segment has area \mathcal{A} and mean curvature M , the areas \mathcal{A}^{in} and \mathcal{A}^{ex} of the in- and the ex-surface are given by $\mathcal{A}^{\text{ex}} \approx (1 + l_{\text{me}}M)\mathcal{A}$

and $\mathcal{A}^{\text{in}} \approx (1 - l_{\text{me}}M)\mathcal{A}$, respectively, where l_{me} denotes the membrane thickness. For both surfaces, we will use normal vectors which point into the adjacent solution which implies $M^\alpha \approx \pm M$ where the plus and the minus sign correspond to $\alpha = \text{ex}$ and $\alpha = \text{in}$, respectively.

In the *absence* of dispersed particles, the interfacial tensions of the two membrane surfaces are given by $\sigma^\alpha = \sigma_W^\alpha$ with $\alpha = \text{ex}, \text{in}$. In this situation, the membrane is taken to have zero spontaneous curvature which implies $\sigma_W^{\text{ex}} = \sigma_W^{\text{in}}$. In general, one has $\sigma^\alpha = \sigma_W^\alpha + \sum_j \sigma_j^\alpha$, where the tensions σ_j^α vanish in the limit of small particle densities N_j^α .

Non-adhesive particles. – First, let us consider particles which are repelled from the membrane surfaces. The depletion of the particles increases the interfacial free energy of these surfaces [15]. Recently, this depletion effect was calculated for solutions of ideal polymers [10] and of hard rods [16].

In the following, the particles are taken to be essentially spherical and thus characterized by a single length scale. For one particle species j with radius $R_{\text{pa}} = R_j$, the excluded volume Ω_j^α in front of the α -surface behaves as $\Omega_j^\alpha \approx \mathcal{A}^\alpha R_j (1 + R_j M^\alpha + \frac{1}{3} R_j^2 G)$ with $\alpha = \text{in}, \text{ex}$ up to second order in the curvatures, where G is the Gaussian curvature.

For dilute solutions, one may ignore the interactions between the particles and treat them as an ideal gas in a confined geometry. In the limit of large particle numbers, one then obtains the interfacial tensions

$$\sigma_j^\alpha = T N_j^\alpha \Omega_j^\alpha / \mathcal{A}^\alpha \approx T N_j^\alpha R_j (1 + R_j M^\alpha) \quad \text{for small } M^\alpha. \quad (2)$$

The total interfacial free energy is now given by $\mathcal{A}^{\text{ex}} \sum_j \sigma_j^{\text{ex}} + \mathcal{A}^{\text{in}} \sum_j \sigma_j^{\text{in}}$. If one subtracts the interfacial free energy of the flat membrane and balances the resulting excess free energy with the bending energy $2\kappa M^2 \mathcal{A}$, one arrives at the “spontaneous” curvature [17]

$$M_{\text{sp}} = -\frac{T}{4\kappa} \sum_j \Delta N_j R_j (l_{\text{me}} + R_j). \quad (3)$$

This expression applies to membrane segments which are large compared to the mean distance of the dispersed particles.

For a closed vesicle, osmotic equilibrium implies $\sum \Delta N_j \simeq 0$ as in (1). Thus, for a solution with a single species, the “spontaneous” curvature as given by (3) vanishes. If one includes the correction terms neglected in (1), one has $\Delta N_1 \sim \kappa / T R_{\text{ve}}^3$ and $M_{\text{sp}} \sim R_1 (l_{\text{me}} + R_1) / R_{\text{ve}}^3 \ll 1/R_{\text{ve}}$, which shows that the approximation used in (1) is indeed justified.

For a binary solution with two particle species $j = 1$ and $j = 2$, the osmotic balance (1) leads to $\Delta N_2 = -\Delta N_1$. When inserted into (3), one obtains the “spontaneous” curvature $M_{\text{sp}} = (T/4\kappa) \Delta N_1 (R_2 - R_1) (l_{\text{me}} + R_1 + R_2)$, which is proportional to the size difference $R_2 - R_1$. Since $\Delta N_1 = N_1^{\text{ex}} - N_1^{\text{in}}$, the membrane segment curves toward the larger particles, see fig. 1(a). For a lipid bilayer with $(T/4\kappa) \simeq 0.01$, the parameter values $\Delta N_1 \simeq 10$ mM and $R_2 = 2R_1 = 2$ nm lead to $M_{\text{sp}} \simeq 0.42/\mu\text{m}$.

In some systems, the densities N_j may change with time. For example, one may simply add particles to the exterior solution and observe the subsequent relaxation processes. Another example is provided by the growth processes mentioned in the introduction for which the mean particle size increases with time. In general, one then has a time-dependent contribution to M_{sp} .

