The statistical mechanics of vesicles

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[summary by Dominique Gouyou-Beauchamps]

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

$$G(x,q) = \sum_{m=1}^{\infty} q^m Z_m(x) \qquad \text{with} \qquad Z_m(x) = \sum_{n=2}^{\infty} c_{n,m} x^n.$$

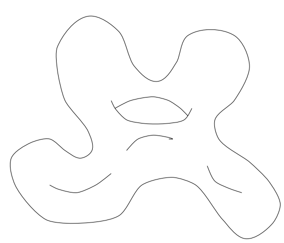

FIGURE 1. A vesicle.

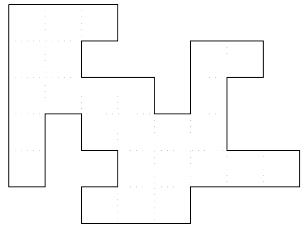

FIGURE 2. A polygon with area $m = 26$ and perimeter $2n = 42$.

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 φ is related to the energy E and the perimeter $2n(\varphi)$ of φ through the relation $H(\varphi) = -E.n(\varphi)$. The partition function $Z_m(x)$ is

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

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:

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

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

$$q_c(x) = e^{\beta f_\infty(x)}, \qquad \text{where} \qquad -\beta f_\infty(x) = \lim_{m\to\infty} \frac{1}{m} \log(Z_m(x)).$$

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* $\lim_{n\to\infty} \frac{1}{n} a_n = \inf_{n\to\infty} \frac{1}{n} a_n$ *exits (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 $q \leq 1$. The minimum area for perimeter $2n$ is $m_{\min} = n-1$ and hence $Z_n(q) \leq Z_n(1) q^{n-1}$ and $x_c(q) \geq \mu_{SAW}^{-2} q^{-1}$, where we write SAW for self-avoiding walk model.

The number of polygons with perimeter $2n$ and area $m_{\min}(n)$ 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

$$\begin{aligned} Z_n(q) Z_m(q) &= \sum_{m_1} c_{n,m_1} q^{m_1} \sum_{m_2} c_{n,m_2} q^{m_2} \\ &\geq \left(\sum_m c_{n,m} (pq)^{\frac{m}{2}} \right)^2 = \left(Z_n(\sqrt{pq}) \right)^2. \end{aligned}$$

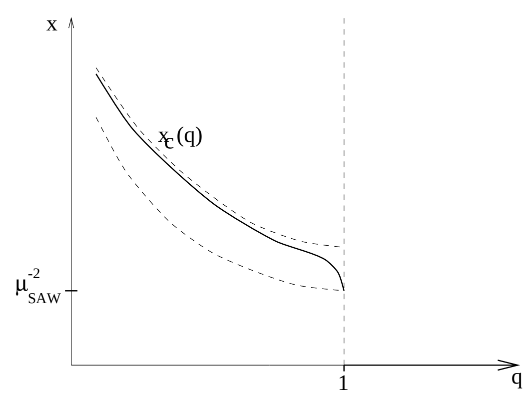

FIGURE 3. Schematic plot of the radius of convergence of the generating function showing the tricritical point.

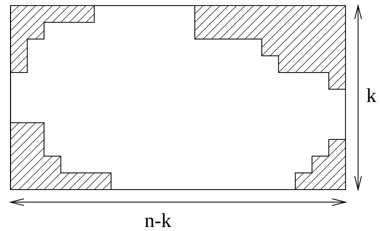

FIGURE 4. Interpretation of $Z_n^{(as)}(q)$.

Case $q \geq 1$. In that case, we have $q^{m_{\max}(n)} \leq Z_n(q) \leq q^{m_{\max}(n)} Z_n(1)$ with $m_{\max}(n) \sim \frac{n^2}{4}$ and $Z_n(1) \sim \mu_{SAW}^{2n}$. Thus $Z_n(q) \sim q^{\frac{n^2}{4}}$ and

$$x_c(q) \equiv 0.$$

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

THEOREM 1 (PRELLBERG, OWCZAREK, 1995).

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

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

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

We can interpret $Z_n^{(as)}(q)$ 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: $\left(\frac{1}{q}; \frac{1}{q}\right)_\infty^{-4}$) 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 a 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 γ_u as $x \to x_t$.
- $G(x_t,q)$ has a singularity with exponent γ_t as $q \to 1$.
- $(x_t, 1)$ is a *tricritical point* with crossover exponent $\phi = \frac{\gamma_t}{\gamma_u}$.

