Exact solution of two friendly walks above a sticky wall with single and double interactions

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Directed walks

- Exact solutions of single and multiple directed walks models
- Recurrence and functional equation
- Rational, algebraic or non Differentially-finite (D-finite) solutions
- Multiple walks: Bethe Ansatz & Lindström-Gessel-Viennot
- LGV Lemma: multiple walks = determinant of single walk
- LGV problems result in generating functions that are D-finite
Functional equation for an expanded generating function
- Uses an extra catalytic variable
- Answer is a ‘boundary’ value
- Fix catalytic variable → ‘bulk’ term disappears (Kernel method)
- Obstinate kernel method: multiple values of catalytic variable
- Solutions are not always D-finite
Polymer Adsorption

The physical motivation is the adsorption phase transition
- Second order phase transition with jump in specific heat
- Crossover exponent $\phi = 1/2$ for directed walks and SAW
- Order parameter is coverage of the surface by the polymer
Exact solution and analysis of single and multiple directed walk models exist

- Single Dyck path in a half space
- Energy $-\varepsilon_a$ for each time (number $m_a$) it visits the surface
- Boltzmann weight $a = \frac{\varepsilon_a}{k_B T}$
A complete solution exists and the generating function is algebraic

Consider the coverage

\[ A = \lim_{n \to \infty} \frac{\langle m_a \rangle}{n} \]

There exists a phase transition at a temperature \( T_a \) given by \( a = 2 \):

- For \( T > T_a \) the walk moves away entropically and \( A = 0 \)
- For \( T < T_a \) the walk is adsorbed onto the surface and \( A > 0 \)
• Exact solution of two directed walks joined making a simple “vesicle”
• Vesicles with interactions for visits of the bottom walk to height 0 and height 1

Single second order transition — similar to the single walk adsorption transition
MORE MOTIVATION: SAW IN A SLIT

• A motivation is a Monte Carlo study of ring polymers in a slit
• Here Both sides of the polygon interact with the surfaces of the slit


(Our Model)

Directed vesicle where both walks can interact with a single surface

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Figure: Two directed walks with single and “double” visits to the surface.

- energy $-\varepsilon_a$ for visits of the bottom walk only (single visits) to the wall,
- energy $-\varepsilon_d$ when both walks visit a site on the wall (double visits)
Model

- number of *single visits* to the wall will be denoted $m_a$,
- number of *double visits* will be denoted $m_d$.

The partition function:

$$Z_n(a, d) = \sum_{\hat{\varphi} \ni |\hat{\varphi}|=n} e^{(m_a(\hat{\varphi}) \cdot \varepsilon_a + m_d(\hat{\varphi}) \cdot \varepsilon_d)/k_BT}$$

where $a = e^{\varepsilon_a/k_BT}$ and $d = e^{\varepsilon_d/k_BT}$.

The thermodynamic reduced free energy:

$$\kappa(a, d) = \lim_{n \to \infty} n^{-1} \log (Z_n(a, d)) .$$
To find the free energy we will instead solve for the generating function

\[ G(a, d; z) = \sum_{n=0}^{\infty} Z_n(a, d)z^n. \]

The radius of convergence of the generating function \( z_c(a, d) \) is directly related to the free energy via

\[ \kappa(a, d) = \log(z_c(a, d)^{-1}). \]

Two order parameters:

\[ \mathcal{A}(a, d) = \lim_{n \to \infty} \frac{\langle m_a \rangle}{n} \quad \text{and} \quad \mathcal{D}(a, d) = \lim_{n \to \infty} \frac{\langle m_d \rangle}{n}, \]
**FUNCTIONAL EQUATION**

We consider walks $\varphi$ in the larger set, where each walk can end at any possible height.

The expanded generating function

$$F(r, s; z) \equiv F(r, s) = \sum_{\varphi \in \Omega} z^{\lfloor \varphi \rfloor} r^{\lfloor \varphi \rfloor} s^{\lceil \varphi \rceil} / 2^{a_m(\varphi) - d_m(\varphi)},$$

where

- $z$ is conjugate to the length $|\varphi|$ of the walk,
- $r$ is conjugate to the distance $\lfloor \varphi \rfloor$ of the bottom walk from the wall and
- $s$ is conjugate to half the distance $\lceil \varphi \rceil$ between the final vertices of the two walks.