Small adhesive particles. – Next, consider small spherical particles with radii $R_j < l_{\text{me}}$ which are attracted toward the membrane. In order to simplify the notation, we will now suppress the index $\alpha = \text{in}, \text{ex}$. The j -coverage Γ_j of a *flat* membrane surface is given by the

Gibbs adsorption equation $\Gamma_j = -(\partial\sigma/\partial\mu_j)_T$. For dilute solutions, the chemical potentials $\mu_j = \mu_{j0} + T \ln(\mathcal{N}_j/\sum_j \mathcal{N}_j)$ and $\Gamma_j = -(N_j/T)(\partial\sigma/\partial N_j)_T$. In order to go beyond this thermodynamic relation, one must consider a more specific adsorption model. In the following, we will use a simple Langmuir-type model for monolayer adsorption [18].

The simplest version of this model is obtained if all particle species are taken to have the same size, R_{pa} . Each *flat* membrane surface then provides the same maximal number of adsorption sites, $n_{\text{ad}} = \mathcal{A}/c_{\text{ad}}R_{\text{pa}}^2$, where c_{ad} is a dimensionsless coefficient of order one. For a densely packed layer of spheres, one has $c_{\text{ad}} = 2\sqrt{3}$. The number of those sites which are *occupied* by particles of species j is denoted by n_j . The coverage by j -particles is then given by $\Gamma_j = n_j/\mathcal{A}$, and the Langmuir adsorption isotherm leads to the interfacial free energy

$$\sigma = -(T/c_{\text{ad}}R_{\text{pa}}^2) \ln \left(1 + \sum_j k_j N_j \right) \approx -(T/c_{\text{ad}}R_{\text{pa}}^2) \sum_j k_j N_j \quad (4)$$

for small N_j with Langmuir constants k_j which are small and large for weak and strong j -adsorption, respectively.

This Langmuir model can be generalized to a curved surface if one takes into account that the centers of the adsorbed particles have a distance R_{pa} from the membrane surfaces. This implies that the ex- and the in-surface have different effective adsorption areas in the curved state. In this way, one finds the interfacial free-energy difference per unit area as given by

$$\Delta\mathcal{F}/\mathcal{A} \approx -(T/c_{\text{ad}}R_{\text{pa}}^2) \sum_j k_j \Delta N_j (l_{\text{me}} + 2R_{\text{pa}}) M. \quad (5)$$

If this interfacial free energy is again balanced against the bending energy of the membrane, one now obtains the “spontaneous” curvature

$$M_{\text{sp}} = +\frac{T}{4\kappa} \sum_j k_j \Delta N_j \frac{l_{\text{me}} + 2R_{\text{pa}}}{c_{\text{ad}}R_{\text{pa}}^2}. \quad (6)$$

which increases monotonically with *decreasing* particle size (a lower cut-off is provided by the molecular roughness of the membrane surface).

A single species of adhesive particles has again no effect on the spontaneous curvature. For a binary solution with two species $j = 1$ and $j = 2$ of adhesive particles, on the other hand, the “spontaneous” curvature as given by (6) becomes $M_{\text{sp}} = (T/4\kappa)(k_1 - k_2)\Delta N_1(l_{\text{me}} + 2R_{\text{pa}})/c_{\text{ad}}R_{\text{pa}}^2$. Thus, the membrane curves away from the more strongly adsorbed particles characterized by a larger k -value as shown in fig. 1(c), where the two particle species have the same size as assumed.

In general, the different species of adhesive molecules will also differ in their size. Now, consider a solution of two adhesive species $j = 1$ and $j = 2$ with different radii R_1 and R_2 , respectively. In order to stay within the simple Langmuir-type model discussed here, let us focus on the special case in which the exterior and the interior compartment contains only particles of species $j = 1$ and $j = 2$, respectively. In this case, the maximal number of adsorption sites per unit area is given by $1/c_{\text{ad}}R_1^2$ and $1/c_{\text{ad}}R_2^2$ for the ex- and the in-surface, respectively. Osmotic balance now implies that $N_1^{\text{ex}} = N_2^{\text{in}} \equiv N$ and the above adsorption model leads to the “spontaneous” curvature $M_{\text{sp}} = (T/4\kappa)N[g(R_1)k_1 - g(R_2)k_2]$ with $g(x) \equiv (l_{\text{me}} + 2x)/c_{\text{ad}}x^2$. For $k_1 = k_2$, *i.e.* if both species have the same adsorption strength, this relation implies that the membrane curves towards the larger particles as in the non-adhesive case.

Within the same approximation scheme, one may also consider dilute solutions containing one non-adhesive species and one adhesive species; in the latter case the membrane curves away from the adhesive particles and toward the non-adhesive ones as shown in fig. 1(b).

