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New Results for Directed Vesicles and Chains near an Attractive Wall

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In this paper we present new exact results for single fully directed walks and fully directed vesicles near an attractive wall. This involves a novel method of solution for these types of problems. The major advantage of this method is that it, unlike many other single-walker methods, generalizes to an arbitrary number of walkers. The method of solution involves solving a set of partial difference equations with a Bethe Ansatz. The solution is expressed as a "constant-term" formula which evaluates to sums of products of binomial coefficients. The vesicle critical temperature is found at which a binding transition takes place, and the asymptotic forms of the associated partition functions are found to have three different entropic exponents depending on whether the temperature is above, below, or at its critical value. The expected number of monomers adsorbed onto the surface is found to become proportional to the vesicle length at temperatures below critical. Scaling functions near the critical point are determined.

KEY WORDS: Polymer networks; vicious walkers; directed vesicles.

1. INTRODUCTION

A vesicle with a preferred direction, or "directed vesicle," can be modeled by a pair of fully directed polymer chains joined in parallel where only configurations in which the chains avoid one another are allowed. In two dimensions the configurations of a single chain can be assumed to be the possible space-time trajectories of a one dimensional random walker who at each tick of a clock moves unit distance in either the positive or negative

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direction. The links of the chain are therefore in the direction of one of the two vectors $\mathbf{e}_1 = \{-1, 1\}$ and $\mathbf{e}_2 = \{1, 1\}$ which form the basis vectors of a directed square lattice which we think of as being oriented at 45 degrees to the horizontal so that time increases from left to right. Since the first and last link in each chain of the vesicle have fixed directions due to the mutual avoidance condition the configurations of a pair of walkers which start at height x^i and $x^i + 2$ and end at x^f and $x^f + 2$ after t steps will be enumerated corresponding to a vesicle of length $t + 2$. The adsorption of the vesicle by an attractive wall will be considered so that in calculating the partition function a vesicle configuration with m monomers adsorbed onto the wall will be given weight κ^m where $\kappa = \exp(-\varepsilon_s/k_B T) \geqslant 1$. The quantity ε_s is the energy of contact with the wall. The wall will be positioned along the line $x = 0$ with the vesicle restricted to the half space $x \geqslant 0$ and if the beginning of the vesicle is grafted to the wall only monomers at even distances along the chain may be adsorbed (see Fig. 1). Earlier work on polymer networks made from long chains in a good solvent both in the bulk and with a surface has recently been reviewed by De'Bell and Lookman.[1] Adsorption of directed polymer chains onto a surface has been reviewed by Privman and Švrakić.[2] They determined the grand partition function of a partially directed polymer chain near an attractive wall and the same system with additional attractive monomer–monomer interactions was solved exactly by Veal *et. al.*[3] The adsorption of vesicles formed from two partially directed chains was investigated numerically using a transfer matrix method by Micheletti and Yeomans.[4] They also included the effect of a pressure difference between the inside and outside of the vesicle by introducing an area fugacity. Their vesicle configurations correspond to row convex polygons whereas the ones considered here are staircase polygons.

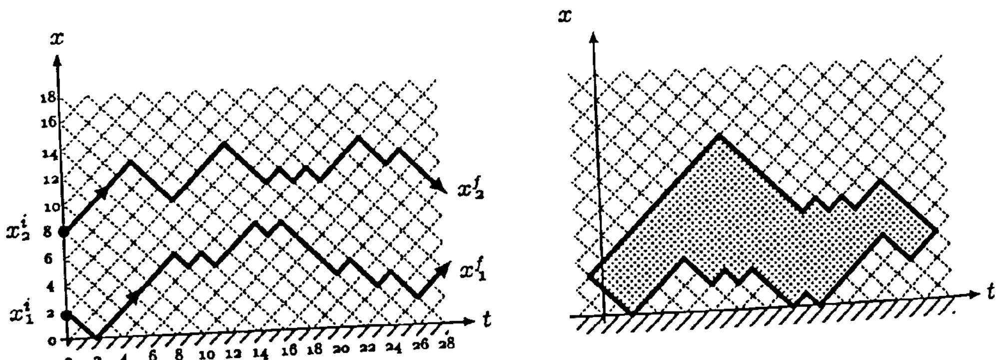

Fig. 1. Two non-intersecting directed walks above a wall (left) and (right) a vesicle made by adding two pairs of steps (grey) to two non-intersecting walks starting and ending a distance two apart.

In this paper we calculate the partition functions for various configurations of vesicles constructed from two fully directed walks as explained above. Before doing this we tackle the problem of a single chain made from a single directed walk. The problem of a single polymer chain has been considered previously: this problem has been modeled in several other ways such as continuous chains[5] and partially-directed walks (see ref. 2 and references therein). In this paper we consider another way of modeling a single chain which is the fully directed walk. The principal advantage of this model is that it leads to the solution of the vesicle model. It also provides a confirmation of universality in this problem. We give a complete list of results for the actual partition functions (and critical analysis) for these fully directed walks: such explicit formulae have not been published previously. The sections on the single walk then serve several purposes. They firstly give these explicit results for the partition functions of various standard single chain scenarios. They explain the method we later use to solve the vesicle and two chain problems. In this regard they also give intermediate results we later use in those two chain sections. Some of these intermediate results also have interesting combinatorial meanings and we explore some of these in this paper. The central single chain results for the partition function of a walk with one end attached, $\acute{Z}^{\mathscr{S}}_{2r}(\kappa)$, and both ends attached to the surface, $\hat{Z}^{\mathscr{S}}_{2r}(\kappa)$, are given by

$$\acute{Z}^{\mathscr{S}}_{2r}(\kappa) = \kappa \sum_{m=0}^{r} (\kappa - 1)^m \binom{2r}{r-m} \tag{1.1}$$

and

$$\hat{Z}^{\mathscr{S}}_{2r}(\kappa) = \kappa \sum_{n=0}^{r} \frac{2n+1}{r+n+1} \binom{2r}{r-n} (\kappa - 1)^n \tag{1.2}$$

respectively.

We now summarise the most important results for the vesicle scenarios. We shall denote the partition function for vesicles of length $t+2$ beginning at height $x^i + 1$ and ending at height $x^f + 1$ by $Z^{\mathscr{V}}_t(x^f \mid x^i; \kappa)$. (Generically in this paper we shall use the superscript $\mathscr{V}$ to denote quantities associated with vesicles, $\mathscr{S}$ for quantities associated with one walker (a single polymer chain) and $\mathscr{T}$ for quantities associated with two walkers (polymer chains). Also, we shall use an acute accent for quantities associated with walkers attached to the surface from one end with the other end free (summed over), while the hat shall denote cases where both ends are fixed to a surface.) In this paper we obtain exact expressions for these partition functions, as well as the special cases when one end of the vesicle is grafted to the wall and the other is either free to move, $\acute{Z}_{2r}^{\mathscr{V}}(\kappa)$, or fixed at distance x^f from the wall, $Z_t^{\mathscr{V}}(x^f \mid 0; \kappa)$. In the latter case

$$Z_t^{\mathscr{V}}(x^f \mid 0; \kappa) = \kappa \binom{t+2}{q} \sum_{n=0}^{q} \frac{(x^f+1)(n+1)(x^f+n+2)(x^f+2n+3)}{(q+1)(t+1)(t+2)(t+3)} \times \binom{t+3}{q-n} (\kappa-1)^n \tag{1.3}$$

where $q = \frac{1}{2}(t - x^f)$. When one end is free we find, for t even,

$$\acute{Z}_{2r}^{\mathscr{V}}(\kappa) = \sum_{x^f \geqslant 0} Z_t^{\mathscr{V}}(x^f \mid 0; \kappa) = \kappa C_r \sum_{n=0}^{r} \frac{n+1}{r+1} \binom{2r+2}{r-n} (\kappa-1)^n \tag{1.4}$$

where C_r is the rth Catalan number,

$$C_r = \frac{1}{r+1} \binom{2r}{r} \tag{1.5}$$

and $\acute{Z}_{2r+1}^{\mathscr{V}}(\kappa)$ is given by the same formula with C_r replaced by C_{r+1}. If both ends are fixed on the wall we obtain, setting $x^f = 0$ in (1.3),

$$\hat{Z}_{2r}^{\mathscr{V}}(\kappa) = Z_{2r}^{\mathscr{V}}(0 \mid 0; \kappa) = \kappa \binom{2r+2}{r} \sum_{n=0}^{r} \frac{(n+1)(n+2)(2n+3)}{(r+1)(2r+1)(2r+2)(2r+3)} \times \binom{2r+3}{r-n} (\kappa-1)^n \tag{1.6}$$

The above sums have hypergeometric terms and using a program of Paule and Schorn,[6] which is an implementation of Zeilberger's algorithm,[7,8] we find, writing $z_r(\kappa) = \acute{Z}_{2r}^{\mathscr{V}}(\kappa)$ or $\hat{Z}_{2r}^{\mathscr{V}}(\kappa)$, that in both cases

$$\frac{(\kappa-1)}{\kappa} \frac{g(\kappa) + r h(\kappa)}{2(2r-1)} z_r(\kappa) - \kappa \frac{g(\kappa) + (r+1) h(\kappa)}{r+2} z_{r-1}(\kappa) = -z_{r-1}(1) \tag{1.7}$$

where in the first case $g(\kappa) = h(\kappa) = 1$ and in the second case

$$g(\kappa) = \kappa^2 + 2\kappa - 2 \qquad \text{and} \qquad h(\kappa) = (\kappa - 2)^2 \tag{1.8}$$

It follows that, for $t \to \infty$, the partition functions have the asymptotic forms[3]

$$\acute{Z}_t^{\mathscr{V}}(\kappa) \sim \mu^t t^{g_1} \qquad \text{and} \qquad \hat{Z}_t^{\mathscr{V}}(\kappa) \sim \mu^t t^{g_{11}} \tag{1.9}$$

[3] Note, in this paper we take $f(x) \sim g(x)$ to mean $\lim_{x \to x_0} f/g = \text{constant} \neq 0$ (rather than one). This avoids the frequent introduction of constants.

Table I. Summary of Vesicle Growth Parameter and Critical Exponents

	μ	g_{11}	g_1	Δ_s
$\kappa<2$	4	-5	-3	0
$\kappa=2$	4	-3	-2	$\frac{1}{2}$
$\kappa>2$	$2\kappa/\sqrt{\kappa-1}$	$-\frac{3}{2}$	$-\frac{3}{2}$	1

where the growth parameter μ and exponents g_1, g_{11} are given in Table I. The notation γ_1-1 and $\gamma_{11}-1$ are often also used in place of g_1 and g_{11} respectively.

Notice that the growth parameter and exponents for $\kappa<2$ are independent of κ and hence must have their $\kappa=1$ values. Fisher[9] solved the $\kappa=1$ problem for fixed x^f in the continuum limit when the walks become Brownian motion paths and the exponent we find for the discrete problem is in agreement with his. Fisher's work on one and two walkers was generalised to p walkers by Forrester[10] who found

$$g_1=-(3p^2+p-2)/4 \qquad \text{and} \qquad g_{11}=-p(2p+1)/2 \tag{1.10}$$

which yields $g_1=-3$ for $p=2$. Fisher[9] also considered the effect of an attractive wall on a single chain but his "necklace" technique does not extend to vesicles. It is one of the main purposes of this paper to illustrate a powerful combinatorial technique[11] known as a "constant term formula" which we have used to obtain equations (1.3) and (1.4). The growth factor for $\kappa<2$ is the same as for a vesicle with no wall. However when $\kappa>2$ the asymptotic form is dominated by the solution of the homogeneous part of (1.7) and has a factor 2 arising from the entropy of the chain which is furthest from the wall and a temperature dependent factor arising from the nearest chain, a macroscopic part of which is adsorbed onto the wall. As $\kappa\to\infty$ the adsorption becomes complete leaving only the Boltzmann factor $\kappa^{1/2}$ arising from the single configuration with half of the monomers adsorbed and the entropy of a single chain.

In the adsorbed region the critical exponent is independent of whether or not the end of the vesicle is fixed to the surface or free to move, and is equal to that of a single chain with both ends grafted onto the surface in the desorbed regime. We find $g=-\frac{3}{2}$ which agrees with setting $p=1$ in the g_{11} formula of (1.10). At the critical point, $\kappa=2$, we shall show that $\hat{Z}_t^{\mathscr{V}}(2)=\acute{Z}_t^{\mathscr{V}}(1)$ in agreement with $g_{11}(\kappa=2)=g_1(\kappa=1)$. Also we show that $\hat{Z}_t^{\mathscr{V}}(2)$ is equal to the $\kappa=1$ partition function of a two-chain star polymer attached to the wall for which the exponent, $g=-2$, was given by

Forrester.[10] These results are respectively special cases of equations (4.16) and (4.14) with $\bar{\kappa}=1$.

