The statistical mechanics of vesicles

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1. Polygons as vesicle models

Biological membranes consist of lipid bilayers and, when closed, form vesicles as blood cells or bi-lipid layer membranes. These 3-dimensional vesicles form a variety of shapes depending on the surface tension, osmotic pressure, etc (see Fig. 1).

A convenient model for the boundary of the two-dimensional vesicle is a polygon either in the continuum or on a lattice. The polygon is taken to be self-avoiding and one asks, in the lattice version, for the number of polygons with $2n$ edges enclosing area $m$. Here, we consider polygons on the square lattice (see Fig. 2).

We denote $c_{n,m}$ the number of all polygons with $2n$ steps which enclose an area of size $m$, and define the polygon-generating function $G(x, q)$ to be

$$G(x, q) = \sum_{n,m} c_{n,m} x^n q^m.$$

Each class of polygons (staircase polygons, bar-graph polygons, column-convex polygons) defines a model of vesicles. We want to give an explicit formula for $G(x, q)$ and information on its singularity structure for all the models.

2. Statistical mechanics, some rigorous results

Mathematically, the model requires the calculation of the same object, the generalized partition function $G(x, q)$, where

$$G(x, q) = \sum_{m=1}^{\infty} q^m Z_m(x) \quad \text{with} \quad Z_m(x) = \sum_{n=1}^{\infty} c_{n,m} x^n.$$

\begin{figure}
\centering
\includegraphics[width=0.3\textwidth]{vesicle.png}
\caption{A vesicle.}
\end{figure}
Physically it is of interest to understand the behavior of the partition function $Z_m(x)$ of vesicles of fixed area $m$ as the perimeter fugacity $x$ is varied [6, 7, 4]. The behavior of the partition function for large vesicles is determined by the mathematical behavior of the generating function near its radius of convergence.

For a fixed area $m$, the free energy $H(\varphi)$ of a vesicle $\varphi$ is related to the energy $E$ and the perimeter $2n(\varphi)$ of $\varphi$ through the relation $H(\varphi) = -E.n(\varphi)$. The partition function $Z_m(x)$ is

$$Z_m(x) = \sum_{|\varphi|=m} e^{-\beta H(\varphi)} = \sum_{n \geq 2} c_{m,n} e^{\beta E_n}$$

with $x = e^{\beta E}$.

The total free energy is

$$-\beta f_m(x) = \frac{1}{m} \log Z_m(x)$$

and assuming the thermodynamic limit exists, we have for the thermodynamic free energy per step

$$f_\infty(x) = \lim_{m \to \infty} \frac{1}{m} \log(Z_m(x))$$

We can also consider the internal energy

$$\frac{1}{E} u_m(x) = x \frac{d}{dx} \left( \frac{1}{m} \log Z_m(x) \right)$$

or the specific heat

$$\frac{1}{\beta E^2} c_m(x) = \left( x \frac{d}{dx} \right)^2 \left( \frac{1}{m} \log Z_m(x) \right).$$

Let $q_c(x)$ be the radius of convergence of the generating function $G(x,q)$ for fixed $x$:

$$q_c(x) = \lim_{m \to \infty} (Z_m(x))^{1/m}.$$ 

For vesicles this is related to the free energy per unit length of vesicles of fixed area in the limit of large areas through the relation

$$q_c(x) = e^{\beta f_\infty(x)}, \quad \text{where} \quad -\beta f_\infty(x) = \lim_{m \to \infty} \frac{1}{m} \log(Z_m(x)).$$
3. Proof of the existence of the thermodynamic limit

We give here a sketch of the proof. For more details, see [9]. We use the following lemma:

**Lemma 1.** Let \( \{a_n\}_{n \geq 0} \) be a sequence in \( \mathbb{R} \). If the sequence is sub-additive \( (a_{n+m} \leq a_n + a_m) \) then \( \lim_{n \to -\infty} \frac{1}{n} a_n = \inf_{n \to -\infty} \frac{1}{n} a_n \) exists (may be \(-\infty\)).

By a standard concatenation construction in which two vesicles are joined by a ‘neck’ consisting of a single square, we obtain a larger vesicle and thereby find:

\[
Z_{n+m}(q) \geq q Z_n(q) Z_m(q)
\]

where \( Z_n(q) = \sum_m c_{n,m} q^m \). Moreover, if we define

\[
a_n = -\log(q Z_n(q))
\]

then \( \{a_n\} \) verifies \( a_{n+m} \leq a_n + a_m \) and \( \lim_{n \to -\infty} (Z_n(q))^{\frac{1}{n}} \) exists.

