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Adsorption transition of directed vesicles in two dimensions

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Abstract. We discuss the behaviour of two-dimensional directed vesicles in the presence of an attractive surface. The variation of the binding potential with osmotic pressure difference is calculated and shown to exhibit surprisingly complex behaviour.

1. Introduction

Our aim in this paper is to study the statistical properties of vesicles attracted to an adsorbing substrate. Vesicles are closed surfaces, isomorphic to the sphere [1]. They are relevant as a model system for the studies of the configurational properties of biological cell membranes, such as the red blood cells [2]. Moreover, artificial vesicles have potential applications in drug delivery.

Given the complexity of the behaviour of vesicles in three dimensions much of the current research is focused on two-dimensional models of closed rings. One of the important parameters is the osmotic pressure difference, Δp, between the inside and outside of the ring. If this is negative the vesicles are deflated and are thought to have the same critical behaviour as branched polymers. For $\Delta p = 0$ the models behave as a self-avoiding ring. For a positive difference the vesicles are inflated with maximal area [3,4].

Recently Foster and Seno [5] presented results obtained from series analysis for the effect of the pressure difference on the adsorption transition of two-dimensional vesicles. They encountered numerical difficulties that prevented them from obtaining definitive results for the shape of the adsorption phase boundary. The problems were particularly severe for $\Delta p \to 0^-$ where it was not possible to tell whether or not the boundary was continuous.

In an attempt to clarify this behaviour we study here the adsorption transition of directed vesicles. Results are obtained by extrapolating exact answers for finite strips of widths s which follow from diagonalizing the transfer matrix. Because of the directed nature of the vesicle, strip widths of $s \leqslant 65$ and, for a restricted version of the model, $s \leqslant 165$ are accessible. This enables us to obtain very precise results for the position of the binding transition and to investigate its behaviour as the pressure difference tends to zero.

The vesicles we consider are directed in that they are bounded by two solid-on-solid walks, that is walks without overhangs. We also impose the condition that the two walks enclosing the membrane must never touch. The shape obtained by following these rules is known as a row-convex polygon; an example is shown in figure 1.

The vesicle is placed on a strip of infinite length and width s. Rows of the lattice are labelled by integers, with rows 1 and s being attractive walls. The position of the walks in column i is labelled by n_i, m_i with $n_i > m_i$. We shall consider two different models; unrestricted where $n_{i+1} - n_i$ and $m_{i+1} - m_i$ can take any value and restricted where $n_{i+1} - n_i = \pm 1, 0$; $m_{i+1} - m_i = \pm 1, 0$.

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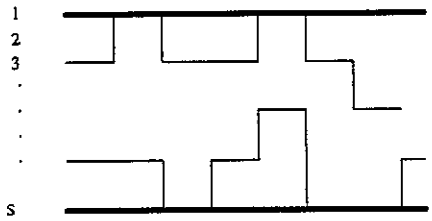

Figure 1. A directed vesicle on a strip of width s.

Assigning a fugacity α to each plaquette, ω to each monomer, and κ to each contact with the walls the transfer matrix $T_{i,j}$ linking two subsequent columns i, j is readily written as

$$\mathcal{T}_{ij} = \omega^l \alpha^p \kappa^q \tag{1.1}$$

where

$$l = (2 + |n_i - n_j| + |m_i - m_j|) \tag{1.2}$$

$$p = \tfrac{1}{2}(n_i - m_i + n_j - m_j) \tag{1.3}$$

$$q = \tfrac{1}{2}(\delta(m_i, 1) + \delta(m_j, 1) + \delta(n_i, s) + \delta(n_j, s)) \tag{1.4}$$

if the matrix element corresponds to an allowed configuration.

Denote by λ_0 the maximum eigenvalue of T. If $\lambda_0 < 1$ the generating function for vesicles of all lengths on the lattice is [6]

$$Z = \langle v | \frac{T}{1 - T} | u \rangle \tag{1.5}$$

where $|v\rangle, |u\rangle$ are vectors depending on the initial and final configuration of the vesicles. As usual the fugacity ω controls the average length of the vesicle

$$\langle L(\kappa, \omega) \rangle = \omega \frac{\partial \ln Z}{\partial \omega} \tag{1.6}$$

and the critical fugacity $\omega^*(\kappa, \alpha)$ is obtained by imposing $\lambda_0(\omega^*, \kappa, \alpha) = 1$.