The critical point may be characterized as the temperature lower than which the expected number of adsorbed monomers, $\langle m\rangle_t^{\mathscr{V}}(x^f\mid 0;\kappa)$ becomes of order t. This quantity may be obtained in the usual way by differentiating the partition function. Thus, for fixed x^f, with the definition

$$Z_t^{\mathscr{V}}(x^f\mid 0;\kappa)=\sum_{m=0}^{q}\sum_{v\in\mathscr{V}_t(x\mid 0;m)}\kappa^m \tag{1.11}$$

where $\mathscr{V}_t(x^f\mid 0;m)$ is the set of vesicle configurations with m adsorbed monomers, we have

$$\langle m\rangle_t^{\mathscr{V}}(x^f\mid 0;\kappa)=M_t^{\mathscr{V}}(x^f\mid 0;\kappa)/Z_t^{\mathscr{V}}(x^f\mid 0;\kappa) \tag{1.12}$$

where

$$M_t^{\mathscr{V}}(x^f\mid 0;\kappa)=\sum_{m=0}^{q}\sum_{v\in\mathscr{V}_t(x^f\mid 0;m)}m\kappa^m=\kappa\frac{d}{d\kappa}Z_t^{\mathscr{V}}(x^f\mid 0;\kappa) \tag{1.13}$$

An explicit formula for $M_t^{\mathscr{V}}(x^f\mid 0;\kappa)$ may be obtained by differentiating (1.3) and, for $x^f=0$, from an asymptotic analysis of the recurrence relation which results from using Zeilberger's algorithm we find, on dividing by $Z_t^{\mathscr{V}}(0\mid 0;\kappa)$,

$$\langle m\rangle_t^{\mathscr{V}}(0\mid 0;\kappa)\sim t^{\Delta_s} \tag{1.14}$$

where the values of the "adsorption" exponent Δ_s are listed in Table I. This exponent is equal to the "crossover" exponent ϕ_s (defined below) when $\kappa=2$. The same result is found for the case when one end is free by using (1.4).

The scaling theory which applies near the binding transition has been discussed in the case of the adsorption of undirected polymer chains by Eisenreigler *et al.*[5,12,13] For the present problem we find the following scaling forms which are valid for $\kappa\to 2$ and $t\to\infty$. When both ends of the vesicle are grafted to the surface

$$\hat{Z}_t^{\mathscr{V}}(\kappa)\approx 4^t t^{g_{11}^c}\hat{\varphi}^{\mathscr{V}}\left(\frac{(\kappa-2)}{2}t^{\phi_s}\right) \tag{1.15}$$

where $g_{11}^c=-3$, the value of g_{11} at $\kappa=2$, and $\phi_s=1/2$. Also, as expected,[14] the scaling function $\hat{\varphi}^{\mathscr{V}}(z)$ is an entire function with

$$\hat{\varphi}^{\mathscr{V}}(z)\sim\begin{cases}z^3e^{z^2}, & z\to\infty\\ (-z)^{-4}, & z\to-\infty\end{cases} \tag{1.16}$$

The symbol $\asymp$ defines the assumed two-variable scaling conditions associated with critical points.[14]

There is a similar scaling form in the case of a vesicle with one free end with $g_1^c = -2$ and $\hat{\varphi}^{\mathscr{V}}(z)$ replaced by

$$\acute{\varphi}^{\mathscr{V}}(z) \sim \begin{cases} ze^{z^2}, & z \to \infty \\ (-z)^{-2}, & z \to -\infty \end{cases} \tag{1.17}$$

Notice that the factor multiplying $\kappa - 2$ in the argument of the φ functions comes from $\langle m \rangle_t^{\mathscr{V}}(\kappa = 2)$. These scaling forms together imply all of the data in Table I. The complete scaling functions are defined in terms of integrals given in Section 4.

The grand partition function is often used as a computational aid in the theory of polymer adsorption.[5] This is defined by

$$\acute{G}^{\mathscr{V}}(u, \kappa) = \sum_{t=0}^{\infty} \acute{Z}_t^{\mathscr{V}}(\kappa)\, u^t \tag{1.18}$$

where u is called the length fugacity. It may be deduced from the form of $\acute{Z}_t^{\mathscr{V}}(\kappa)$ that $\acute{G}^{\mathscr{V}}(u, \kappa)$ is singular at $u = u_c = 1/\mu$ which is physically the value of u at which the expected polymer length diverges. The form of $\acute{Z}_t^{\mathscr{V}}(\kappa)$ as $t \to \infty$ implies that as u approaches u_c from below

$$\acute{G}^{\mathscr{V}}(u, \kappa) \sim (1 - \mu u)^{-\gamma_1} \tag{1.19}$$

where the critical exponent $\gamma_1 = 1 + g_1$. Note, γ_1 takes on three values, γ_1^-, γ_1^c and γ_1^+ depending on whether $\kappa > 2$, $\kappa = 2$ or $\kappa < 2$ respectively.

Near the critical point, ($\kappa = 2$, $u = \frac{1}{4}$), the grand partition function has the scaling form

$$\acute{G}^{\mathscr{V}}(u, \kappa) \asymp (1 - \mu u)^{-\gamma_1^c}\, \acute{\psi}^{\mathscr{V}}\left(\frac{\kappa - 2}{(1 - \mu u)^{\phi_s}}\right) \tag{1.20}$$

where $\acute{\psi}^{\mathscr{V}}(z)$ is the scaling function, and $\gamma_1^c = g_1^c + 1$. The grand partition function when both ends are grafted to the surface has a similar form with $\acute{\psi}^{\mathscr{V}}$ replaced by $\hat{\psi}^{\mathscr{V}}$.

In Section 2 we write down the partial difference equations to be satisfied by the single chain and vesicle partition functions. In Section 3 we illustrate the use of the constant term method in the case of a single chain and in Section 4 the method is used to produce explicit formulae for the vesicle partition functions. In both cases we deduce the recurrence relations which lead to the determination of the critical exponents and scaling forms.

2. PARTIAL DIFFERENCE EQUATIONS

This section contains the partial difference equations for the partition functions of a single chain and vesicle near an attracting wall on the directed square lattice. Our approach to the vesicle problem will be to first solve the problem of a single chain near an attracting wall using techniques which have immediate extensions to the problem of two non-intersecting chains. The vesicle partition function is then a special case of that for two chains.

2.1. Single Chain

A vesicle is constructed from two chains only one of which makes contacts with the wall so here we consider a single polymer chain (one walker) of length t (having $t+1$ monomers) which starts at $x^i \geqslant 0$ and terminates at $x^f \geqslant 0$. For given x^f the partition function $Z_t^{\mathscr{S}}(x^f \mid x^i; \kappa)$ is defined by (1.11) with the set of vesicle configurations replaced by chain configurations. Since a chain of length t can be made by appending a single step to a chain of length $t-1$ we get the partial difference equations

$$Z_t^{\mathscr{S}}(x \mid x^i; \kappa) = Z_{t-1}^{\mathscr{S}}(x-1 \mid x^i; \kappa) + Z_{t-1}^{\mathscr{S}}(x+1 \mid x^i; \kappa), \qquad x>0, \quad t>0 \tag{2.1}$$

$$Z_t^{\mathscr{S}}(0 \mid x^i; \kappa) = \kappa Z_{t-1}^{\mathscr{S}}(1 \mid x^i; \kappa), \qquad x=0, \quad t>0 \tag{2.2}$$

$$Z_0^{\mathscr{S}}(x \mid x^i; \kappa) = \begin{cases} \delta(x, x^i) & \text{for} \quad x^i > 0 \\ \kappa\delta(x, 0) & \text{for} \quad x^i = 0 \end{cases} \tag{2.3}$$

where the last equation is the initial condition which can also be rewritten more compactly as

$$Z_0^{\mathscr{S}}(x^f \mid x^i; \kappa) = [1 + (\kappa - 1)\, \delta(x^i, 0)]\, \delta(x^f, x^i) \tag{2.4}$$

These equations may be programmed recursively to obtain $Z_t^{\mathscr{S}}(x^f \mid x^i; \kappa)$ for increasing values of t and the computing time is polynomial in the length t. From the exact solution (given below) or by iterating the difference equations, the first few terms when the chain starts and ends on the wall are given in Appendix B.

2.2. Two Chains and Vesicles

In calculating the vesicle partition function it is necessary to consider the configurations of two polymer chains of length t the first of which goes from $x_1^i \geqslant 0$ to x_1^f without crossing the wall and the second goes from x_2^i

to x_2^f, where all intermediate positions satisfy $x_2 > x_1 \geqslant 0$, that is, without touching the first walk. For fixed final positions, and for $t > 0$, the partition function $Z_t^{\mathscr{T}}(x_1^f, x_2^f \mid x_1^i, x_2^i; \kappa)$ satisfies the partial difference equation

$$\begin{aligned} Z_t^{\mathscr{T}}(x_1, x_2 \mid x_1^i, x_2^i; \kappa) = {} & Z_{t-1}^{\mathscr{T}}(x_1 - 1, x_2 - 1 \mid x_1^i, x_2^i; \kappa) \\ & + Z_{t-1}^{\mathscr{T}}(x_1 + 1, x_2 - 1 \mid x_1^i, x_2^i; \kappa) \\ & + Z_{t-1}^{\mathscr{T}}(x_1 - 1, x_2 + 1 \mid x_1^i, x_2^i; \kappa) \\ & + Z_{t-1}^{\mathscr{T}}(x_1 + 1, x_2 + 1 \mid x_1^i, x_2^i; \kappa), \qquad 0 < x_1 < x_2 \end{aligned} \tag{2.5}$$

$$\begin{aligned} Z_t^{\mathscr{T}}(0, x_2 \mid x_1^i, x_2^i; \kappa) = {} & \kappa Z_{t-1}^{\mathscr{T}}(1, x_2 - 1 \mid x_1^i, x_2^i; \kappa) \\ & + \kappa Z_{t-1}^{\mathscr{T}}(1, x_2 + 1 \mid x_1^i, x_2^i; \kappa), \qquad 0 = x_1 < x_2 \end{aligned} \tag{2.6}$$

$$Z_t^{\mathscr{T}}(x_1, x_1 \mid x_1^i, x_2^i; \kappa) = 0, \qquad x_1 = x_2 \tag{2.7}$$

and for $t = 0$,

$$Z_0^{\mathscr{T}}(x_1, x_2 \mid x_1^i, x_2^i; \kappa) = \begin{cases} \delta(x_1, x_1^i)\, \delta(x_2, x_2^i) & \text{for } \; x_1^i > 0 \\ \kappa \delta(x_1, x_1^i)\, \delta(x_2, x_2^i) & \text{for } \; x_1^i = 0 \end{cases} \tag{2.8}$$

Equation (2.7) ensures the walkers never cross. The last equation is the initial condition. For any given initial and final positions the partition function may again be computed from these equations in a time which is polynomial in t. We now illustrate this in the case of vesicles for which $x_2^i = x_1^i + 2$ and $x_2^f = x_1^f + 2$. Thus the partition function defined in the introduction for which the initial monomer of the lower chain is grafted to the surface and the other end is fixed at distance x is obtained by setting $x_1^f = x$ and calculating

$$Z_t^{\mathscr{V}}(x \mid 0; \kappa) = Z_t^{\mathscr{T}}(x, x + 2 \mid 0, 2; \kappa) \tag{2.9}$$

using the above equations. The first few terms given in the Appendix B.

3. A SINGLE CHAIN NEAR AN ATTRACTIVE WALL

The problem of a single chain interacting with a wall has been tackled previously using different underlying polymer configurations: these being partially-directed walks and restricted Solid-on-Solid walks (see ref. 2 and references therein). It has also been analysed via continuum models.[5]

The results in this section are new for fully-directed walks on a square lattice rotated through 45 degrees. Of course, any universal quantities such as exponents and scaling functions are expected to be the same as those derived previously for the other underlying geometric configurations. We show this is the case. However, the value in explicitly deriving these universal results again is many fold. Firstly, we confirm universality as mentioned above. More importantly, the method as applied to a single chain is of pedagogical value as it demonstrates simply the salient features that are used to solve the vesicle problems and will be used in the future to solve even more complicated cases. Further, several intermediate results are the starting points for further combinatorial investigations and the solution of the vesicle case.

In this section an explicit formula is obtained for the partition function defined by the equations of Section 2.1 using a method which can be generalized to more than one chain.