Now, we examine bounds on \( x_c(q) = \lim_{n \to -\infty} (Z_n(q))^{\frac{1}{n}} \).

**Case q ≤ 1.** The minimum area for perimeter \( 2n \) is \( m_{\text{min}} = n - 1 \) and hence \( Z_n(q) \leq Z_n(1) q^{n-1} \) and \( x_c(q) \geq \mu_{\text{SAW}}^{2} q^{-1} \), where we write SAW for self-avoiding walk model.

The number of polygons with perimeter \( 2n \) and area \( m_{\text{min}}(n) \) is the number of site trees on dual lattice with \( n - 1 \) vertices, say \( d_n \), and hence \( Z_n(q) \geq d_n q^{n-1} \) and \( x_c(q) \leq \tilde{\mu} q^{-1} \) (see Fig. 3).

Since \( Z_n(q) \) is monotone increasing in \( x \), \( x_c(q) \) is monotone non-decreasing. Therefore to prove that \( x_c(q) \) is log-convex it suffices to show that:

\[
\frac{x_c(p) + x_c(q)}{2} \geq x_c(\sqrt{pq}).
\]

This follows immediately from

\[
Z_n(q) Z_m(q) = \sum_{m_1} c_{n,m_1} q^{m_1} \sum_{m_2} c_{n,m_2} q^{m_2} \\
\geq \left( \sum_m c_{n,m} (pq)^{\frac{m}{n}} \right)^2 = (Z_n(\sqrt{pq}))^2.
\]

![Figure 3](image-url)

**Figure 3.** Schematic plot of the radius of convergence of the generating function showing the tricritical point.
Figure 4. Interpretation of $Z_n^{(\alpha)}(q)$.

Case $q \geq 1$. In that case, we have $q^{m_{\text{max}}(n)} \leq Z_n(q) \leq q^{m_{\text{max}}(n)}Z_n(1)$ with $m_{\text{max}}(n) \sim \frac{n^2}{q}$ and $Z_n(1) \sim \mu_{\text{SAW}}^{2n}$. Thus $Z_n(q) \sim q^{\frac{n^2}{q}}$ and $x_c(q) = 0$.

In fact, the ‘blown-up’ configurations completely dominate the asymptotics.

Theorem 1 (Prellberg, Owczarek, 1995).

$$Z_n(q) \sim Z_n^{(\alpha)}(q) = \left(\frac{1}{q}; \frac{1}{q}\right)_{\infty}^{-\frac{4}{q}} \sum_{k=-\infty}^{+\infty} q^{k(n-k)}$$

in the sense that for all $q > 1$ there are $C > 0$ and $0 < \rho < 1$ such that for all $n$

$$\left|Z_n(q)/Z_n^{(\alpha)}(q) - 1\right| < C\rho^n$$

We can interpret $Z_n^{(\alpha)}(q)$ as the generating functions of $k \times (n - k)$ rectangles ($\sum_{k=1}^{n-1} q^{k(n-k)}$) where 4 corners (4 Ferrers diagrams: $\left(\frac{1}{q}; \frac{1}{q}\right)_{\infty}^{-\frac{4}{q}}$) are removed, which are in fact convex polygons (see Fig. 4).

4. Tricritical phase diagram

We show that, for $q < 1$, $G(x, q)$ converges for $x < x_c(q)$. For $q > 1$, $G(x, q)$ converges only for $x = 0$. These results can be expressed in terms of a phase diagram in the space of the two fugacities $x$ and $q$. The form of this phase diagram is shown in figure 3. For $x < x_c(q)$ and $q < 1$ the polygons are ramified objects, closely resembling branched polymers. As $q$ approaches unity less ramified configurations predominate; at $q = 1$ one has standard self-avoiding polygons. This region, $\{x < x_c(q), y \leq 1\}$ might be referred to as the ‘droplet’ or ‘compact’ phase. For $q > 1$ the polygons become ‘expanded’ or ‘inflated’ and approximate squares, their average areas scaling as the square of their perimeters. For $q < 1$ and $x > x_c(q)$, we expect that this phase can be described as a single convoluted polygon that ‘fills’ the whole lattice rather like a closed Hamiltonian path: one might describe it as a ‘seaweed phase’ [9].