For each value of $0 \leqslant \alpha \leqslant 1$ a binding transition is expected to occur for some $\kappa \equiv \kappa_c(\alpha)$. For $\kappa < \kappa_c(\alpha)$ the vesicle is not bound to the surface and $\omega^*(\kappa, \alpha)$ is equal to a value $\omega_c(\alpha)$ which is independent of κ. For $\kappa > \kappa_c(\alpha)$ the largest eigenvalue corresponds to a bound eigenstate and $\omega^*(\kappa, \alpha)$ decreases with increasing κ [7].

Our aim here is to understand how the position of the binding transition $(\omega_c(\alpha), \kappa_c(\alpha))$ depends on α. We do this by using a numerical approach based on a crossing-point method first introduced by Veal *et al* [8]. This is described and justified in section 2. In particular we compare numerical and exact results for a soluble model. Results for restricted and unrestricted vesicles are presented and discussed in section 3.

2. The numerical approach

Very precise results for the dependence of the position of the binding transition on the area fugacity $(\omega_c(\alpha), \kappa_c(\alpha))$ have been obtained using a crossing-point method first introduced by Veal *et al* [8]. Indicating by $\omega_s^*(\alpha, \kappa)$ the critical value of ω for a vesicle on a strip of width s, it becomes apparent that if $\omega_s^*(\alpha, \kappa)$ is plotted as a function of κ for fixed $\alpha < 1$, a crossing point occurs between curves for different s. Examples are shown in figure 2. Using $(\tilde{\omega}_s(\alpha), \tilde{\kappa}_s(\alpha))$ to denote the crossing point of $\omega_s^*(\alpha, \kappa)$ and $\omega_{s+2}^*(\alpha, \kappa)$ we shall assume that

$$\lim_{s\to\infty} (\tilde{\omega}_s(\alpha), \tilde{\kappa}_s(\alpha)) = (\omega_c(\alpha), \kappa_c(\alpha)). \tag{2.1}$$

Our aim in this section is to summarize the evidence for this assumption and to discuss its physical meaning.