3.1. Solution of a Single Chain with Both Ends Fixed

3.1.1. Derivation of $Z_t^{\mathscr{S}}(x^f \mid x^i; \kappa)$. To solve (2.1) we begin by separating the variables with a trial solution of $Z_t^{\mathscr{S}}(x \mid x^i; \kappa) = P_t(x, k) = \Lambda^t \exp(ikx)$ which requires

$$\Lambda = \lambda(k) = \exp(ik) + \exp(-ik) \tag{3.1}$$

If we substitute this trial solution into (2.2) then the equation is satisfied only provided $\Lambda = \Lambda_p = \kappa/\sqrt{\kappa - 1}$ and $\exp(ik_p) = \sqrt{\kappa - 1}$. This gives us a particular solution. However, $P_t(x, k) = \Lambda^t \exp(ikx)$ and $P_t(x, -k) = \Lambda^t \exp(-ikx)$ satisfy the bulk equation so we try a more general form of solution, $R_t(x, k) = \lambda(k)^t (\mathscr{A}(k) \exp(ikx) + \mathscr{B}(k) \exp(-ikx))$ for $Z_t^{\mathscr{S}}(x \mid x^i; \kappa)$. If this is substituted into (2.2) then we must have $\mathscr{A}/\mathscr{B} = \mathscr{S}(e^{ik})$, where the "surface scattering" amplitude, $\mathscr{S}(z)$ is given by

$$\mathscr{S}(z) = -\frac{z + \bar{z} - \kappa \bar{z}}{z + \bar{z} - \kappa z}, \qquad \bar{z} := \frac{1}{z} \tag{3.2}$$

Thus the most general form of the solution for $Z_t^{\mathscr{S}}(x \mid x^i; \kappa)$ satisfying the bulk and boundary equations is

$$\begin{aligned} W_t(x; \kappa) &= \int_0^{\pi} R_t(x, k)\, dk + \mathscr{C} \Lambda_p^t \exp(ik_p x) \\ &= \int_0^{\pi} \lambda(k)^t\, \mathscr{B}(k) [\exp(-ikx) + \mathscr{S}(e^{ik}) \exp(ikx)]\, dk \\ &\quad + \mathscr{C}(\kappa/\sqrt{\kappa - 1})^t (\kappa - 1)^{x/2} \end{aligned} \tag{3.3}$$

It remains to choose the two arbitrary constants $\mathscr{B}(k)$ and $\mathscr{C}$ such that the initial condition (2.3) is satisfied. If we choose $\mathscr{B}=\mathscr{B}_0[\exp(ikx^i)+\mathscr{S}(e^{-ik})\times\exp(-ikx^i)]$ and call the integral with that choice in (3.3), $\mathscr{K}_t(x \mid x^i)$, then by a few changes of variable we can rewrite the integral as

$$\mathscr{K}_t(x \mid x^i)=\mathscr{B}_0\int_{-\pi}^{\pi}\lambda(k)^t\,[\exp(ik(x-x^i))+\mathscr{S}(e^{ik})\exp(ik(x+x^i))]\,dk \quad (3.4)$$

When $t=0$ this integral can be evaluated using the contour illustrated in Fig. 2. It has a pole at

$$k=\frac{i}{2}\log(\kappa-1) \qquad \text{(Binding pole)} \qquad (3.5)$$

We find that

$$\mathscr{K}_0(x \mid x^i)=2\pi\mathscr{B}_0(\delta(x, x^i)+(\kappa-1)\,\delta(x, -x^i)) + \pi\mathscr{B}_0\theta(\kappa-2)(2\kappa-\kappa^2)(\kappa-1)^{-(x+x^i+2)/2} \qquad (3.6)$$

where θ is the Heaviside step function. The last term arising from the residue of the pole. Thus we see that in order to satisfy (2.3) we have two cases depending on whether κ is greater than or less than 2, i.e. whether the pole is outside or inside the contour. Case a: $1<\kappa<2-$ no interior pole (unbound phase). In this case we must have $\mathscr{C}=0$ and $\mathscr{B}_0=1/2\pi$. Case b:

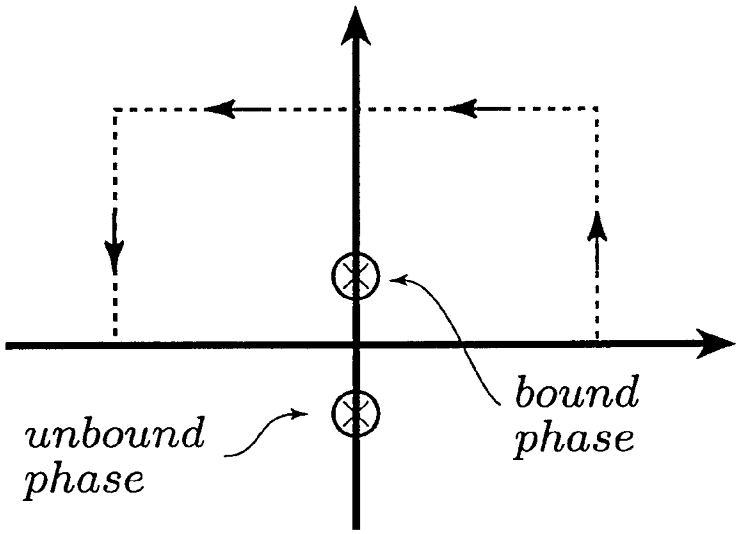

Fig. 2. The contour and pole structure in the complex k-plane, used to evaluate the integral (3.4).

$\kappa > 2-$ an interior pole (bound phase). In this case we must have $\mathscr{B}_0 = 1/2\pi$ and

$$\mathscr{C} = \frac{\kappa}{2}(\kappa - 2)(\kappa - 1)^{-(x^i+2)/2} \tag{3.7}$$

We denote the solution which satisfies (2.3), the initial condition, by $Z_t^{\mathscr{S}}(x \mid x^i; \kappa) = S_t(x \mid x^i; \kappa)$. For $1 < \kappa < 2$, to find $S_t(x \mid x^i; \kappa)$ for $t > 0$ we need to evaluate the integral in (3.4) by a different means. First, make the change in variable to $z = \exp(ik)$, then expand the denominator of the $\mathscr{S}$ amplitude to give

$$\begin{aligned} S_t(x \mid x^i; \kappa) = {} & \frac{1}{2\pi i} \oint_{|z|=1} \Bigg[\Lambda^t (z^{x-x^i} - z^{x+x^i}) - (1 - 1/z^2) \\ & \times \sum_{m=1}^{t} (\kappa z)^m \Lambda^{t-m} z^{x+x^i} \Bigg] \frac{dz}{z} \\ & + \frac{\kappa}{2\pi i} \oint_{|z|=1} \frac{(\kappa z)^t (z - 1/z)}{\Lambda - \kappa z} z^{x+x^i} \frac{dz}{z} \end{aligned} \tag{3.8}$$

Now, using the result $\oint_{|z|=1} z^M \, dz/z = 2\pi i \, \delta(M, 0)$, with M an integer, as well as the fact that the last term vanishes, gives

$$S_t(x \mid x^i; \kappa) = S_t^{(0)}(x \mid x^i) + S_t^{(1)}(x \mid x^i; \kappa) \tag{3.9}$$

where

$$S_t^{(0)}(x \mid x^i) = \binom{t}{(t - x + x^i)/2} - \binom{t}{(t - x - x^i)/2} \tag{3.10}$$

and

$$S_t^{(1)}(x \mid x^i; \kappa) = \sum_{m \geqslant 1} \kappa^m \left\{ \binom{t-m}{(t + x + x^i - 2)/2} - \binom{t-m}{(t + x + x^i)/2} \right\} \tag{3.11}$$

Since the binomial coefficients vanish outside their natural domain of definition $S_t(x \mid x^i; \kappa)$ is, as expected, a polynomial in κ. Also note that $t \pm x^i \pm x^f$ is always even due to the formulation of the problem we have chosen. Now, since $S_t^{(0)}(x^f \mid x^i)$ is simply the $\kappa = 0$ value of $S_t(x^f \mid x^i; \kappa)$ it is therefore the number of walks which avoid the wall. Hence we can also interpret $S_t^{(1)}(x^f \mid x^i; \kappa)$ as the partition function for walks which touch the wall at least once. These equations correctly reproduce the $t \leqslant 10$ polynomials given in Appendix B so that although they were derived for $1 < \kappa < 2$ they are therefore valid for all κ. Note that equation (3.10) follows from the well-known reflection principle.[15]

In conclusion, our solution is

$$Z_t^{\mathscr{S}}(x^f \mid x^i; \kappa) = S_t(x^f \mid x^i; \kappa) \tag{3.12}$$

where $S_t(x^f \mid x^i; \kappa)$ is given in equations (3.9), (3.10) and (3.11).

3.1.2. The Constant Term Formulation. We illustrate the method for a single chain. The action of the integral in (3.8) is formally equivalent to extracting the constant term of the integrand in (3.4). If $z := \exp(ik)$ is regarded as a formal variable then

$$Z_t^{\mathscr{S}}(x^f \mid x^i; \kappa) = S_t(x^f \mid x^i; \kappa) = \mathrm{CT}[(z+\bar{z})^t (z^{x^f - x^i} + \mathscr{S}(z)\, z^{x^f + x^i})] \tag{3.13}$$

where $\mathrm{CT}[\,\cdot\,]$ denotes the constant term of the argument, i.e., the coefficient of z^0. Separating the parts which correspond to walks which touch the wall, and those that do not, gives the $\kappa = 0$ term as

$$S_t^{(0)}(x^f \mid x^i) = \mathrm{CT}[(z+\bar{z})^t (z^{x^f - x^i} - z^{x^f + x^i})] \tag{3.14}$$

and the complement as

$$S_t^{(1)}(x^f \mid x^i; \kappa) = \kappa \mathrm{CT}[(z+\bar{z})^t D(z)\, z^{x^f + x^i}] \tag{3.15}$$

where

$$D(z) = \kappa^{-1}(1 + \mathscr{S}(z)) = \frac{1 - z^2}{1 - (\kappa - 1)\, z^2} \tag{3.16}$$

When $\kappa = 2$, $D(z) = 1$ and we obtain the simple form

$$S_t^{(1)}(x^f \mid x^i; \kappa = 2) = 2 \binom{t}{(t - x^f - x^i)/2} \tag{3.17}$$

This result has an interesting combinatorial interpretation—see Section 3.4. For future reference we note from (3.15) that $S^{(1)}(x^f \mid x^i; \kappa)$ depends on x^i and x^f only through their sum $(x^f + x^i)$, so that

$$S_t^{(1)}(x^f \mid x^i; \kappa) = S_t^{(1)}(x^f + x^i \mid 0; \kappa) \tag{3.18}$$

3.1.3. Formulae for Walks Beginning on the Surface. Interesting and convenient formulae can be obtained for the special cases where walks begin at the surface, that is $x^i = 0$. Let us define

$$U_t(x^f; \bar{\kappa}) := S_t^{(1)}(x^f \mid 0; \bar{\kappa} + 1)/(\bar{\kappa} + 1) = Z_t^{\mathscr{S}}(x^f \mid 0; \kappa)/\kappa \tag{3.19}$$

which is proportional to the partition function for walks that finish at x^f after beginning at 0 (by definition this implies that the walks touch the surface), where

$$\bar{\kappa} = \kappa - 1 \tag{3.20}$$

Using (3.15) we have

$$U_t(x; \bar{\kappa}) = \mathrm{CT}\left[(z+\bar{z})^t \frac{1-z^2}{1-\bar{\kappa}z^2} z^x \right] \tag{3.21}$$

Expanding the denominator in (3.21) gives

$$U_t(x; \bar{\kappa}) = \sum_{m=0}^{(1/2)(t-x)} \bar{\kappa}^m \, \mathrm{CT}[(z+\bar{z})^t (1-z^2) z^{2m+x}] \tag{3.22}$$

However we note

$$\begin{aligned} U_t(x; 0) &= \mathrm{CT}[(z+\bar{z})^t (1-z^2) z^x] \\ &= \binom{t}{(t-x)/2} - \binom{t}{(t-x-2)/2} = \frac{2(1+x)}{t+x+2} \binom{t}{(t-x)/2} \end{aligned} \tag{3.23}$$

so that we can identify the coefficient

$$\mathrm{CT}[(z+\bar{z})^t (z-z^2) z^{2m+x}] \tag{3.24}$$

of $\bar{\kappa}^m$ in the expansion (3.22) of $U_t(x; \bar{\kappa})$ as $U_t(x+2m; 0)$. Hence we can write

$$U_t(x; \bar{\kappa}) = \sum_{m=0}^{(1/2)(t-x)} \bar{\kappa}^m U_t(x+2m; 0) \tag{3.25}$$

The fact that the expansion of $U_t(x; \bar{\kappa})$ in the variable $\bar{\kappa}$ has as its coefficients positive numbers suggests they have a combinatorial interpretation. Indeed they can be interpreted in terms of "terraced walks".[16]

We will use the function $U_t(x; \bar{\kappa})$ as the basis for our analysis of the behaviour of $\hat{Z}^{\mathscr{S}}_{2r}(\kappa)$, the partition function for walks that begin and end on the surface. We have from (3.19),

$$\hat{Z}^{\mathscr{S}}_{2r}(\kappa) = Z^{\mathscr{S}}_{2r}(0 \mid 0; \kappa) = \kappa U_{2r}(0; \kappa - 1) = \kappa \sum_{m=0}^{r} (\kappa - 1)^m \, U_{2r}(2m; 0) \tag{3.26}$$

with

$$U_{2r}(2m;\,0) = \frac{1+2m}{r+m+1}\binom{2r}{r-m} \tag{3.27}$$

For $\dot{Z}_t^{\mathscr{S}}(\kappa)$, the partition function for walks that start on the surface with the other end free (i.e. summed over), we have

$$\dot{Z}_t^{\mathscr{S}}(\kappa) = \sum_{x^f \geqslant 0} Z_t^{\mathscr{S}}(x^f \mid 0;\,\kappa) = \kappa \sum_{x^f \geqslant 0} U_t(x^f;\,\kappa - 1) \tag{3.28}$$