**G(a,d;z)= F(0,0)**
Consider adding steps onto the ends of the two walks

This gives the following functional equation

\[
F(r, s) = 1 + z \left( r + \frac{1}{r} + \frac{s}{r} + \frac{r}{s} \right) \cdot F(r, s) \\
- z \left( \frac{1}{r} + \frac{s}{r} \right) \cdot [r^0]F(r, s) - z\frac{r}{s} \cdot [s^0]F(r, s) \\
+ z(a - 1)(1 + s) \cdot [r^1]F(r, s) + z(d - a) \cdot [r^1s^0]F(r, s).
\]

Figure: Adding steps to the walks when the walks are away from the wall.
The Kernel

Rewrite equation as “Bulk = Boundary”

\[
K(r, s) \cdot F(r, s) = \frac{1}{d} + \left(1 - \frac{1}{a} - \frac{zs}{r} - \frac{z}{r}\right) \cdot F(0, s) - \frac{zr}{s} \cdot F(r, 0) + \left(\frac{1}{a} - \frac{1}{d}\right) \cdot F(0, 0)
\]

where the kernel \( K \) is

\[
K(r, s) = \left[1 - z \left(r + \frac{1}{r} + \frac{s}{r} + \frac{r}{s}\right)\right].
\]

Recall, we want \( F(0, 0) \) so we try to find values that kill the kernel

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Symmetries of the Kernel

The kernel is symmetric under the following two transformations:

\[(r, s) \mapsto \left( r, \frac{r^2}{s} \right), \quad (r, s) \mapsto \left( \frac{s}{r}, s \right)\]

Transformations generate a family of 8 symmetries (‘group of the walk’)

\[(r, s), \left( r, \frac{r^2}{s} \right), \left( \frac{s}{r}, \frac{s}{r^2} \right), \left( \frac{r}{s}, \frac{1}{s} \right), \left( \frac{1}{r}, \frac{1}{s} \right), \left( \frac{1}{r}, \frac{s}{r^2} \right), \left( \frac{r}{s}, \frac{r^2}{s} \right), \text{ and } \left( \frac{s}{r}, s \right)\]

We make use of 4 of these which only involve positive powers of \(r\).

This gives us four equations.
Following Bousquet-Mélou when \( a = 1 \) we form the simple alternating sum

\[ \text{Eqn1} - \text{Eqn 2} + \text{Eqn 3} - \text{Eqn 4}. \]

- When \( a \neq 1 \) one needs to generalise that approach
- Multiply by rational functions,

The form of the Left-hand side of the final equation being

\[
a^2 rK(r, s) \left( sF(r, s) - \frac{r^2}{s} F \left( r, \frac{r^2}{s} \right) + \frac{Lr^2}{s^2} F \left( \frac{r}{s}, \frac{r^2}{s} \right) - \frac{L}{s^2} F \left( \frac{r}{s}, \frac{1}{s} \right) \right)
\]

where

\[
L = \frac{zas - ars + rs + zar^2}{zas - ar + r + zar^2}.
\]
Extracting the solution $a = 1$

\[ K(r, s) \cdot (\text{linear combination of } F) = \]
\[ \frac{r(s - 1)(s^2 + s + 1 - r^2)}{s^2} \left( 1 + (d - 1)F(0, 0) \right) \]
\[ - zd(1 + s)sF(0, s) + \frac{zd(1 + s)}{s^2} F \left( 0, \frac{1}{s} \right). \]

- The kernel has two roots
- choose the one which gives a positive term power series expansion in $z$
- with Laurent polynomial coefficients in $s$:

\[ \hat{r}(s; z) \equiv \hat{r} = \frac{s \left( 1 - \sqrt{1 - 4 \left( \frac{1+s}{s} \right)^2 z^2} \right) }{2(1 + s)z} = \sum_{n \geq 0} C_n \frac{(1 + s)^{2n+1} z^{2n+1}}{s^n}, \]

where $C_n = \frac{1}{n+1} \binom{2n}{n}$ is a Catalan number.
Make the substitution $r \mapsto \hat{r}$

rewrite to remove $z$: $z = (\hat{r} + 1/\hat{r} + \hat{r}/s + s/\hat{r})^{-1}$.

Setting $r \mapsto \hat{r}$ gives

$$0 = ds^4F(0, s) - dsF \left(0, \frac{1}{s}\right) - (s - 1)(s^2 + s + 1 - \hat{r}^2)(s + \hat{r}^2) (1 + (d - 1)F(0, 0))$$

Note coefficients of $F(0, s)$ and $F(0, 1/s)$ are independent of $\hat{r}$.