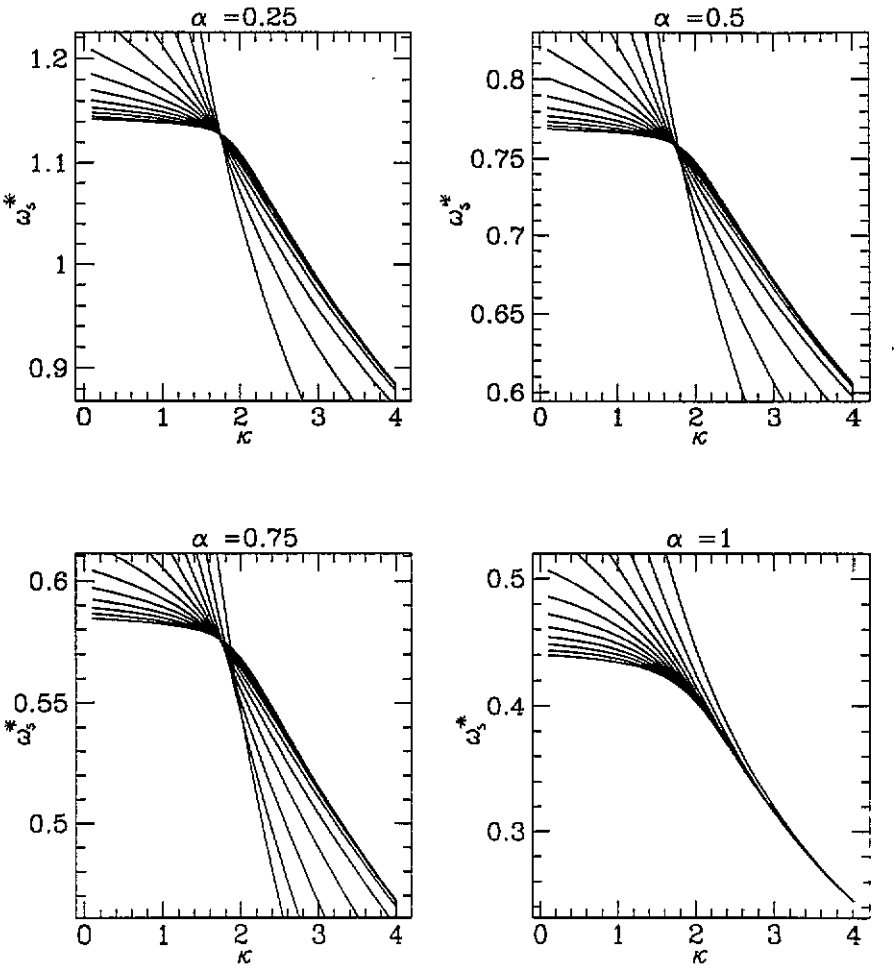

Figure 2. Variation of critical bond fugacity ω_s^* with binding potential κ for different values of area fugacity α. Results are presented for strip widths $s = 3 - 15$. Note that the crossing point of the curves disappears for $\alpha = 1$.

Equation (2.1) has been found to hold true for several exactly soluble models. These are directed polymers with and without attractive monomer–monomer interactions near an attractive wall [8] and the adsorption transition of strongly-embedded restricted walks [9]. The latter model corresponds to the $\alpha = 0$ limit of the restricted vesicles considered here.

Brak and Guttmann [10] have solved the unrestricted model of convex polygons exactly. This corresponds to $\kappa = 1$ and $s = \infty$. However $\omega^*(\kappa, \alpha)$ can be proved to be independent of κ for $\kappa \leqslant \kappa_c(\alpha)$ [11, 12] and hence their calculation provides a check on the numerical results for the binding fugacity presented here. They give a numerical fit for $\omega^*(1, \alpha) \equiv \omega_c(\alpha)$ which is indistinguishable from our results to within the accuracy of the fit itself [10]†.

A further check on the numerical approximations to both κ_c and ω_c throughout the range of α can be made by considering a vesicle built using only the column configurations appearing in figure 3. This model can be solved exactly following the approach outlined in previous work [9]. The exact results and those obtained from the crossing-point method are compared in table 1. The numerical values $(\tilde{\kappa}_c, \tilde{\omega}_c)$ follow from extrapolating finite-size data for strip widths up to $s = 15$. Despite the small strip widths the agreement is excellent.

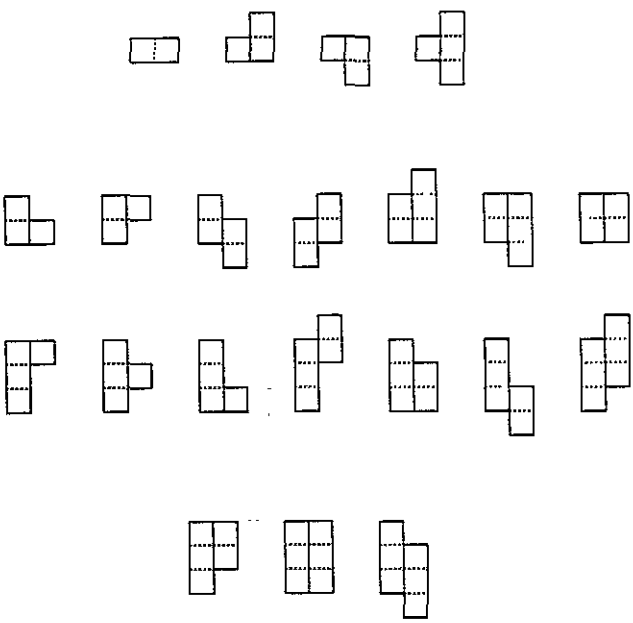

Figure 3. Allowed configurations in two neighbouring columns of the lattice for an exactly soluble model of directed vesicles. This model was used to check the numerical procedure described in the text.