3.2. Single Chain with Both Ends Fixed, One End on the Surface: Recurrence Relations and Critical Exponents

From inspection of (3.26) and (3.27) we see that $U_t(0;\,\bar{\kappa})$ is a sum of hypergeometric terms and the same can be seen for the more general $U_t(x;\,\bar{\kappa})$ by inspecting the combination of (3.25) with (3.23). Using Zeilberger's algorithm(7) $U_t(x;\,\bar{\kappa})$ is found, for $t \geqslant x$, to satisfy the recurrence relation

$$(\kappa - 1)\,U_t(x;\,\bar{\kappa}) - \kappa^2 U_{t-2}(x;\,\bar{\kappa}) = -A_t(x;\,\bar{\kappa}) \tag{3.29}$$

where

$$A_t(x;\,\bar{\kappa}) = U_{t-2}(x;\,0)\,\frac{q_t(x;\,\bar{\kappa})}{q_t(x;\,0)} = \frac{(t-2)!\;q_t(x;\,\bar{\kappa})}{2\left(\dfrac{t-x}{2}\right)!\left(\dfrac{t+x}{2}\right)!} \tag{3.30}$$

with

$$q_t(x;\,\bar{\kappa}) = (x+1)(t-x) - \bar{\kappa}(x-1)(t+x) \tag{3.31}$$

and $U_t(t;\,\bar{\kappa}) = 1$. Equation (3.29) has a direct combinatorial derivation.(16) In Appendix A we show that the equation

$$u_r - G(r)\,u_{r-1} = H(r) \tag{3.32}$$

has two solutions with the asymptotic form

$$u_r \sim \rho^r r^g \tag{3.33}$$

where the constant ρ may take values ρ_1 and ρ_2 with corresponding exponents g' and g'' obtained from the expansions

$$G(r) \sim \rho_1 \left(1 + \frac{g'}{r} + \frac{h_1}{r^2} + \cdots\right) \quad \text{and} \quad H(r)/H(r-1) \sim \rho_2 \left(1 + \frac{g''}{r} + \frac{h''}{r^2} \cdots\right) \tag{3.34}$$

In the case that $\rho_1 = \rho_2$ it is shown that the critical exponent may take values g' or $g'' + 1$ normally depending on which of these values is greater. Now

$$\frac{A_t(x; \bar{\kappa})}{A_{t-2}(x; \bar{\kappa})} = \frac{4(t-2)(t-3)\, q_t(x; \bar{\kappa})}{(t-x)(t+x)\, q_{t-2}(x; \bar{\kappa})} \tag{3.35}$$

and

$$\frac{q_{2r}(x; \bar{\kappa})}{q_{2r-2}(x; \bar{\kappa})} \sim 1 + \frac{1}{r} + O\left(\frac{1}{r^2}\right) \tag{3.36}$$

Since $H(r) = A_{2r}(x; \bar{\kappa})/(\kappa - 1)$ we find

$$\frac{H(r)}{H(r-1)} \sim 4\left(1 + \frac{3}{2r} + O\left(\frac{1}{r^2}\right)\right) \tag{3.37}$$

It is interesting to note that to order $1/r$ the coefficients are independent of κ and x as expected from universality but the order $1/r^2$ term is a rational function of both of these variables. This will also be true of all subsequent recurrence relations to be considered. Setting $u_r = U_{2r}(x; \bar{\kappa})$ or $U_{2r+1}(x; \bar{\kappa})$, depending on whether x is even or odd, gives $G(r) = \kappa^2/(\kappa - 1)$ and the critical parameters are therefore $\rho_1 = \kappa^2/(\kappa - 1)$, $\rho_2 = 4$, $g' = 0$ and $g'' = -\frac{3}{2}$. The value ρ_1 in the regime $\kappa > 1$ is convex having its minimum value 4 when $\kappa = 2$. For $\kappa < 2$, ρ_1 is decreasing and since from its definition the partition function increases with κ the asymptotic behavior must be governed by the bulk value $\rho = \rho_2 = 4$ which is the same as when no wall is present and the restriction to $x \geqslant 0$ just changes the exponent g from $-\frac{1}{2}$ for a free walk fixed at both ends to $-\frac{3}{2}$ in agreement with Forrester's formula (1.10) with $p = 1$. For $\kappa > 2$, ρ_1 is an increasing function of κ and $\rho = \rho_1 = \kappa^2/(\kappa - 1)$ determines the asymptotic form with exponent $g = 0$ corresponding to a bound phase in which the walk sticks close to the wall. The critical value $\kappa = 2$ at which this binding transition takes place corresponds to the second pole moving inside the contour in the integral formulation of the

Table II. Summary of the Growth Parameter and Critical Exponents for a Single Walk Grafted to a Surface at One (Subscript 1) or Both (Subscript 11) Ends.[a]

	μ	g_{11}	g_1	h_{11}	h_1
$\kappa<2$	2	$-\frac{3}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$
$\kappa=2$	2	$-\frac{1}{2}$	0	0	$\frac{1}{2}$
$\kappa>2$	$\kappa/\sqrt{\kappa-1}$	0	0	1	1

[a] The g exponents are associated with the partition function and the h exponents with the first moment of the distribution of the number of contacts.

previous section. When $\kappa=2$ the relation (3.29) has a particular solution satisfying

$$U_t(x;\,1)=\frac{4t(t-1)}{t^2-x^2}\,U_{t-2}(x;\,1) \tag{3.38}$$

with together with $U_x(x;\,\bar{\kappa})=1$ gives another route to (3.17). The solution $U_t=2^t$ of the homogeneous equation is therefore not required in this case. From (3.38) it follows that the critical exponent is $g=-\frac{1}{2}$ which is equal to $g''+1$. This is an expection to the rule found in Appendix 1 since the solution having the more dominant exponent $g'=0$ does not contribute. The other special case is $\kappa=1$. In this case equation (3.29) gives the explicit formula $U_t(x;\,1)=-A_{t+2}(x;\,1)$ having the bulk critical point and exponent. The exponents are summarised in Table II in the column headed g_{11}.

3.3. Single Chain: One End Free

We now consider the partition function

$$\tilde{Z}_t^{\mathscr{S}}(x^i;\,\kappa)=\sum_{x^f\geqslant 0} Z^{\mathscr{S}}(x^f\mid x^i;\,\kappa) \tag{3.39}$$

for walks of length t with the beginning fixed at distance x^i from the wall and the other end free to be at any value of $x^f\geqslant 0$. The usual "free end" partition function $\dot{Z}_{2r}^{\mathscr{S}}(\kappa)=\tilde{Z}_{2r}^{\mathscr{S}}(0;\,\kappa)$ is simply a sub-case. Now using (3.9) we can write

$$\tilde{Z}_t^{\mathscr{S}}(x^i;\,\kappa)=\tilde{S}_t^{(0)}(x^i)+\tilde{S}_t^{(1)}(x^i;\,\kappa) \tag{3.40}$$

where

$$\tilde{S}_t^{(0)}(x^i) = \sum_{x^f \geqslant 0} S_t^{(0)}(x^f \mid x^i) \tag{3.41}$$

and

$$\tilde{S}_t^{(1)}(x^i; \kappa) = \sum_{x^f \geqslant 0} S_t^{(1)}(x^f \mid x^i; \kappa) \tag{3.42}$$

Note that firstly

$$\tilde{S}_t^{(0)}(0) = 0 \tag{3.43}$$

and that further for $x^i > 0$ the asymptotic form of $\tilde{S}_t^{(0)}(x^i)$, which is the $\kappa = 0$ solution, as $t \to \infty$ is either sub-dominant (for $\kappa > 2$) or co-dominant (for $\kappa \leqslant 2$) to $\tilde{S}_t^{(1)}(x^i; \kappa)$. Hence we shall examine $\tilde{S}_t^{(1)}(x^i; \kappa)$ more closely.

Let us choose $x^i = 2y$ to be even and $t = 2r$ also to be even. Summing (3.18) over (even) $x^f = 2\ell$ and using (3.25) with definition (3.19) gives, using $r - y = q$,

$$\tilde{S}_{2r}^{(1)}(2y; \bar{\kappa}) = (\bar{\kappa} + 1) \sum_{m=0}^{q} \bar{\kappa}^m \sum_{\ell=0}^{q-m} U_t(2y + 2\ell + 2m; 0) \tag{3.44}$$

and using (3.23) we find that the inner sum telescopes to give

$$\tilde{S}_{2r}^{(1)}(2y; \bar{\kappa}) = (\bar{\kappa} + 1) \sum_{m=0}^{r-y} \bar{\kappa}^m \binom{2r}{r - y - m} \tag{3.45}$$

Application of Zeilberger's algorithm gives the same recurrence relation (3.29) as when both ends are fixed with $A_t(x; \kappa)$ replaced by

$$B_{2r}(2y, \bar{\kappa}) = (\bar{\kappa} + 1) \frac{(2r-2)!\, q_{2r}(2y; \bar{\kappa})}{2(r-y)!\, (r+y-1)!} \tag{3.46}$$

with $q_{2r}(2y; \bar{\kappa})$ given by

$$q_{2r}(2y; \bar{\kappa}) = 2[r - y - \bar{\kappa}(r + y - 1)] \tag{3.47}$$

and $\tilde{S}_{2r}^{(1)}(2r; \bar{\kappa}) = 1 + \bar{\kappa}$. The asymptotic form of $q_{2r}(2y; \bar{\kappa})$ is again given by (3.36) but now

$$\frac{B_{2r}(2y; \bar{\kappa})}{B_{2r-2}(2y; \kappa)} = \frac{2(r-1)(2r-3)\, q_{2r}(2y; \bar{\kappa})}{(r-y)(r+y-1)\, q_{2r-2}(2y; \bar{\kappa})} \tag{3.48}$$

The discussion of the previous section therefore applies to $\tilde{S}_{2r}^{(1)}(2y; \bar{\kappa})$ except that now $g'' = -\frac{1}{2}$ in agreement with the value obtained by setting $p = 1$ in the formula (1.10) for g_1. Comparing (3.35) and (3.48) we notice that when $\kappa = 2$ and $x^i = y = 0$ the recurrence relation becomes the same as for the chain with both ends attached to the wall but now the partition function is a linear combination of both solutions. To satisfy the initial conditions each of the two solutions has $U_0(0; \bar{\kappa}) = 1$ and the partition function is sum of the resulting functions

$$\tilde{S}_{2r}^{(1)}(0; \bar{\kappa} = 1) = 2^{2r} + \binom{2r}{r} \tag{3.49}$$

The critical exponent is therefore $g = 0$ since the bulk solution 2^{2r} is dominant. The exponents are summarised in Table II in the column headed g_1.

A simpler recurrence relation results if both x^i and t are allowed to vary with $q = (t - x^i)/2$ fixed: now allowing t and x^i to be either both odd or both even, which implies that x^f is still even.

$$\begin{aligned} \bar{\kappa}\tilde{S}_t^{(1)}(x^i; \bar{\kappa}) - (1 + \bar{\kappa})\, \tilde{S}_{t-1}^{(1)}(x^i - 1; \bar{\kappa}) &= -\tilde{S}_{t-1}^{(1)}(x^i - 1; 0) \\ &= -(1 + \bar{\kappa}) \binom{t-1}{(t - x^i)/2} \end{aligned} \tag{3.50}$$

with the boundary condition $\tilde{S}_t^{(1)}(-t; \bar{\kappa}) = (1 + \bar{\kappa})^{t+1}$. However this relation cannot yield the required asymptotic form for $t \to \infty$ with x^i fixed.