*Divide by equation by $s$ — $F(0, 0)$ is a constant term in the variable $s$.**
Hence extracting the coefficient of $s^1$ gives

$$0 = -\left(1 + \sum_{n=0}^{\infty} \frac{12(2n + 1)}{(n + 2)^2(n + 3)} C_n^2 z^{2n+2}\right) \cdot (1 + (d - 1)F(0, 0)) - d \cdot F(0, 0).$$

Solving the above when $d = 1$ gives

$$G(1, 1; z) = 1 + \sum_{n=0}^{\infty} \frac{12(2n + 1)}{(n + 2)^2(n + 3)} C_n^2 z^{2n+2},$$

and hence for general $d$ we have

$$F(0, 0) = G(1, d; z) = \frac{G(1, 1; z)}{d + (1 - d)G(1, 1; z)}.$$
$a = d$

Need to extract coefficients term by term in $a$ to give

$$[a^k z^{2n}] F(0, 0) = \sum_{k' = 0}^{k} \frac{k'(k' + 1)(2 + 4n - k'n - 2k')}{(k' - 1 - n)(n + 1)^2(-2n + k')(n + 2)} \binom{2n - k'}{n} \binom{2n}{n}$$

$$= \frac{k(k + 1)(k + 2)}{(2n - k)(n + 1)^2(n + 2)} \binom{2n - k}{n} \binom{2n}{n}$$

which gives us

$$G(a, a) = \sum_{n \geq 0} z^{2n} \sum_{k=0}^{n} a^k \frac{k(k + 1)(k + 2)}{(n + 1)^2(n + 2)(2n - k)} \binom{2n}{n} \binom{2n - k}{n}.$$ 

Agrees with Brak et al. (1998) that used LGV

One can now consider $d \neq a$:

$$G(a, d; z) = \frac{aG(a, a; z)}{d + (a - d)G(a, a; z)}.$$
• Combinatorial structure the underlying the functional equation.
• Breaking up our configurations into pieces between double visits gives

\[ G(a, d; z) = \frac{1}{1 - dP(a; z)} \]

where \( P(a; z) \) is the generating function of so-called primitive factors.
• Rearranging this expression gives

\[ P(a; z) = \frac{G(a, d; z) - 1}{dG(a, d; z)} = \frac{G(a, a; z) - 1}{aG(a, a; z)}. \]

• This allows us to calculate \( P(a; z) \) from a known expression for \( G(a, a; z) \)
The phases determined by dominant singularity of the generating function

The singularities of $G(a, d; z)$ are

- those of $P(a; z)$ and
- the simple pole at $1 - dP(a; z) = 0$ and
- the singularities of $P(a; z)$ are related to those of $G(a, a; z)$.

There are two singularities of $G(a, a; z)$ giving rise to two phases:

- A desorbed phase: $A = D = 0$
- The bottom walk is adsorbed (an $a$-rich phase): $A > 0$ with $D = 0$

The simple pole in $1 - dP(a; z) = 0$ gives rise to the third phase

- Both walks are adsorbed and this is a $d$-rich phase: $D > 0$, and $A > 0$
Figure: The first-order transition is marked with a dashed line, while the two second-order transitions are marked with solid lines. The three boundaries meet at the point \((a, d) = (a^*, d^*) = (2, 11.55 \ldots)\).
Phase transitions

- The *Desorbed* to *a-rich* transition is
  - the standard second order adsorption transition
  - on the line $a = 2$ for $d < d^*$
- On the other hand the *Desorbed* to *d-rich* transition is *first order*
- While the *a-rich* to *d-rich* transition is also second order.

The other two phase boundaries are solutions to equations involving $G(a, a)$

The point where the three phase boundaries meet can be computed as

$$(a^*, d^*) = \left(2, \frac{16(8 - 3\pi)}{64 - 21\pi}\right)$$

Note that $d^*$ is not algebraic.
**Nature of the Solution**

Desorbed to $d$-rich transition occurs at a value of $d_c(a)$ for $a < 2$. We found

$$d_c(1) = \frac{8(512 - 165\pi)}{4096 - 1305\pi}$$

which is not algebraic.

- If generating function was D-finite the $d_c(1)$ must be algebraic
- Hence generating function is not D-finite
- it is a calculated in terms of one.
**Fixed energy ratio model family**

*Family of models parameterised by $-\infty < r < \infty$ where*

\[ \varepsilon_d = r\varepsilon_a \quad \text{and so} \quad d = a' \]

- $r = 2$ model has *two* phase transitions as temperature changed.
- At very low temperatures the model is in a $d$-rich phase.
- While at high temperatures the model is in the desorbed state.
- At intermediate temperatures the system is in an $a$-rich phase.
- Both transitions are second-order with jumps in specific heat.
Conclusions

- Vesicle above a surface — both sides of the vesicle can interact
- Exact solution of generating function
- Obstinate kernel method with a minor generalisation
- Solution is not D-finite — LGV lemma does not apply directly
- There are two low temperature phases
- Line of first order transition and usual second order adsorption.