It is of importance to the understanding of the crossing point to note that it only occurs when both walls of the strip are attractive. Moreover, even if this is the case, for $\alpha = 1$ no crossing point is found. As α approaches unity it is necessary to take into account increasingly large strip widths s before the crossing point occurs. A typical behaviour of $(\tilde{\kappa}_s, \tilde{\omega}_s)$ is given in figure 4 where the behaviour of the average area per column a_s has also

† In the last equation of [10] y^2 and z should be interchanged.

Table 1. Comparison between the exact and numerical solutions of a soluble vesicle model (see figure 3). The numerical values $(\tilde{\kappa}, \tilde{\omega})$ follow from extrapolating the position of the crossing point $(\tilde{\kappa}_s, \tilde{\omega}_s)$ for strips of width $s \leqslant 15$ to infinite width.

α	κ_c(exact)	$\tilde{\kappa}$	ω_c(exact)	$\tilde{\omega}$
0.1	1.352 984 30	1.352 985 39	2.019 126 48	2.019 126 33
0.2	1.354 458 41	1.354 462 12	1.407 032 86	1.407 032 340
0.3	1.354 057 58	1.354 061 48	1.131 380 44	1.131 379 91
0.4	1.351 576 22	1.351 577 98	0.964 167 46	0.964 166 97
0.5	1.346 842 83	1.346 850 95	0.847 902 18	0.847 901 86
0.6	1.339 746 26	1.339 749 02	0.760 351 05	0.760 350 91
0.7	1.330 262 46	1.330 261 70	0.690 860 62	0.690 860 21
0.8	1.318 475 53	1.318 477 35	0.633 606 99	0.633 606 70
0.9	1.304 587 46	1.304 595 13	0.585 108 35	0.585 107 76

been plotted. Note that the position of $(\tilde{\kappa}_s, \tilde{\omega}_s)$ only reaches its asymptotic behaviour for $s > a_s$. The system is then behaving as a vesicle attracted to a single surface rather than two walks attracted to the two surfaces of the strip.

The crossing point occurs because, for fixed $\alpha < 1$, $\omega_s^*(\kappa, \alpha)$ is a decreasing function of s for $\kappa < \kappa_c$ and an increasing function of s for $\kappa > \kappa_c$. It can be shown formally that this is the case for directed polymers [11]. Here we give a physical argument that indicates that this also occurs in the vesicle case. In the extended regime the vesicle is restricted and loses entropy on a strip of finite width. Therefore it needs to increase its step fugacity ω to attain a given length and ω_s^* increases with decreasing s. In the bound regime the symmetry of the problem dictates that the vesicle tunnels between the two sides of the strip. The second surface thus enables it to increase its entropy and, for a given κ, this effect dominates and ω_s^* decreases with decreasing s.

3. The adsorption phase boundaries

Results for the adsorption phase boundaries of the restricted and unrestricted models are shown in figures 5 and 7 respectively. The limiting value $(\tilde{\kappa}, \tilde{\omega})$ was obtained using a standard Padé analysis [13] for the convergence of the finite-size data $(\tilde{\kappa}_s, \tilde{\omega}_s)$. Only values for which $s > a_s$ (see figure 4) for which the finite-size behaviour appeared to have reached an asymptotic regime were included in the analysis. The value of s for which this occurred increased with increasing s and, indeed, the crossing point is not expected to occur for $\alpha = 1$.

For the restricted model it was possible to consider strip widths $s \leqslant 165$ and to obtain reliable numerical data for $(\tilde{\kappa}, \tilde{\omega})$ for $\alpha \lesssim 0.9999$. These are presented in figures 5 and 6. For $\alpha = 0$ the numerical results reproduce the analytic solution $\kappa_c = 1.3095$ exactly. For $\alpha \to 1$ they are consistent with a trend towards the exact value $(\kappa_c, \omega_c) = (\frac{4}{3}, \frac{1}{2})$ [7].

As $\alpha \to 0$ $\tilde{\omega}$ diverges as $\alpha^{-1/2}$. The value then decreases smoothly with increasing α and there is some numerical evidence for a power law dependence of $\tilde{\omega}$ on $(1 - \alpha)$ as $\alpha \to 1$. This is as expected [4, 14].