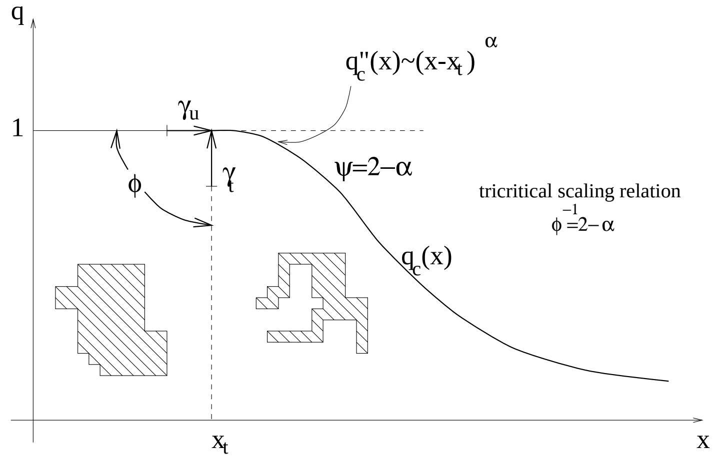

FIGURE 5. The singularity diagram.

– The scaling function f is:

$$G^{Sing}(x,q) \sim (1-q)^{-\gamma_t} f\left(\{1-q\}^{-\phi}\{x_t - x\}\right)$$

with $f(z) \sim z^{-\gamma_u}$ as $z \to \infty$ and $f(z) \sim 1$ as $z \to 0$.

– The shape exponent is $\psi = \frac{1}{\phi}$ and $q_c(x) \sim 1 - a(x-x_t)^{\frac{1}{\psi}}$.

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.

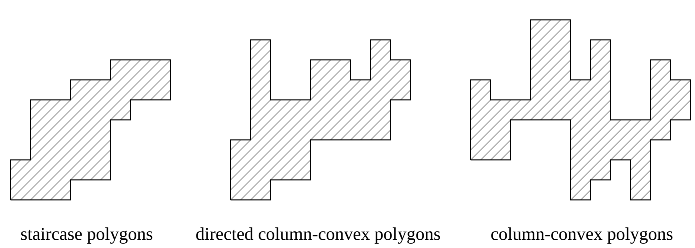

FIGURE 6. Partially convex polygons.

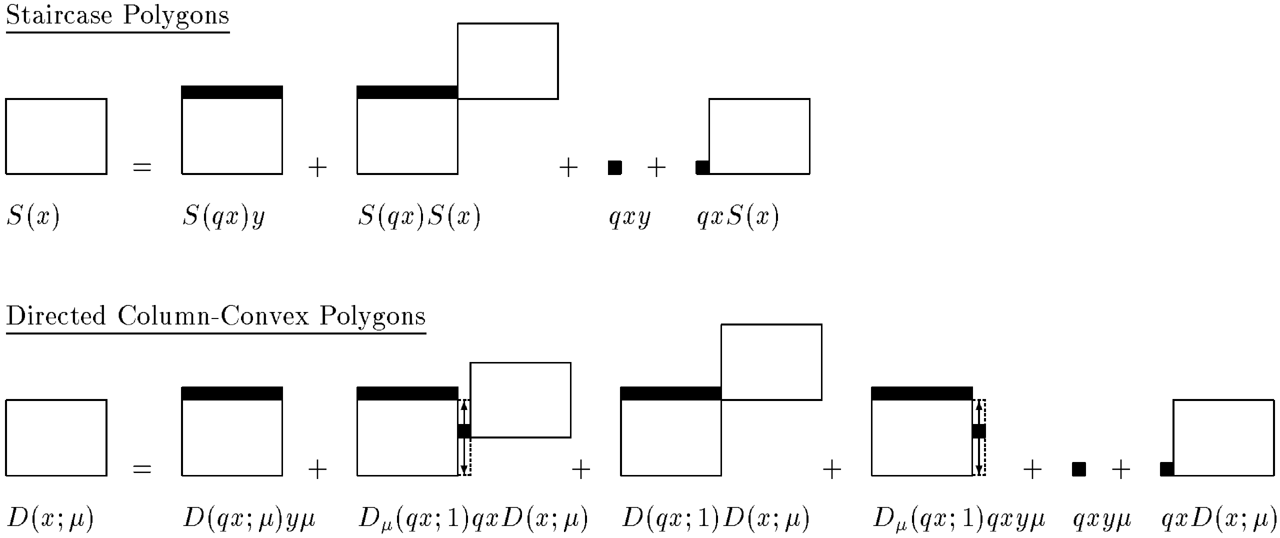

FIGURE 7. The diagrammatic form of the functional equations for staircase polygons and directed column-convex polygons.