In the above estimates for Langmuir-type adsorption, it was tacitly assumed that the membrane structure is not strongly perturbed by the adhesive particles. If these particles are as small as or smaller than the head groups of the membrane molecules, they may intercalate between these head groups and, in this way, expand the area of the membrane surfaces. This area expansion will increase with the number of intercalated particles. If two different particle species intercalate on both sides of the membrane, one has an additional bending moment which curves the membrane away from the more strongly adsorbed particles and thus exhibits the same tendency as the contribution from the Langmuir-type adsorption.

Large adhesive particles. – For adhesive particles with $R_{\text{pa}} \gg l_{\text{me}}$, the attractive interaction between the membrane and the particle surface will be characterized by the adhesion energy per unit area, $W < 0$. If the membrane segment is essentially tensionless, this adhesion energy is balanced by the bending energy of the membrane.

If the membrane covers a certain fraction X of the surface of a spherical particle, its contact area is given by $\mathcal{A}_{\text{ca}} = X4\pi R_{\text{pa}}^2$, its adhesion energy is $\mathcal{E}_{\text{ad}} = -\mathcal{A}_{\text{ca}}|W|$, and the bending energy of the adhering membrane segment is $\mathcal{E}_{\text{be}} = \mathcal{A}_{\text{ca}}2\kappa/R_{\text{pa}}^2$. The state of lowest energy then corresponds to complete encapsulation with $X = 1$ as soon as [19]

$$R_{\text{pa}} > R_* \equiv [2\kappa/|W|]^{1/2}, \quad (7)$$

and to complete detachment with $X = 0$ for $R_{\text{pa}} < R_*$. For $0 < X < 1$, the deformation of the membrane along the contact line will contribute an additional bending energy term to the contact line energy \mathcal{E}_{cl} which acts as an energy barrier for the encapsulation process [20]. This process resembles domain-induced budding, another transformation of the membrane shape arising from intramembrane domains [21].

For attractive van der Waals forces between the bilayer membrane and the particle, the adhesion energy W per unit area is typically of the order of T/a_{\parallel}^2 , where a_{\parallel} represents a molecular length scale. For lipid bilayers $\kappa \simeq 20T$, this leads to the estimate $R_* \simeq 6a_{\parallel}$. If a_{\parallel} is comparable to the size of the lipid head group, one has $a_{\parallel} \simeq 0.8$ nm and thus $R_* \simeq 5$ nm which must be compared with the bilayer thickness $l_{\text{me}} \simeq 4$ nm.

The encapsulation of a single particle with $R_{\text{pa}} > R_*$ leads to the energy gain $\Delta\mathcal{E}_{\text{ep}} = -|W|4\pi(R_{\text{pa}}^2 - R_*^2)$. For attractive van der Waals forces with $|W| \simeq T/a_{\parallel}^2$, one has $\Delta\mathcal{E}_{\text{ep}} \simeq -T4\pi(R_{\text{pa}}^2 - R_*^2)/a_{\parallel}^2$. Thus, as soon as $R_{\text{pa}}^2 - R_*^2 \lesssim a_{\parallel}^2$, the energy gain $\Delta\mathcal{E}_{\text{ep}}$ is large compared to T . Thus, the encapsulation of large particles with $R_{\text{pa}} \gg l_{\text{me}}$ is irreversible in contrast to the reversible adsorption of small particles with $R_{\text{pa}} \ll l_{\text{me}}$.

If the solution contains *many* adhesive particles with $R_{\text{pa}} \gg R_*$, the membrane will encapsulate a large number of them. In order to be specific, let us consider two particle species, $j = 1$ and $j = 2$. The particles of species $j = 1$ are adhesive with $R_{\text{pa}} = R_1 \gg l_{\text{me}}$; the particles of species $j = 2$ are non-adhesive and act as a “buffer” for the osmotic equilibrium, *i.e.* one has $N_2^{\text{ex}} \gg N_1^{\text{ex}}$ and $N_2^{\text{in}} \gg N_1^{\text{in}}$.