$\tilde{\kappa}$ decreases with increasing $\alpha < 0.8$; then increases sharply to its limiting value at $\alpha = 1$. Note, however that the variation in $\tilde{\kappa}$ over the range $0 \leqslant \alpha \leqslant 1$ is only $\sim 3\%$.

These results should be compared to those for the unrestricted model shown in figures 7 and 8. In this case the maximum strip width that we have been able to attain is $s = 65$ and therefore reliable data for the crossing point could be obtained only for $\alpha \lesssim 0.998$.

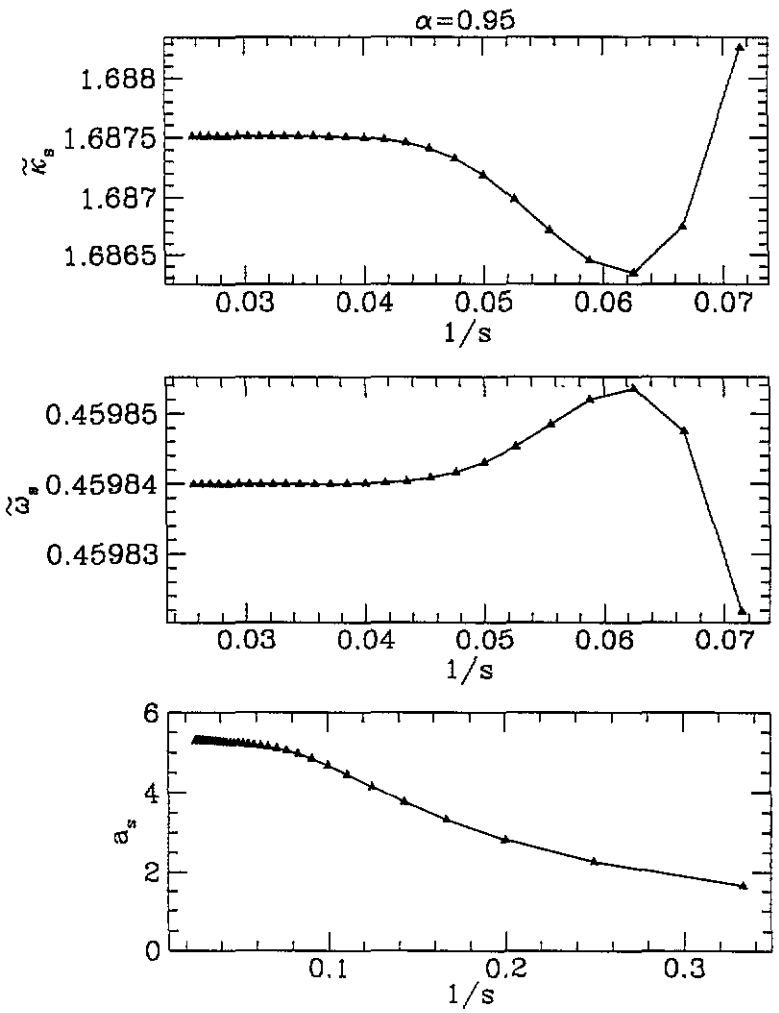

Figure 4. Variation of the position of the crossing point $(\tilde{\omega}_s, \tilde{\kappa}_s)$ and the mean area per column a_s of the vesicle with the width of the strip s for an area fugacity $\alpha = 0.95$.

$\tilde{\omega}$ behaves in a similar way to the restricted model approaching the exact value $\omega_c = \sqrt{2} - 1$ [15] as $\alpha \to 1^-$. $\tilde{\kappa}$, however, initially increases with increasing α, then decreases, until for $\alpha > 0.99$ there is an increase which is very sharp but consistent with a continuous approach to the exact limiting value $\kappa_c = 1 + 1/\sqrt{2}$. It should be borne in mind that the variation of $\tilde{\kappa}$ with α is only $\sim 2\%$.

In both models $\tilde{\kappa}$ changes little in magnitude as the area fugacity is varied, but shows considerable structure. We believe this to be the result of subtle competition between the change in shape of the vesicle from flaccid to branched polymer-like as α decreases and the interaction of the binding surface with the second vesicle surface further from the wall. Strong effects may be expected when $\alpha \lesssim 1$ where the area of the vesicle grows quickly with α.