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

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

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

$$S(x,y,q) = (S(qx,y,q) + qx)\,(y + S(x,y,q)).$$

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

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

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:

$$D(x,y,q;\mu) = (1 + D_\mu(qx,y,q;1))\,qx\,(y\mu + D(x,y,q;\mu)) \\ + D(qx,y,q;\mu)y\mu + D(qx,y,q;1)D(x,y,q;\mu).$$

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

$$0 = D(q^2x)D(qx)D(x) + yD(q^2x)D(qx) + yD(q^2x)D(x) - (1+q)D(qx)D(x) + y^2D(q^2x) \\ - y(1+q)D(qx) + q(1 + qx(y-1))D(x) + yq^2x(y-1).$$

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

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

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

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

LEMMA 2. *The solution of*

$$0 = xH(qx) + \sum_{k=0}^{N} \alpha_k H(q^k x) \qquad \textit{with} \qquad \sum_{k=0}^{N} \alpha_k = 0$$

regular at $x = 0$ is given by

$$H(x) = \sum_{n=0}^{\infty} \frac{(-x)^n q^{\binom{n}{2}}}{\prod_{m=1}^{n} \Lambda(q^m)} \qquad \textit{with} \qquad \Lambda(t) = \sum_{k=0}^{N} \alpha_k t^k.$$

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

$$S(x) = y\left(\frac{T(qx)}{T(x)} - 1\right) \qquad \text{with} \qquad T(x) = \sum_{n=0}^{\infty} \frac{(-qx)^n q^{\binom{n}{2}}}{(q, qy; q)_n}.$$

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

$$D(x) = y\left(\frac{E(qx)}{E(x)} - 1\right) \qquad \text{with} \qquad E(x) = \sum_{n=0}^{\infty} \frac{((y-1)qx)^n q^{\binom{n}{2}}}{(q, qy, y; q)_n}.$$

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

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

and

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

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

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

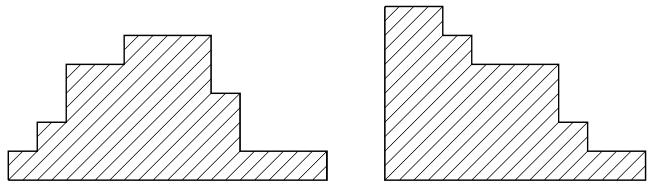

FIGURE 8. Typical configurations of stacks and Ferrers diagrams.

and a rational function for the perimeter-generating function

$$G_s(x, y, 1) = \frac{xy(1-x)^{s-1}}{(1-x)^s - y}.$$

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

[1] Binder (P. M.), Owczarek (A. L.), Veal (A. R.), and Yeomans (J. M.). – Collapse transition in a simple polymer model : exact results. *Journal of Physics Series A*, vol. 23, 1990, p. L975.

[2] Bousquet-Mélou (Mireille). – Codage des polyominos convexes et équations pour l'énumération suivant l'aire. *Discrete Applied Mathematics*, vol. 48, 1994, pp. 21–43.

[3] Bousquet-Mélou (Mireille). – A method for the enumeration of various classes of column-convex polygons. *Discrete Mathematics*, vol. 154, 1996, pp. 1–25.

[4] Brak (R.), Enting (I. G.), and Guttmann (A. J.). – Exact solution of the row-convex polygon perimeter generating function. *Journal of Physics Series A*, vol. 23, 1990, pp. 2319–2326.

[5] Brak (R.) and Guttmann (A. J.). – Exact solution of staircase and row-convex polygon perimeter and area generating function. *Journal of Physics Series A*, vol. 23, 1990, pp. 4581–4588.

[6] Brak (R.), Owczarek (A. L.), and Prellberg (T.). – A scaling theory of the collapse transition in geometric cluster models of polymers and vesicles. *Journal of Physics Series A*, vol. 26, 1993, pp. 4565–4579.

[7] Brak (R.), Owczarek (A. L.), and Prellberg (T.). – Exact scaling behavior of partially convex vesicles. *Journal of Statistical Physics*, vol. 76, 1994, pp. 1101–1128.

[8] Delest (M. P.). – Generating functions for column-convex polyominoes. *Journal of Physics Series A*, vol. 48, 1988, pp. 12–31.

[9] Fisher (Michael E.), Guttmann (Anthony J.), and Whittington (Stuart G.). – Two-dimensional lattice vesicles and polygons. *Journal of Physics Series A*, vol. 24, 1991, pp. 3095–3106.

[10] Prellberg (T.) and Brak (R.). – Critical exponents from nonlinear functional equations for partially directed cluster models. *Journal of Statistical Physics*, vol. 78, 1995, pp. 701–730.

[11] Prellberg (Thomas) and Owczarek (Aleksander L.). – Staking models of vesicles and compact clusters. *Journal of Statistical Physics*, vol. 80, n° 3/4, 1995, pp. 755–779.

[12] Temperley (H. N. V.). – Combinatorial problems suggested by the statistical mechanics of domains and rubber-like molecules. *Physical Review*, vol. 103, n° 1, 1956, pp. 1–16.