Now, consider a vesicle of volume \mathcal{V}^{in} and surface area \mathcal{A} . The shape of its membrane depends on the reduced volume $v \equiv 3\sqrt{\pi}\mathcal{V}^{\text{in}}/\mathcal{A}^{3/2} \leq 1$ [13]. If we ignore the excess area stored in the shape fluctuations, the membrane can only encapsulate adhering particles for $v < 1$. The encapsulation will proceed until the membrane forms a large spherical “mother” vesicle with many spherical buds, see fig. 2. As far as this limit shape is concerned, one must distinguish two different situations: i) for relatively slow flip flops between the two leaflets of the bilayer, the area difference $\Delta\mathcal{A}$ between these two leaflets is subject to another constraint [22, 11]; and

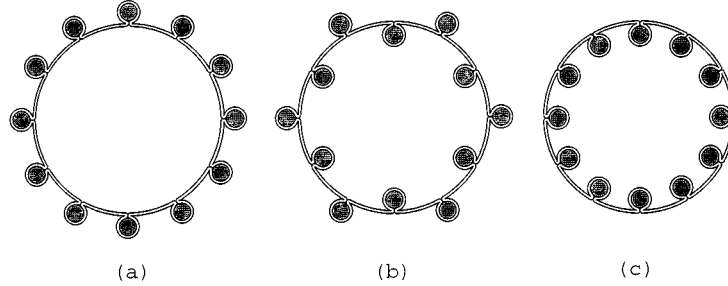


Fig. 2. – Vesicle with several encapsulated particles adsorbed (a) from the interior compartment; (b) from both the interior and the exterior solution; and (c) from the exterior compartment. The membrane thickness and the particle size have been exaggerated for illustrative purposes; in the theoretical work described here, the vesicle size is assumed to be much larger than the size of the particles.

ii) for relatively fast flip flops as present, *e.g.*, in lipid/cholesterol bilayers, such a constraint will not be effective.

For relatively fast flip flops, the limit shapes as shown in fig. 2 depend only on the reduced volume v of the initial state of the vesicle without any encapsulated particles. In general, the particle buds may point toward the exterior and interior compartment, respectively. In all cases, the total number \mathcal{N}_{ep} of encapsulated particles behaves as

$$\mathcal{N}_{\text{ep}} = (1 - v^{2/3})(R_{\text{ve}}/R_1)^2 + \mathcal{O}(R_{\text{ve}}/R_1) \quad \text{for large } R_{\text{ve}}/R_1. \quad (8)$$

The correction term of $\mathcal{O}(R_{\text{ve}}/R_1)$ is positive for a majority of exterior buds as in fig. 2(a), negative for a majority of interior buds as in fig. 2(c), and vanishes if the numbers of exterior and interior buds are equal as in fig. 2(b). For a large vesicle with $R_{\text{ve}} \simeq 10 \mu\text{m}$ and nanoparticles with $R_{\text{pa}} = R_1 \simeq 10 \text{ nm}$, the above formula leads to the estimate $\mathcal{N}_{\text{ep}} \simeq (1 - v^{2/3})10^6$.

If flip flops are slow on the time scales which govern the encapsulation process, the constraint on the area difference $\Delta\mathcal{A}$ favors states as in fig. 2(b) for which the numbers of interior and exterior buds are equal and the area difference remains essentially unchanged during encapsulation. The asymmetric states shown in fig. 2(a) and 2(c), on the other hand, will be suppressed by this constraint since they involve a large change in $\Delta\mathcal{A}$.

After the completion of this work, we became aware of two recent papers on the interaction of vesicles with large adhesive particles. In ref. [23] by Dinsmore, Wong, Nelson and Yodh, the depletion forces between small and large particles are studied which push the large particles toward the membrane. The authors also discuss the possibility that one large particle is encapsulated by the vesicle membrane and derive a relation which is similar to our eq. (7) above. In ref. [24] by Dietrich, Angelova and Pouligny, the interaction of large Latex particles with vesicles is studied. The size of these particles is in the micrometer regime and is, thus, comparable to the size of the vesicle. The constraints on the area and on the volume of the vesicle then acts to *prevent* the encapsulation of the particles. In contrast, we have focussed here on situations in which the particle size R_1 is much smaller than the vesicle size R_{ve} , see, *e.g.*, our eq. (8).

In summary, we have shown theoretically that dispersed nanoparticles and colloids change the curvature of flexible membranes and that these changes depend on the membrane/particle interactions and the particle size. One issue which deserves further study is the interaction

of flexible membranes with *growing* particles. As mentioned, growing particles which are non-adhesive will typically induce a time-dependent “spontaneous” curvature. Growing adhesive particles, on the other hand, will become encapsulated as soon as the particle size exceeds the critical size R_* . It seems possible to use this encapsulation process in order to interrupt the growth process as soon as the particle size has reached the threshold value $R_{pa} \simeq R_*$ which would provide a systematic method to control this size.

Finally, the curvature effects studied here should also be present for biomembranes. The latter membranes contain many different channels, carriers and pumps which are used in order to transport ions and larger molecules across the membrane. These transport processes change the concentrations of the various molecular species and, thus, determine the osmotic conditions in the two compartments which are separated by the membrane. The results reported here imply, however, that these changes in the molecular concentrations will also contribute to the “spontaneous” curvature of the biomembrane. It remains to be seen if this coupling between membrane transport and curvature has some biological significance.

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