3.4. Single Chain: A Combinatorial Interpretation of $\kappa = 2$

Let $\mathscr{W}_t^{(1)}(x^i, x^f)$ be the set of all walks, from x^i to x^f, having t steps, which do not cross the wall, but have at least one contact with the wall. The contribution of such walks to the partition function is

$$S_t^{(1)}(x^f \mid x^i; \kappa) = \kappa \sum_{w \in \mathscr{W}_t^{(1)}(x^i, x^f)} \kappa^c \tag{3.51}$$

where c is the number of contacts of the walk w with the wall other than the last. When $\kappa = 2$ each contact with the wall contributes a factor of two to the weight of the walk. Thus a given walk with $c + 1$ contacts will contribute 2^c to the sum. Instead of considering the given walk as contributing a weight 2^c one can think of this as 2^c walks each contributing weight one. How are these 2^c new walks constructed? For each contact, other than the last, there is a factor of two, we can get two walks by counting the original configuration as well as the walk obtained by reflecting the segment of the

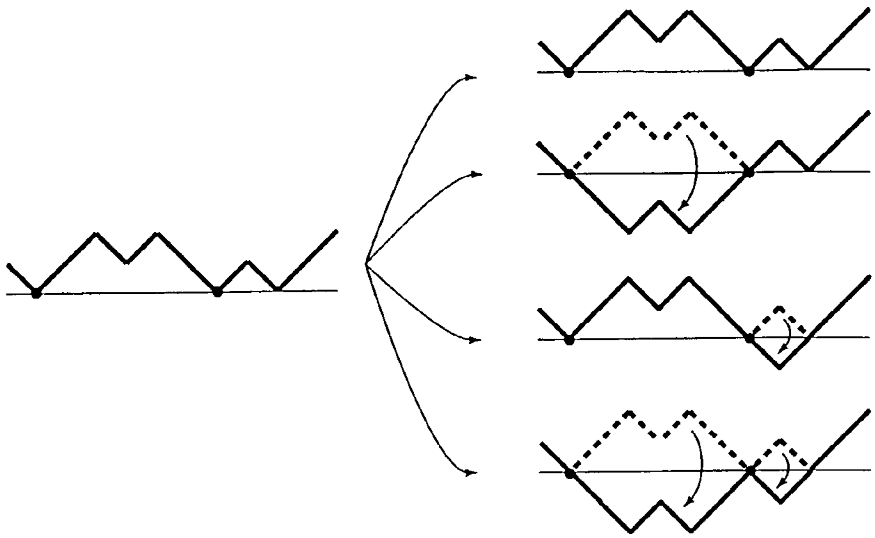

Fig. 3. The figure shows an example of one configuration of weight 2^2 and the corresponding set of 4 walks, each of weight one, obtained by reflecting segments of the walk between surface contacts.

walk between the contact and the next one to the right in the t-axis. This is easiest to explain by illustration—see Fig. 3. If this reflection procedure is carried out for each subset of the wall contacts (excluding the last), then the resulting set of walk configurations is the set of all walks from $x^i \to x^f$ with *no* wall but which visit $x = 0$ at least once. The number of such walks is equal to the number of walks from $-x^i$ to x^f and hence we obtain (3.17). The $\kappa = 2$ partition function for a chain which starts at $x^i = 0$ and ends at any $x^f \geqslant 0$ has a similar interpretation. For a configuration which ends at $x^f > 0$ the last κ factor may be replaced by reflecting the part of the chain between the last contact and the terminal monomer. Configurations which terminate at the wall have an additional factor of κ which will not be included by the reflection procedure. The partition function is therefore the sum of the number of chains with one free end and no wall, i.e., 2^t, and the number of chains which start and end at $x^i = 0$ with no wall, i.e., $\binom{t}{t/2}$, which gives (3.49).

Physically we can interpret these results as corresponding to the wall becoming completely transparent. This is somewhat analogous to what happens at the theta point of interacting self-avoiding walks in three dimensions were the self-avoiding walk behaves rather like a random walk.[17] Intriguingly, this value, $\kappa = 2$ is also weight generated by the appropriate kinetic growth walk near a surface.[18]

An alternative combinatorial interpretation of the $\kappa = 2$ partition function when one end is grafted to the wall follows by setting $\bar{\kappa} = 1$ in (3.25). The left hand side is the required partition function giving weight one to the grafted monomer. The right hand side is the total number of t step walks which start at distance x^i and end anywhere on or above the wall, visiting the wall at least once.

3.5. Single Chain: The Mean Number of Contacts

The mean number of contacts for a vesicle was defined in the introduction as the ratio of $M_t^{\mathscr{V}}(x^f \mid 0; \kappa)$, given by equation (1.13), to the partition function. A similar definition holds for a single chain.

3.5.1. Mean Contact Number of a Single Chain: Both Ends Fixed to the Surface. When both ends are fixed $M_t^{\mathscr{S}}(x^f \mid 0; \kappa)$ is obtained (noting (3.19)) by differentiating (3.25) with respect to $\bar{\kappa}$ and multiplying by κ. We have done this for general x^f but only give the results for $x^f = x = 0$ since the exponents turn out to be independent of x^f as expected:

$$\bar{\kappa}(\kappa + (r-1)(\kappa-2)^2)\, \hat{M}_{2r}^{\mathscr{S}}(\kappa) - \kappa^2(\kappa + r(\kappa-2)^2)\, \hat{M}_{2r-2}^{\mathscr{S}}(\kappa)$$
$$= -\kappa(-3 + \bar{\kappa} + 3r - 2\bar{\kappa}r - \bar{\kappa}^2 r)(2r-2)!/r!\,(r-1)! \qquad (3.52)$$

The values of the critical exponent h_{11} of M_t which follow from this recurrence relation are listed in Table II. The expected number of contacts has critical exponent $\hat{\Delta}_s = h_{11} - g_{11}$.

3.5.2. Mean Contact Number of a Single Chain: One End Free. The function $\tilde{M}_t^{\mathscr{S}}(x^i; \kappa)$ for a chain with one end fixed at x^i, that ends anywhere above or on the wall, is given by differentiating the summand in (3.45) with respect to $\bar{\kappa}$ and multiplying by κ. Note that $\tilde{S}_t^{(0)}(x^i)$ does not depend on κ. With $t = 2r$ and $x^i = 2y$, applying Zeilberger's algorithm to the sum gives the recurrence relation

$$\bar{\kappa}(\kappa y - (r-1)(\kappa-2))\, \tilde{M}_{2r}^{\mathscr{S}}(2y; \kappa) - \kappa^2(\kappa y - r(\kappa-2))\, M_{2r-2}(2y; \kappa)$$
$$= \kappa^2 \binom{2r-2}{r-y-1} (\kappa y + (r-1)(\kappa-2)) \qquad (3.53)$$

When $\kappa = 2$ this reduces to

$$\tilde{M}_{2r}^{\mathscr{S}}(2y; 2) - 4\tilde{M}_{2r-2}^{\mathscr{S}}(2y; 2) = 4\binom{2r-2}{r-y-1} \qquad (3.54)$$

and if further $y=0$ we obtain the explicit form

$$\tilde{M}_{2r}^{\mathscr{S}}(0;2)=4r\binom{2r-1}{r} \tag{3.55}$$

Proceeding as in the case of the partition function we find for $x^i=0$, with $\acute{M}_t^{\mathscr{S}}(\kappa)=\tilde{M}_t^{\mathscr{S}}(0;\kappa)$,

$$\acute{M}_t^{\mathscr{S}}\sim\mu^t t^{h_1} \tag{3.56}$$

where the values of h_1 are given in Table II. The expected number of contacts has critical exponent $\acute{\Delta}_s=h_1-g_1$, and satisfies $\acute{\Delta}_s=\hat{\Delta}_s\equiv\Delta_s$. This adsorption exponent also has the same value as for the equivalent exponent in the case of vesicles (see Table I), as expected.

3.6. Single Chain Scaling Form Near $\kappa=2$

In the case of even $t=2r$ and $x^f=2y$ we consider $U_{2r}(2y;\bar{\kappa})$ and the solution of (3.29) subject to $U_{2r}(2r;\bar{\kappa})=1$ may then be written in the form

$$U_{2r}(2y;\bar{\kappa})=\omega^{y-r}\left(1-\frac{1}{\bar{\kappa}}\sum_{s=y+1}^{r}A_{2s}(2y;\bar{\kappa})\,\omega^{s-y}\right) \tag{3.57}$$

where $\omega=\bar{\kappa}/(\bar{\kappa}+1)^2=(\kappa-1)/\kappa^2$. Noting that

$$Z_{2r}^{\mathscr{S}}(2y\,|\,0;\kappa)=\kappa U_{2r}(2y;\bar{\kappa}) \tag{3.58}$$

we can analyse the scaling behavior of $\acute{Z}_{2r}^{\mathscr{S}}$ and $\hat{Z}_{2r}^{\mathscr{S}}$ via (3.28) and (3.26) respectively.

3.6.1. Single Chain Scaling Form: Both Ends Fixed to the Surface. Setting $x=0$ in (3.30) gives $A_{2r}(0;\bar{\kappa})=\kappa C_{r-1}$ and hence the partition function for chains with both ends grafted to the surface is given by

$$\hat{Z}_{2r}^{\mathscr{S}}(\kappa)=\kappa\omega^{-r}\left(1-\frac{1}{\kappa}\sum_{s=0}^{r-1}C_s\omega^s\right) \tag{3.59}$$

Now for $\kappa>1$ (that is, $0\leqslant\omega\leqslant\frac{1}{4}$) ω as a function of κ passes through a maximum at $\kappa=2$ which is the value at which the polymer first sticks to the wall. It is a property of the Catalan numbers that for $|\omega|\leqslant\frac{1}{4}$

$$\sum_{s=0}^{\infty}C_s\omega^s=\frac{1-\sqrt{1-4\omega}}{2\omega}=\frac{\kappa(\kappa-|\kappa-2|)}{2\bar{\kappa}} \tag{3.60}$$

and hence

$$\hat{Z}^{\mathscr{S}}_{2r}(\kappa)=\frac{\kappa(\kappa-2)}{\bar{\kappa}}\,\omega^{-r}\theta(\kappa-2)+\sum_{s=r}^{\infty} C_s\omega^{s-r} \tag{3.61}$$

The Catalan numbers have asymptotic form

$$C_s\sim\frac{4^s}{\pi^{1/2}s^{3/2}} \qquad \text{as} \quad s\to\infty \tag{3.62}$$

which on substitution in (3.61), replacing the sum by an integral gives

$$\hat{Z}^{\mathscr{S}}_{2r}(\kappa)\sim\frac{\kappa(\kappa-2)}{\bar{\kappa}}\,\omega^{-r}\theta(\kappa-2)+\frac{4^r}{\sqrt{\pi r}}\,\chi\left(r\log\left(\frac{1}{4\omega}\right),\frac{3}{2}\right) \tag{3.63}$$

where

$$\chi(y,n)=\int_1^{\infty}\frac{e^{-y(u-1)}}{u^n}\,du \tag{3.64}$$

As $\kappa\to 2$, $\log(1/4\omega)\approx\frac{1}{4}(\kappa-2)^2$ and hence near the binding transition ($\kappa\to 2$ and $t\to\infty$) the partition function has the scaling form

$$\hat{Z}^{\mathscr{S}}_{2r}(\kappa)\approx\frac{4^r}{r^{1/2}}\,\hat{\varphi}^{\mathscr{S}}\left(\frac{(\kappa-2)}{2}\,r^{1/2}\right) \tag{3.65}$$

where

$$\hat{\varphi}^{\mathscr{S}}(z)=\frac{1}{\sqrt{\pi}}\,\chi(z^2,\tfrac{3}{2})+\theta(z)\,ze^{z^2} \tag{3.66}$$

Integration by parts gives

$$\chi(z^2,\tfrac{3}{2})=2-2z^2\chi(z^2,\tfrac{1}{2}) \tag{3.67}$$

and for $z\leqslant 0$ the substitution $u^{1/2}=-v/z$ in the definition of $\chi(z^2,\frac{1}{2})$ gives

$$\begin{aligned}\hat{\varphi}^{\mathscr{S}}(z)&=\frac{2}{\sqrt{\pi}}+2ze^{z^2}\,\frac{2}{\sqrt{\pi}}\int_{-z}^{\infty}e^{-v^2}\,dv\\&=\frac{2}{\sqrt{\pi}}+2ze^{z^2}\,\mathrm{erfc}(-z)\end{aligned} \tag{3.68}$$

This form of $\hat{\varphi}^{\mathscr{S}}(z)$ also gives the $z>0$ branch correctly. Note that $\hat{\varphi}^{\mathscr{S}}(z)$ is analytic for all z as expected.

Now $\operatorname{erfc}(-\infty)=2$, $\operatorname{erfc}(0)=1$ and (see [19]) for $z\to\infty$

$$\sqrt{\pi}\, z e^{z^2} \operatorname{erfc}(z) = 1 - \frac{1}{2z^2} + \frac{3}{4z^4} - \frac{15}{8z^6} + O\left(\frac{1}{z^4}\right) \tag{3.69}$$

thus

$$\hat{\varphi}^{\mathscr{S}}(z) \sim \begin{cases} \dfrac{1}{\sqrt{\pi}\, z^2} & \text{for} \quad z\to-\infty \\ \dfrac{2}{\sqrt{\pi}} + 2z & \text{for} \quad z\to 0 \\ 4ze^{z^2} & \text{for} \quad z\to\infty \end{cases} \tag{3.70}$$

which gives values of g_{11} and μ in agreement with Table II.

3.6.2. Single Chain Scaling Form: One Free End. In the case of chains of length $2r$ which terminate at any even value of $x^f = 2\ell \geqslant 0$, if the initial monomer is grafted to the surface then setting $x^i=0$ in (3.46) given $B_{2r}(0;\bar{\kappa}) = (\bar{\kappa} - r(\bar{\kappa}-1))\, C_{r-1}$. Substituting in (3.57) gives

$$\acute{Z}^{\mathscr{S}}_{2r}(\kappa) = \kappa\omega^{-r}\left(1 - \frac{1}{\bar{\kappa}}\sum_{s=0}^{r-1} C_s(1-(\kappa-2)\,s)\,\omega^{s+1}\right) \tag{3.71}$$

and using (3.60)

$$\acute{Z}^{\mathscr{S}}_{2r}(\kappa) = \kappa\omega^{-r}\theta\,(\kappa-2) + \frac{1}{\kappa}\sum_{s=r}^{\infty} C_s(1-(\kappa-2)\,s)\,\omega^{s-r} \tag{3.72}$$

where the step function is defined such that $\theta(0)=1$. Proceeding as in the previous section we see that near the binding transition the partition function has the scaling form

$$\acute{Z}^{\mathscr{S}}_{2r}(\kappa) \approx 4^r \acute{\varphi}^{\mathscr{S}}\left(\frac{(\kappa-2)}{2}\, r^{1/2}\right) \tag{3.73}$$

where

$$\acute{\varphi}^{\mathscr{S}}(z) = \frac{-z}{\sqrt{\pi}}\,\chi\left(z^2, \frac{1}{2}\right) + 2\theta(z)\, e^{z^2} \tag{3.74}$$

$$= e^{z^2} \operatorname{erfc}(-z) \tag{3.75}$$

Using the above properties of erfc gives values of g_1 in agreement with Table II.