In summary we have presented phase diagrams for the dependence of the binding fugacity on area fugacity for directed vesicles. The results are subtle and large strip widths

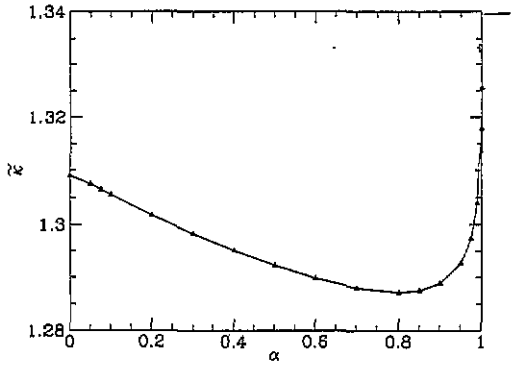

Figure 5. Dependence of the binding potential $\tilde{\kappa}$ on the area fugacity α for the restricted directed model. The exact value for $\alpha = 1$ is indicated by a star.

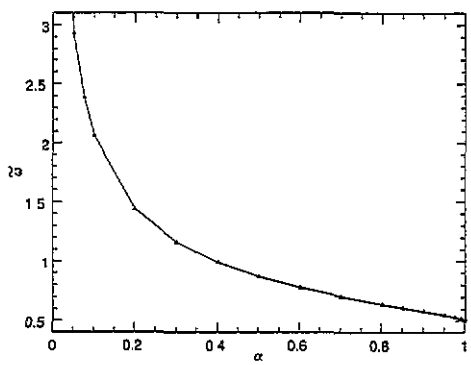

Figure 6. Dependence of the bond fugacity at the binding transition $\tilde{\omega}$ on the area fugacity α for the restricted directed model.

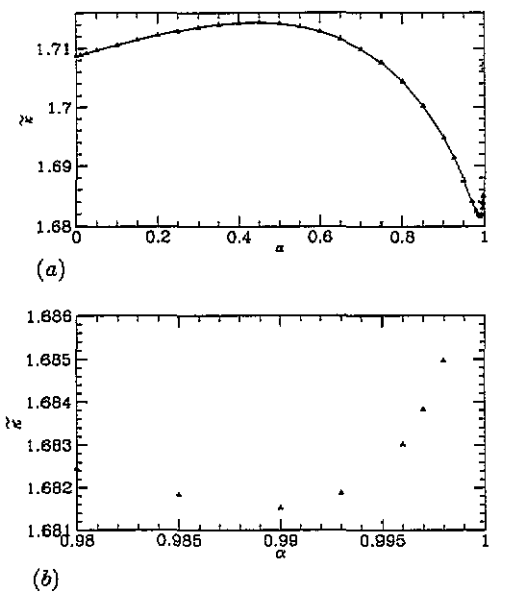

Figure 7. (*a*) Dependence of the binding potential $\tilde{\kappa}$ on the area fugacity α for the unrestricted directed model. The exact value for $\alpha = 1$ is indicated by a star. (*b*) A close-up of the phase boundary shown in figure 7(*a*) for $\alpha < 1$.

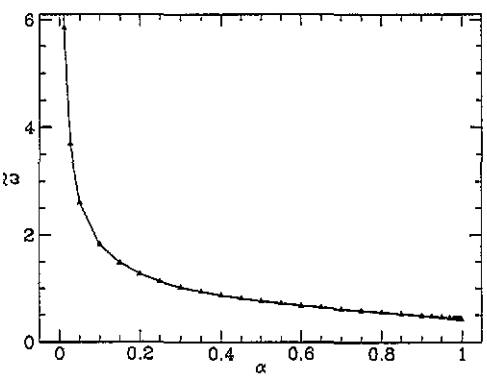

Figure 8. Dependence of the bond fugacity at the binding transition $\tilde{\omega}$ on the area fugacity α for the unrestricted directed model.

are needed to obtain meaningful curves. Numerical work for the binding of non-directed vesicles, even in two-dimensions, will be difficult.

Acknowledgments

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