Here we give main results about the singularity diagram (see Fig. 5):

- $q_c(x)$ is singular in $x = x_t$ thus we have a phase transition.
- $G(x, q)$ diverges at $q_c(x)$ for $x > x_t$.
- $G(x, q)$ is singular at $q_c(x) = 1$ for $x < x_t$.
- $G(x, 1)$ is finite with singularity exponent $\gamma_\nu$ as $x \to x_t$.
- $G(x_t, q)$ has a singularity with exponent $\gamma_t$ as $q \to 1$.
- $(x_t, 1)$ is a tricritical point with crossover exponent $\phi = \frac{\gamma_t}{\gamma_\nu}$.
The scaling function $f$ is:
\[ G_{r\rightarrow s}(x, q) \sim (1 - q)^{-\eta} f \left( \left\{ 1 - q \right\}^{-\psi} (x_L - x) \right) \]
with $f(z) \sim z^{-\gamma}$ as $z \to \infty$ and $f(z) \sim 1$ as $z \to 0$.
- The shape exponent is $\psi = \frac{1}{\phi}$ and $q_c(x) \sim 1 - a(x - x_t)^{1b}$.

5. Partially convex polygons: a solvable model

The analysis of partially convex subsets of self-avoiding polygons confirms results of the previous section. These partially convex polygons form a universality class with the same crossover exponent as expected in the unrestricted problem. The particular models we consider are subsets of column-convex polygons: staircase polygons, directed column-convex polygons and column-convex polygons (see Fig. 6).

These models have been studied by a variety of methods:
- mapping to a $q$-extension of an algebraic language [8],
- recurrence relations [12, 5],
- linear functional equations [3, 2],
- transfer matrix techniques [1].

All these models possess the characteristic feature that their single-variable generating functions are algebraic, while the two-variable generating functions are expressed in term of quotients of $q$-series.

Figure 5. The singularity diagram.

Figure 6. Partially convex polygons.
Staircase Polygons

\[
\begin{align*}
S(x) & = S(qx)y + S(qx)S(x) + qxy + qxS(x) \\

\text{Directed Column-Convex Polygons} & = \]

\[
D(x; \mu) & = D(qx; \mu)y + D(qx; 1)qxD(x; \mu) + D(qx; 1)D(x; \mu) + D(qx; 1)qxy\mu + qxy\mu + qxD(x; \mu)
\]

\text{Figure 7.} The diagrammatic form of the functional equations for staircase polygons and directed column-convex polygons.

We define the polygon generating function \(G(x, y, q)\) to be

\[
G(x, y, q) = \sum_{n_x, n_y, n} c_{n_x, n_y, n} x^{n_x} y^{n_y} q^n.
\]

We derive the generating function for each models by using an inflation process [10, 11, 3]: the height of the polygon is increased by one lattice spacing and concatenated with rows of height one (see Fig. 7).

Denoting the generating function for the staircase polygons by \(S(x, y, q)\), we therefore get immediately

\[
S(x, y, q) = \left( S(qx, y, q) + qx \right) \left( y + S(x, y, q) \right).
\]

In order to write down a functional equation for the column-convex polygons, we need to keep track of the height \(r\) of the rightmost column of these polygons. We define the generating function \(D(x, y, q; \mu)\) to be

\[
D(x, y, q; \mu) = \sum_{n_x, n_y, n} c_{n_x, n_y, n} x^{n_x} y^{n_y} q^n \mu^r.
\]

If we denote \(\frac{\partial}{\partial \mu} D(qx, y, q; \mu)\big|_{\mu=1}\) by \(D_\mu(qx, y, q; 1)\), we get the following functional-differential equation:

\[
D(x, y, q; \mu) = \left( 1 + D_\mu(qx, y, q; 1) \right) qx \left( y\mu + D(x, y, q; \mu) \right)
\]

\[
+ D(qx, y, q; \mu) y\mu + D(qx, y, q; 1) D(x, y, q; \mu).
\]

We can transform this equation to one functional equation in \(D(x) = D(x, y, q; 1)\) by partially differentiating with respect to \(\mu\) and setting \(\mu = 1\). This leads to

\[
0 = D(q^2 x) D(qx) D(x) + y D(q^2 x) D(qx) + y D(q^2 x) D(x) - (1 + q) D(qx) D(x) + y^2 D(q^2 x)
\]

\[
- y(1 + q) D(qx) + q(1 + qx(y - 1)) D(x) + yq^2 x(y - 1).
\]

Setting \(q = 1\) gives the perimeter generating function which satisfies a cubic equation and has a square-root singularity at

\[
y_c = \frac{\sqrt{100} - 4}{3} \quad \text{for} \quad x = y
\]

\[80\]
implying that $\gamma_u = -\frac{1}{2}$.