Equations (3.68) and (3.75) agree with those obtained for a continuous chain interacting with a wall by Eisenreigler *et al.*[5] as one would expect from universality considerations. The form (3.75) is also identical to that calculated for the partially-directed partition function scaling form[20] derived using the theorem of Brak and Owczarek in [14]. This then serves as another example of the scope of this theorem.

4. VESICLES NEAR AN ATTRACTIVE WALL

4.1. Constant Term Formula for the Two Chain Partition Function.

We now derive a constant term formula for the partition function of two chains. The formula will "automatically" produce both the method of images involution and the Gessel–Viennot involution for non-intersecting chains.[21] We must solve equations (2.5) to (2.7), to do this we try the Ansatz

$$Z_t^{\mathscr{T}}(\mathbf{x} \mid \mathbf{x}^i; \kappa) = Q_t(\mathbf{x}; \kappa) = \Lambda(k_1, k_2)^t \sum_{\varepsilon_1 = \pm 1} \sum_{\varepsilon_2 = \pm 1} \sum_{\sigma \in P_2} A_{(\varepsilon_1, \varepsilon_2)}^{(\sigma_1, \sigma_2)} \times \exp(i\varepsilon_{\sigma_1} k_1 x_1 + i\varepsilon_{\sigma_2} k_2 x_2) \tag{4.1}$$

where $\sigma = (\sigma_1, \sigma_2)$, and $P_2 = \{(1, 2), (2, 1)\}$ (we use the vector notation $\mathbf{x} = (x_1, x_2)$). This satisfies (2.5) if

$$\Lambda(k_1, k_2) = \lambda_1 \lambda_2, \qquad \lambda_j = \exp(ik_j) + \exp(-ik_j) \tag{4.2}$$

Equation (2.6) is satisfied provided

$$\frac{A_{(\varepsilon_1, \varepsilon_2)}^{(1, 2)}}{A_{(\varepsilon_1, \varepsilon_2)}^{(2, 1)}} = -1 \tag{4.3}$$

$$\frac{A_{(+, \varepsilon_2)}^{(1, 2)}}{A_{(-, \varepsilon_2)}^{(1, 2)}} = \mathscr{S}(\exp(ik_1)) \tag{4.4}$$

$$\frac{A_{(\varepsilon_1, +)}^{(2, 1)}}{A_{(\varepsilon_1, -)}^{(2, 1)}} = \mathscr{S}(\exp(ik_2)) \tag{4.5}$$

where $\mathcal{S}(z)$ is defined by (3.2). Thus we have the general solution

$$Z_t^{\mathcal{T}}(\mathbf{x} \mid \mathbf{x}^i; \kappa) = T_t(\mathbf{x}; \kappa) = \int_0^{\pi} \int_0^{\pi} \mathcal{B}(k_1, k_2)\, \Lambda(k_1, k_2)^t\, \mathcal{F}(k_1, k_2)\, dk_1\, dk_2 \tag{4.6}$$

where

$$\begin{aligned}\mathcal{F}(k_1, k_2) = {} & \exp(ik_1 x_1 + ik_2 x_2) + \mathcal{S}(\exp(ik_1)) \exp(-ik_1 x_1 + ik_2 x_2) \\ & - \exp(ik_2 x_1 + ik_1 x_2) - \mathcal{S}(\exp(ik_2)) \exp(-ik_2 x_1 + ik_1 x_2) \\ & + \mathcal{S}(\exp(ik_1))\, \mathcal{S}(\exp(ik_2)) \exp(-ik_1 x_1 - ik_2 x_2) \\ & + \mathcal{S}(\exp(ik_2)) \exp(ik_1 x_1 - ik_2 x_2) \\ & - \mathcal{S}(\exp(ik_1))\, \mathcal{S}(\exp(ik_2)) \exp(-ik_2 x_1 - ik_1 x_2) \\ & - \mathcal{S}(\exp(ik_1)) \exp(ik_2 x_1 - ik_1 x_2)\end{aligned} \tag{4.7}$$

Once again we choose $\mathcal{B}(k_1, k_2)$ as $1/2\pi$ times the complex conjugate of $\mathcal{F}(k_1, k_2)$. This gives an integrand with 64 terms. As in the case for a single chain the number of terms can be reduced, resulting in an integral over only eight terms. Thus we obtain the result

$$Z_t^{\mathcal{T}}(\mathbf{x} \mid \mathbf{x}^i; \kappa) = \mathrm{CT}[(z_1 + \bar{z}_1)^t (z_2 + \bar{z}_2)^t z_1^{x_1^f} z_2^{x_2^f} D(z_1, z_2; x_1^i, x_2^i)] \tag{4.8}$$

where

$$\begin{aligned}D(z_1, z_2; x_1^i, x_2^i) & \\ = \bar{z}_1^{x_1^i} \bar{z}_2^{x_2^i} & + \mathcal{S}(z_1)\, z_1^{x_1^i} \bar{z}_2^{x_2^i} + \mathcal{S}(z_2)\, \bar{z}_1^{x_1^i} z_2^{x_2^i} + \mathcal{S}(z_1)\, \mathcal{S}(z_2)\, z_1^{x_1^i} z_2^{x_2^i} \\ - \bar{z}_1^{x_2^i} \bar{z}_2^{x_1^i} & - \mathcal{S}(z_1)\, z_1^{x_2^i} \bar{z}_2^{x_1^i} - \mathcal{S}(z_2)\, \bar{z}_1^{x_2^i} z_2^{x_1^i} - \mathcal{S}(z_1)\, \mathcal{S}(z_2)\, z_1^{x_2^i} z_2^{x_1^i}\end{aligned} \tag{4.9}$$

and $z_j = e^{ik_j}$ with $\bar{z}_j = 1/z_j$. Each term can be interpreted diagrammatically as shown in Fig. 4. Combining the terms illustrated in the figure leads to the determinantal form

$$D(z_1, z_2; x_1^i, x_2^i) = \begin{vmatrix} \bar{z}_1^{x_1^i} + \mathcal{S}(z_1)\, z_1^{x_1^i} & \bar{z}_1^{x_2^i} + \mathcal{S}(z_1)\, z_1^{x_2^i} \\ \bar{z}_2^{x_1^i} + \mathcal{S}(z_2)\, z_2^{x_1^i} & \bar{z}_2^{x_2^i} + \mathcal{S}(z_2)\, z_2^{x_2^i} \end{vmatrix} \tag{4.10}$$

If we generate on t then, with $G^{\mathcal{T}}(\mathbf{x}^f \mid \mathbf{x}^i; u, \kappa) = \sum_{t \geqslant 0} Z_t^{\mathcal{T}}(\mathbf{x}^f \mid \mathbf{x}^i; \kappa)\, u^t$, we get

$$G^{\mathcal{T}}(\mathbf{x}^f \mid \mathbf{x}^i; u, \kappa) = \mathrm{CT} \left| z_1^{x_1^f} z_2^{x_2^f} \frac{D(z_1, z_2; x_1^i, x_2^i)}{1 - u(z_1 + \bar{z}_1)(z_2 + \bar{z}_2)} \right| \tag{4.11}$$

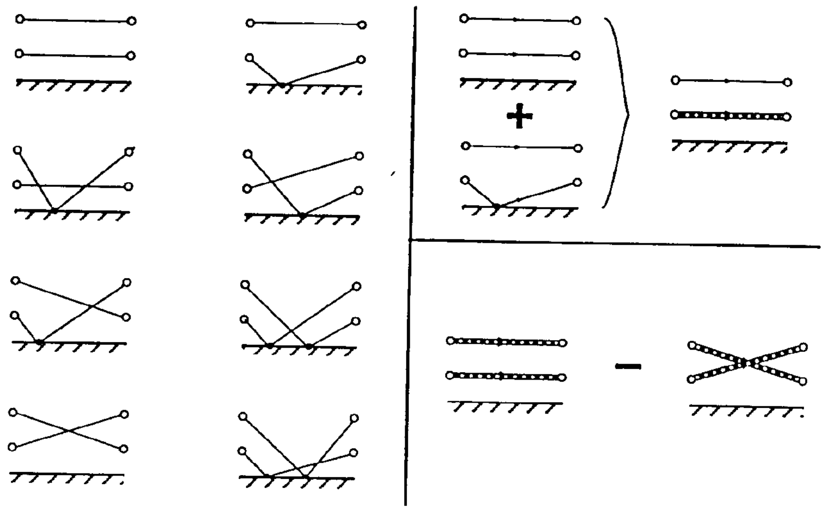

Fig. 4. (a) All eight terms of the constant term formula for vesicles—each horizontal line represents a directed walk with no constraints. (b) Pairs of terms can be combined and interpreted as one walker not going below the wall—this is the method of images involution. (c) All eight terms can be combined into two terms (of two factors each—each of which represents a walker not going below the wall)—these two terms give correspond the determinant for non-intersecting walkers.

4.2. Explicit Form of the Partition Function for Vesicles Grafted to a Wall.

As a first step of finding the partition function for vesicles with one or both ends attached to the wall we set $x_1^i = 0$ and $x_2^i = 2$ in the formulae of the previous section. The determinant in (4.10) may then be evaluated to give a simple generalisation of the constant term formula for a single chain attached to the wall. As in the case of the one chain problem we also remove a factor of κ, which is always present for vesicles attached to the wall. Defining a specialised partition function by

$$U_t(x_1^f, x_2^f; \bar{\kappa}) = \kappa^{-1} Z_t^{\mathscr{T}}(x_1^f, x_2^f \mid 0, 2; \kappa) \tag{4.12}$$

gives

$$U_t(x_1, x_2; \bar{\kappa}) = \mathrm{CT}[\Lambda_1^t \Lambda_2^t D(z_1)\, D(z_2)(z_1^2 - z_2^2)(\bar{z}_1^2 - z_2^2)\, z_1^{x_1} z_2^{x_2 - 2}] \tag{4.13}$$

where $D(z)$ is given by (3.16) and $\Lambda_i = z_i + \bar{z}_i$. Expanding the denominators in $D(z_1)$ and $D(z_2)$ shows that $U_t(x_1, x_2; \bar{\kappa})$ may be expressed in powers of $\bar{\kappa}$ with the coefficients determined by the "$\kappa = 1$" solution

$$U_t(x_1, x_2; \bar{\kappa}) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \bar{\kappa}^{m+n} U_t(x_1 + 2m, x_2 + 2n; 0) \tag{4.14}$$

For a vesicle we write $x=x_1=x_2-2$ and separating the $m=0$ term the partition function may be written in the equivalent form

$$U_t(x, x+2; \bar{\kappa}) = \sum_{n=0}^{\infty} \bar{\kappa}^n U_t(x, x+2n+2; 0)$$
$$+ \sum_{m=0}^{\infty} \sum_{n'=0}^{\infty} \bar{\kappa}^{m+n'-1} U_t(x+2m, x+2n'; 0) \tag{4.15}$$

where $U_t(x_1, x_2; \bar{\kappa})$ is defined in terms of the constant term formula (4.13).

If we formally extend the definition of $U_t(x, x+2; \bar{\kappa})$ to $x_1 > x_2$ using (4.13) then it follows that $U_t(x_1, x_2; \bar{\kappa}) = -U_t(x_2, x_1; \bar{\kappa})$. Using this shows that the second summation in (4.15) is zero and thus we obtain the final result

$$U_t(x, x+2; \bar{\kappa}) = \sum_{n=0}^{\infty} \bar{\kappa}^n U_t(x, x+2n+2; 0) \tag{4.16}$$

The general vesicle partition function is

$$Z_t^{\mathscr{V}}(x \mid y; \kappa) = Z_t^{\mathscr{T}}(x, x+2 \mid y, y+2; \kappa) \tag{4.17}$$

Hence the partition function for vesicles started at the surface and finishing at some height is

$$Z_t^{\mathscr{V}}(x \mid 0; \kappa) = Z_t^{\mathscr{T}}(x, x+2 \mid 0, 2; \kappa) = \kappa U_t(x, x+2); \bar{\kappa}) \tag{4.18}$$

Also, we have

$$\hat{Z}_t^{\mathscr{V}}(\kappa) = Z_t^{\mathscr{V}}(0 \mid 0; \kappa) = Z_t^{\mathscr{T}}(0, 2 \mid 0, 2; \kappa) = \kappa U_t(0, 2; \bar{\kappa}) \tag{4.19}$$

Further

$$\tilde{Z}_t^{\mathscr{V}}(y; \kappa) = \sum_{x \geqslant 0} Z_t^{\mathscr{V}}(x \mid y; \kappa) = \sum_{x \geqslant 0} Z_t^{\mathscr{T}}(x, x+2 \mid y, y+2; \kappa) \tag{4.20}$$

and so

$$\acute{Z}_t^{\mathscr{V}}(\kappa) = \tilde{Z}_t^{\mathscr{V}}(0; \kappa) = \sum_{x \geqslant 0} Z_t^{\mathscr{V}}(x \mid 0; \kappa)$$
$$= \sum_{x \geqslant 0} Z_t^{\mathscr{T}}(x, x+2 \mid 0, 2; \kappa)$$
$$= \kappa \sum_{x \geqslant 0} U_t(x, x+2; \bar{\kappa}) \tag{4.21}$$

Notice that the sum in (4.16) is finite since the summand vanishes for $x+2n>t$. To determine the summand in (4.16) we set $\bar{\kappa}=0$ in (4.13) to obtain the constant term form

$$U_t(x_1, x_2; 0) = \mathrm{CT}[\Lambda_1^t \Lambda_2^t (1-z_1^2)(1-z_2^2)(z_1^2 - z_2^2)(\bar{z}_1^2 - \bar{z}_2^2)\, z_1^{x_1} z_2^{x_2-2}] \tag{4.22}$$

Taking the constant term after expanding the brackets gives a sum of sixteen products of binomial coeffients which simplifies to

$$U_t(x_1, x_2; 0) = \frac{((x_2-x_1)/2)((x_1+x_2)/2+1)(x_1+1)(x_2+1)}{(t+1)(t+2)(t+3)^2} \times \binom{t+3}{(t+x_1)/2+2}\binom{t+3}{(t+x_2)/2+2} \tag{4.23}$$

which together with (4.16) gives formula (1.3) for $Z_t^{\mathscr{V}}(x \mid 0; \kappa)$. For vesicles of even length $t=2r$ ending anywhere the partition function $\dot{Z}_{2r}^{\mathscr{V}}(\kappa)$ may be found by summing (4.16) over even values of x from 0 to $2r$. With the aid of Zeilberger's algorithm this gives,

$$\dot{Z}_{2r}^{\mathscr{V}}(\kappa) = \kappa C_r \sum_{n=0}^{r} \frac{n+1}{r+1} \binom{2r+2}{r-n} \bar{\kappa}^n \tag{4.24}$$

where C_r is defined by (1.5), which is equation (1.4). Similarly, for vesicles of odd length, summing (4.16) over odd values of x from 1 to $2r+1$ gives

$$\dot{Z}_{2r+1}^{\mathscr{V}}(\kappa) = \kappa C_{r+1} \sum_{n=0}^{r} \frac{n+1}{r+1} \binom{2r+2}{r-n} \bar{\kappa}^n \tag{4.25}$$

We note that the above, together with (3.26), shows the following relations

$$\dot{Z}_{2r+1}^{\mathscr{V}}(\kappa) = \frac{C_{r+1}}{C_r} \dot{Z}_{2r}^{\mathscr{V}}(\kappa) \qquad \text{and} \qquad \dot{Z}_{2r}^{\mathscr{V}}(\kappa) = \frac{C_r}{\kappa} \hat{Z}_{2r+2}^{\mathscr{S}}(\kappa) \tag{4.26}$$

4.3. Recurrence Relations and Critical Exponents for Vesicles Grafted to a Wall.

As in the case of a single walk the critical exponents are most easily found from recurrence relations. From equations (4.16) and (4.23) we see that $U_t(x, x+2; \bar{\kappa})$ is a sum of hypergeometric terms and Zeilberger's algorithm may therefore be used to find its recurrence relation. We find

$$\bar{\kappa}(r+2)(g(\kappa)+rh(\kappa))\, U_{2r}(0,2;\kappa) \\ -2\kappa^2(2r-1)(g(\kappa)+h(\kappa)(1+r))\, U_{2r-2}(0,2;\kappa) = -\kappa B_r \tag{4.27}$$

where

$$g(\kappa)=\kappa^2+2\kappa-2, \qquad h(\kappa)=(\kappa-2)^2 \tag{4.28}$$

and

$$B_r=\frac{4(2r-1)^2}{(r+1)^2}B_{r-1}=6C_r^2, \tag{4.29}$$

with $B_0=6$ and $U_0(0,2;\kappa)=1$. This may be written in the form (1.7) quoted in the introduction. In the notation of Appendix 1,

$$G(r)=\frac{2\kappa^2(2r-1)(g(\kappa)+(r+1)\,h(\kappa))}{\bar{\kappa}(r+2)(g(\kappa)+rh(\kappa))}=\rho_1\left(1-\frac{3}{2r}+O\left(\frac{1}{r^2}\right)\right) \tag{4.30}$$

where $\rho_1=4\kappa^2/\bar{\kappa}$. The corresponding exponent $g'=-\frac{3}{2}$. Also

$$\frac{H(r)}{H(r-1)}=\frac{4(2r-1)^2\,(g(\kappa)+(r-1)\,h(\kappa))}{(r+1)(r+2)(g(\kappa)+rh(\kappa))}=16\left(1-\frac{5}{r}+O\left(\frac{1}{r^2}\right)\right) \tag{4.31}$$

so that $\rho_2=16$ and $g'=-5$. Similarly, for vesicles with one end free, we find the recurrence relation for

$$V_r(\bar{\kappa})=\acute{Z}_{2r}^{\mathscr{V}}(\bar{\kappa}+1)/[(\bar{\kappa}+1)\,C_r]=\acute{Z}_{2r+1}^{\mathscr{V}}(\bar{\kappa}+1)/[(\bar{\kappa}+1)\,C_{r+1}] \tag{4.32}$$

to be

$$\bar{\kappa}V_r(\bar{\kappa})-(1+\bar{\kappa})^2\,V_{r-1}(\bar{\kappa})=-C_r \tag{4.33}$$

and so

$$\bar{\kappa}(r+1)\,\acute{Z}_{2r}^{\mathscr{V}}(\kappa)-2(1+\bar{\kappa})^2(2r-1)\,\acute{Z}_{2r-2}^{\mathscr{V}}(\kappa)=-(\bar{\kappa}+1)\,A_r^{\text{even}} \tag{4.34}$$

Here $A_r^{\text{even}}=(r+1)\,C_r^2$ and hence

$$A_r^{\text{even}}=\frac{4(2r-1)^2}{r(r+1)}A_{r-1}^{\text{even}} \tag{4.35}$$

This result may be rearranged to give equation (1.7) with $g(\kappa)=h(\kappa)=1$. Similarly,

$$\bar{\kappa}(r+2)\,\acute{Z}^{\mathscr{V}}_{2r+1}(\kappa)-2(1+\bar{\kappa})^2\,(2r+1)\,\acute{Z}^{\mathscr{V}}_{2r-1}(\kappa)=-(\bar{\kappa}+1)\,A^{\text{odd}}_r \tag{4.36}$$

where $A^{\text{odd}}_r=(r+2)\,C_rC_{r+1}$ and hence

$$A^{\text{odd}}_r=\frac{4(2r+1)(2r-1)}{(r+1)^2}\,A^{\text{odd}}_{r-1} \tag{4.37}$$

This result is similar to but not exactly of the form (1.7). The asymptotic form of the solution in the case of vesicles of even length is determined by

$$G^{\text{even}}(r)=\frac{2\kappa^2(2r-1)}{\bar{\kappa}(r+1)}=\rho_1\left(1-\frac{3}{2r}+O\left(\frac{1}{r^2}\right)\right) \tag{4.38}$$

which is asymptotically the same as when both ends are fixed, and

$$\frac{H^{\text{even}}(r)}{H^{\text{even}}(r-1)}=\frac{4(2r-1)^2}{(r+1)^2}=16\left(1-\frac{3}{r}+O\left(\frac{1}{r^2}\right)\right) \tag{4.39}$$

so that again $\rho_2=16$ but $g''=-3$. For vesicles of odd length the relevant ratios are

$$G^{\text{odd}}(r)=\frac{2\kappa^2(2r+1)}{\bar{\kappa}(r+2)}\qquad\text{and}\qquad\frac{H^{\text{odd}}(r)}{H^{\text{odd}}(r-1)}=\frac{4(2r+1)(2r-1)}{(r+1)(r+2)} \tag{4.40}$$

which have the same asymptotic forms as in the even case. Using the same argument as for a single chain the asymptotic form of the partition functions is determined by ρ_2 for $\kappa>2$ and ρ_1 for $\kappa>2$ so that again the binding transition is at $\kappa=2$. In the case $\kappa<2$ the exponents agree with the $\kappa=1$ result of equation (1.10).

When $\kappa=2$ and $x^f=0$, that is we try a solution for $\hat{Z}^{\mathscr{V}}_{2r}(2)=2u_r$, the solutions of the inhomogeneous and homogeneous equations may be seen to satisfy the relations

$$u^{(1)}_r=\frac{4(2r-1)(2r+1)}{(r+1)(r+2)}\,u^{(1)}_{r-1}\qquad\text{and}\qquad u^{(2)}_r=\frac{8(2r-1)}{(r+2)}\,u^{(2)}_{r-1} \tag{4.41}$$

respectively. Only the first of these solutions is required to match the coefficients and has $\rho=16$ and $g=-3$ which is not equal to $g''+1$ due to the vanishing of $h(\kappa)$ at the transition point. Similarly for vesicles with one end free and $\kappa = 2$, that is, we try a solution for $\acute{Z}_{2r}^{\mathscr{V}}(2) = 2v_r$, the coefficients are generated by the first of the two solutions satisfying the relations

$$v_r^{(1)} = \frac{4(2r-1)(2r+1)}{(r+1)^2} v_{r-1}^{(1)} \qquad \text{and} \qquad v_r^{(2)} = \frac{8(2r-1)}{(r+2)} v_{r-1}^{(2)} \tag{4.42}$$

and hence the asymptotic form of v_r has parameters $\rho = 16$ and $g = -2$ which this time is equal to $g'' + 1$. The critical exponents are summarised in Table I.

We noted that when $\kappa = 1$ or 2, vesicles which start and end at the wall satisfy first order recurrence relations. We now give the generalisation of these relations to vesicles which terminate at arbitrary fixed x^f:

$$Z_t^{\mathscr{V}}(x^f \mid 0; 1) = \frac{16(t-1)(t+1)(t+2)}{(t-x^f)(t-x^f+2)(t+x^f+4)(t+x^f+6)} Z_{t-2}^{\mathscr{V}}(x^f \mid 0; 1) \tag{4.43}$$

In both cases $Z_t^{\mathscr{V}}(x^f \mid 0; 1)$ is zero for $t < x^f$ which is consistent with the zeros of the denominator. The critical points and exponents are independent of x^f.

4.4. Vesicles: The Mean Number of Contacts

4.4.1. The Mean Number of Contacts of Vesicles: One End Free. Differentiating (1.4) with respect to $\log \kappa$ gives $\acute{M}_t^{\mathscr{V}}(\kappa)$, and applying Zeilberger's algorithm to the resulting sum gives

$$\begin{aligned} &\kappa(r+1)(2+(r-1)(\kappa-2)^2)\, \acute{M}_{2r}^{\mathscr{V}}(\kappa) - 2\kappa^2(2r-1)(2+r(\kappa-2)^2)\, \acute{M}_{2r-2}^{\mathscr{V}}(\kappa) \\ &\quad = 4\kappa(1+r(\kappa-2)) \frac{(2r)!\,(2r-1)!}{r!^2\,(r-1)!\,(r+1)!} \end{aligned} \tag{4.44}$$

which, applying the analysis of Appendix A, yields critical exponents which give rise to the values of Δ_s in Table I.

4.4.2. The Mean Number of Contacts of Vesicles: Both Ends Fixed to the Surface. The same procedure applied to (1.3) with $x = 0$ gives the rather more complicated expression

$$\begin{aligned} &\kappa(r+2)(8-22\kappa+18\kappa^2-\kappa^3-\kappa^4+3r(\kappa-2)^2(3\kappa-2)+r^2(\kappa-2)^4)\, \hat{M}_{2r}^{\mathscr{V}}(\kappa) \\ &\quad - 2\kappa^2(2r-1)(6\kappa+r(\kappa-2)^2(2+\kappa+2\kappa^2)+r^2(\kappa-2)^4)\, \hat{M}_{2r-2}^{\mathscr{V}}(\kappa) \\ &\quad = 12\kappa H(r)(8+2\kappa-r(4+7\kappa-6\kappa^2)+r^2(\kappa-2)(2+3\kappa)) \end{aligned} \tag{4.45}$$

where

$$H(r)=\frac{(2r)!\,(2r-1)!}{(r-1)!\,r!\,(r+1)!\,(r+2)!} \tag{4.46}$$

When $\kappa=2$ this simplifies to

$$\hat{M}_{2r}^{\mathscr{V}}(2)-8\,\frac{2r-1}{r+2}\,\hat{M}_{2r-2}^{\mathscr{V}}(2)=12H(r) \tag{4.47}$$

The critical exponents derived from these equations give the same values of Δ_s as when one end of the vesicle is free. Similar equations may be obtained for $x>0$ but this would not be expected to change the critical behavior by analogy with the single chain calculations.