First we note that the functional equation for staircase polygons is of the form

$$G(x)G(qx) + a(x)G(x) + b(x)G(qx) + c(x) = 0$$

which can be linearized by the use of the transformation

$$G(x) = \alpha \frac{H(qx)}{H(x)} - b(x)$$

where $\alpha$ has to be chosen to match the initial condition. This leads to a linear functional equation in $H(x)$,

$$\alpha^2 H(q^2 x) + \alpha [a(x) - b(qx)] H(qx) + [c(x) - a(x)b(x)] H(x) = 0.$$  

**Lemma 2.** The solution of

$$0 = x H(qx) + \sum_{k=0}^{N} \alpha_k H(q^k x) \quad \text{with} \quad \sum_{k=0}^{N} \alpha_k = 0$$

regular at $x = 0$ is given by

$$H(x) = \sum_{n=0}^{\infty} \frac{(-x)^n q^{(\gamma)}_n}{\prod_{m=1}^{n} \Lambda(q^{m})} \quad \text{with} \quad \Lambda(t) = \sum_{k=0}^{N} \alpha_k t^k.$$  

We apply lemma 2 to staircase polygons, we choose $\alpha = y$ and we get the solution

$$S(x) = y \left( \frac{T(qx)}{T(x)} - 1 \right) \quad \text{with} \quad T(x) = \sum_{n=0}^{\infty} \frac{(-qx)^n q^{(\gamma)}_n}{(q, qy; q)_n}.$$  

Surprisingly, this works also for directed column-convex polygons:

$$D(x) = y \left( \frac{E(qx)}{E(x)} - 1 \right) \quad \text{with} \quad E(x) = \sum_{n=0}^{\infty} \frac{(y - 1)qx^n q^{(\gamma)}_n}{(q, qy; y; q)_n}.$$  

M. Bousquet-Mélou [3] found by other means that for column-convex polygons

$$G(x, y, q) = y \frac{(1 - y)A}{1 + B + yA}$$

where

$$A = \frac{xq}{(1 - y)(1 - yq)} + \sum_{n=2}^{\infty} \frac{(-1)^{n+1} x^n (1 - y)^{2n-4} q^{\binom{n+1}{2}} (y^2 q; q)_{2n-2}}{(q; q)_{n-1}(yq; q)_{n-2}(yq; q)_n(y^2 q; q)_n(y^2 q; q)_{n-1}}$$

and

$$B = \sum_{n=1}^{\infty} \frac{(-1)^n x^n (1 - y)^{2n-3} q^{\binom{n+1}{2}} (y^2 q; q)_{2n-1}}{(q; q)_{n}(yq; q)_{n-1}(yq; q)_n(y^2 q; q)_{n-1}(y^2 q; q)_{n-1}}.$$  

In [11] we consider simpler models of partially convex polygons as stacks and Ferrers diagrams (see Fig. 8).

For stacks ($s = 2$) and Ferrers diagram ($s = 1$), we obtain a non-alternating $q$-series for the generating function

$$G_s(x, y, q) = \sum_{n=1}^{\infty} \frac{x(yq)^n}{(xq; q)_n(1 - xq^n)}$$

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and a rational function for the perimeter-generating function

\[ G_z(x, y, 1) = \frac{xy(1 - x)^z - 1}{(1 - x)^z - y}. \]

These models are interesting, as they show “pathological behavior”. We have seen that considered as a function of \( x \), the radius of convergence is a continuous function, while considered as a function of \( q \), it has a jump discontinuity at \( q = 1 \) in the generic case for the vesicle models. But in the generic case we have left continuity at \( x_c(1) \) whereas for stacks \( (x_c(q) = 1/q) \) there is an isolated point \( x_c(1) \) at \( q = 1 \) \( (x_c(1^-) = 1 > x_c(1) > x_c(1^+) = 0) \). Thus stacks and Ferrers diagram are too simplified to give a reasonable physical model.

Bibliography