4.5. Vesicles: Scaling Form Near $\kappa=2$

We first consider the free energy of vesicles with one free end. The scaling form of $\dot{Z}_{2r}^{\mathscr{V}}(\kappa)$ may be derived from that of $\hat{Z}_{2r}^{\mathscr{S}}(\kappa)$ since solving (4.33) we find

$$\dot{Z}_{2r}^{\mathscr{V}}(\kappa)=\kappa C_r\omega^{-r}\left(1-\frac{1}{\bar{\kappa}}\sum_{s=1}^{r}C_s\omega^s\right) \tag{4.48}$$

which on comparison with (3.59) shows that

$$\dot{Z}_{2r}^{\mathscr{V}}(\kappa)=\frac{C_r}{\kappa}\,\hat{Z}_{2r+2}^{\mathscr{S}}(\kappa) \tag{4.49}$$

and this agrees with the previously noted relation (4.26). Combining (4.49), (3.65) and (3.62) gives the scaling form

$$\dot{Z}_{2r}^{\mathscr{V}}(\kappa)\approx 2\,\frac{16^r}{\sqrt{\pi}\,r^2}\,\dot{\varphi}^{\mathscr{V}}\left(\frac{(\kappa+2)}{2}\,r^{1/2}\right) \tag{4.50}$$

where $\dot{\varphi}^{\mathscr{V}}=\hat{\varphi}^{\mathscr{S}}$ and using (3.66) gives values of g_1 in agreement with Table I. Note, at a mathematical level the equality of the scaling functions for a single chain attached at both ends and the scaling function for vesicles fixed at one end whose other end is free (summed over) arises from the functional relation (4.49) between the associated partition functions. However, one would expect the equality of the scaling functions should be independent, via universality, of this particular relationship and hence be based on some physical argument. What this physical argument might be is unclear to us.

Using $\acute{Z}^{\mathscr{V}}_{2r+1}(\kappa) = (C_{r+1}/\kappa)\,\hat{Z}^{\mathscr{S}}_{2r+2}(\kappa)$ gives the same scaling form for $\acute{Z}^{\mathscr{V}}_{2r+1}(\kappa)$ and hence we have the general form (1.15) with $\hat{\varphi}^{\mathscr{V}}$ replaced by $\acute{\varphi}^{\mathscr{V}}$ of equation (1.17). The asymptotic form given in (1.17) follows from (3.70).

To find the partition function when both ends are grafted to the surface we substitute

$$\hat{Z}^{\mathscr{V}}_{2r}(\kappa) = \frac{2\omega^{-r}(g(\kappa)+(r+1)\,h(\kappa))\,C_r}{(r+2)(g(\kappa)+h(\kappa))}\,u_r(\kappa) \tag{4.51}$$

into (4.27) and solving the resulting difference equation gives

$$\begin{aligned} u_r(\kappa) &= 1 - \frac{3\kappa}{\bar{\kappa}}\,(g(\kappa)+h(\kappa)) \sum_{s=1}^{r} \frac{C_s\omega^s}{(g(\kappa)+sh(\kappa))(g(\kappa)+(s+1)\,h(\kappa))} \\ &= \frac{\kappa-2}{\bar{\kappa}}\,\theta(\kappa-2) + \frac{3\kappa}{\bar{\kappa}} \sum_{s=r+1}^{\infty} \frac{(g(\kappa)+h(\kappa))\,C_s\omega^s}{(g(\kappa)+sh(\kappa))(g(\kappa)+(s+1)\,h(\kappa))} \end{aligned} \tag{4.52}$$

Following the analysis for a single walker this leads to the following scaling form near the binding transition,

$$\hat{Z}^{\mathscr{V}}_{2r}(\kappa) \approx \frac{16^r}{r^3}\,\hat{\varphi}^{\mathscr{V}}\left(\frac{(\kappa-2)}{2}\,r^{1/2}\right) \tag{4.53}$$

where for $z \leqslant 0$

$$\hat{\varphi}^{\mathscr{V}}(z) = e^{z^2}(3+2z^2)\,\frac{6}{\pi} \int_1^{\infty} \frac{e^{-uz^2}}{u^{3/2}(3+2uz^2)^2}\,du \tag{4.54}$$

and substituting $u^{1/2} = -v/z$ gives

$$\hat{\varphi}^{\mathscr{V}}(z) = -e^{z^2}(3+2z^2)\,\frac{12z}{\pi} \int_{-z}^{\infty} \frac{e^{-v^2}}{v^3(3+2v^2)^2}\,dv \tag{4.55}$$

$$= \frac{4(1+z^2)}{\pi} + \frac{e^{z^2}z(6+4z^2)\,\mathrm{erfc}(-z)}{\sqrt{\pi}} \tag{4.56}$$

which provides the continuation to $z > 0$. Using the properties of the erfc function, equation (3.69) and before, gives the asymptotic forms

$$\hat{\varphi}^{\mathscr{V}}(z) \sim \begin{cases} \dfrac{3}{\pi}\dfrac{1}{z^4} & \text{for} \quad z \to -\infty \\[2ex] \dfrac{4}{\pi} + \dfrac{6z}{\sqrt{\pi}} & \text{for} \quad z \to 0 \\[2ex] \dfrac{8z^3 e^{z^2}}{\sqrt{\pi}} & \text{for} \quad z \to \infty \end{cases} \tag{4.57}$$

which is in agreement with the form (1.15) quoted in the introduction. These forms also confirm the critical exponents in Table I which we previously obtained from the recurrence relation.

APPENDIX A. CRITICAL EXPONENTS FROM RECURRENCE RELATIONS

The recurrence relations which arise in this paper are of the form

$$f(r)\, u_r - g(r)\, u_{r-1} = h(r) \tag{A.1}$$

which we rewrite as

$$u_r - G(r)\, u_{r-1} = H(r) \tag{A.2}$$

or as the equivalent second order relation

$$u_r - \left(G(r) + \frac{H(r)}{H(r-1)} \right) u_{r-1} + \frac{H(r)}{H(r-1)}\, G(r-1)\, u_{r-2} = 0 \tag{A.3}$$

Here $G(r) = g(r)/f(r)$ and $H(r) = h(r)/f(r)$ are rational functions which may be expanded to give the asymptotic forms

$$G(r) \sim \rho_1 \left(1 + \frac{g'}{r} + \frac{h'}{r^2} + \cdots \right) \quad \text{and} \quad H(r)/H(r-1) \sim \rho_2 \left(1 + \frac{g''}{r} + \frac{h''}{r^2} \cdots \right) \tag{A.4}$$

We seek solutions having the asymptotic form $u_r \sim \rho^r r^g$. Substitution in (A.3) and expanding the coefficients to order $1/r^2$ gives

$$\rho^2 - \rho(\rho_1 \phi_1(r) + \rho_2 \phi_2(r)) + \rho_1 \rho_2 \psi(r) = 0 \tag{A.5}$$

where

$$\phi_i(r) \sim 1 + \frac{g_i - g}{r} + \frac{h_i - gg_i + g(g-1)}{r^2} + \cdots \tag{A.6}$$

with $g_1 := g'$, $g_2 := g''$, $h_1 := h'$, $h_2 := h''$ and

$$\psi(r) \sim 1 + \frac{g' + g'' - 2g}{r} + \frac{g' + h' + h'' + 2g(g-1) + g'g'' - 2g(g' + g'')}{r^2} + \cdots \tag{A.7}$$

Equating the constant terms in (A.5) gives a quadratic ρ having roots ρ_1 and ρ_2. Setting $\rho = \rho_i$ in the coefficient of $1/r$ gives $(\rho_1 - \rho_2)(g - g_i) = 0$. If $\rho_1 \neq \rho_2$ then the exponent corresponding to ρ_i is g_i. On the other hand, if the roots are equal then the coefficient of $1/r$ is automatically zero and equating the coefficient of $1/r^2$ to zero gives a quadratic for g having solutions $g = g'$ and $g = g'' + 1$ and the asymptotic form of u_r will be governed by the larger of these two values. Notice that h' and h'' cancel out at this order.

APPENDIX B. PARTITION FUNCTION POLYNOMIALS

B.1. Single Chain Starting and Ending on the Wall

$$\begin{aligned}
\hat{Z}_0^{\mathscr{S}}(0 \mid 0; \kappa) &= \kappa \\
\hat{Z}_2^{\mathscr{S}}(0 \mid 0; \kappa) &= \kappa^2 \\
\hat{Z}_4^{\mathscr{S}}(0 \mid 0; \kappa) &= \kappa^2 + \kappa^3 \\
\hat{Z}_6^{\mathscr{S}}(0 \mid 0; \kappa) &= 2\kappa^2 + 2\kappa^3 + \kappa^4 \\
\hat{Z}_8^{\mathscr{S}}(0 \mid 0; \kappa) &= 5\kappa^2 + 5\kappa^3 + 3\kappa^4 + \kappa^5 \\
\hat{Z}_{10}^{\mathscr{S}}(0 \mid 0; \kappa) &= 14\kappa^2 + 14\kappa^3 + 9\kappa^4 + 4\kappa^5 + \kappa^6
\end{aligned} \tag{B.1}$$

B.2. Single Chain Starting at the Wall eand Ending at $x^f = 2$

$$\begin{aligned}
Z_0^{\mathscr{S}}(2 \mid 0; \kappa) &= 0 \\
Z_2^{\mathscr{S}}(2 \mid 0; \kappa) &= \kappa \\
Z_4^{\mathscr{S}}(2 \mid 0; \kappa) &= 2\kappa + \kappa^2 \\
Z_6^{\mathscr{S}}(2 \mid 0; \kappa) &= 5\kappa + 3\kappa^2 + \kappa^3 \\
Z_8^{\mathscr{S}}(2 \mid 0; \kappa) &= 14\kappa + 9\kappa^2 + 4\kappa^3 + \kappa^4 \\
Z_{10}^{\mathscr{S}}(2 \mid 0; \kappa) &= 42\kappa + 28\kappa^2 + 14\kappa^3 + 5\kappa^4 + \kappa^5
\end{aligned} \tag{B.2}$$

B.3. Single Chain Starting and Ending at $x=2$

$$
\begin{aligned}
&Z_0^{\mathscr{S}}(2\,|\,2;\kappa)=1\\
&Z_2^{\mathscr{S}}(2\,|\,2;\kappa)=2\\
&Z_4^{\mathscr{S}}(2\,|\,2;\kappa)=5+\kappa\\
&Z_6^{\mathscr{S}}(2\,|\,2;\kappa)=14+4\kappa+\kappa^2\\
&Z_8^{\mathscr{S}}(2\,|\,2;\kappa)=42+14\kappa+5\kappa^2+\kappa^3\\
&Z_{10}^{\mathscr{S}}(2\,|\,2;\kappa)=132+48\kappa+20\kappa^2+6\kappa^3+\kappa^4
\end{aligned}
\tag{B.3}
$$

B.4. Vesicle Grafted to the Wall at each End

$$
\begin{aligned}
&\hat{Z}_0^{\mathscr{V}}(0\,|\,0;\kappa)=\kappa\\
&\hat{Z}_2^{\mathscr{V}}(0\,|\,0;\kappa)=\kappa^2\\
&\hat{Z}_4^{\mathscr{V}}(0\,|\,0;\kappa)=\kappa^2+2\kappa^3\\
&\hat{Z}_6^{\mathscr{V}}(0\,|\,0;\kappa)=3\kappa^2+6\kappa^3+5\kappa^4\\
&\hat{Z}_8^{\mathscr{V}}(0\,|\,0;\kappa)=14\kappa^2+28\kappa^4+28\kappa^5+14\kappa^6\\
&\hat{Z}_{10}^{\mathscr{V}}(0\,|\,0;\kappa)=84\kappa^2+168\kappa^3+180\kappa^4+120\kappa^5+42\kappa^5
\end{aligned}
\tag{B.4}
$$

B.5. Vesicle with one End Free

$$
\begin{aligned}
&\acute{Z}_0^{\mathscr{V}}(\kappa)=\kappa\\
&\acute{Z}_1^{\mathscr{V}}(\kappa)=\kappa\\
&\acute{Z}_2^{\mathscr{V}}(\kappa)=\kappa+\kappa^2\\
&\acute{Z}_3^{\mathscr{V}}(\kappa)=2\kappa+2\kappa^2\\
&\acute{Z}_4^{\mathscr{V}}(\kappa)=4\kappa+4\kappa^2+2\kappa^3\\
&\acute{Z}_5^{\mathscr{V}}(\kappa)=10\kappa+10\kappa^2+5\kappa^3\\
&\acute{Z}_6^{\mathscr{V}}(\kappa)=25\kappa+25\kappa^2+15\kappa^2+5\kappa^4\\
&\acute{Z}_7^{\mathscr{V}}(\kappa)=70\kappa+70\kappa^2+42\kappa^3+14\kappa^4\\
&\acute{Z}_8^{\mathscr{V}}(\kappa)=196\kappa+196\kappa^2+126\kappa^3+56\kappa^4+14\kappa^5\\
&\acute{Z}_9^{\mathscr{V}}(\kappa)=588\kappa+588\kappa^2+378\kappa^3+168\kappa^4+42\kappa^5
\end{aligned}
\tag{B.5}
$$

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