Statistical properties of the 2D attached Rouse chain

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Abstract

We study various dynamical properties (winding angles, areas) of a set of harmonically bound Brownian particles (monomers), one endpoint of this chain being kept fixed at the origin 0. In particular, we show that, for long times $t$, the areas $\{A_i\}$ enclosed by the monomers scale like $t^{1/2}$, with correlated gaussian distributions. This is at variance with the winding angles $\{\theta_i\}$ around fixed points that scale like $t$ and are distributed according to independent Cauchy laws.

In this paper, we will study the planar motion of a chain of $n$ harmonically bound brownian particles. This model is usually referred in the litterature as the Rouse chain [1] and has shown to be historically very important in polymer science [2, 3]. We will consider such a chain attached at the origin 0 and examine some of its properties from the Brownian motion viewpoint.

Representing a given configuration of the chain by a complex $n$-vector $z$ (the components $z_i$, $i = 1, \ldots, n$, are the complex coordinates of the particles), we consider the set of all the closed trajectories of length $t$, i.e. $z(t) = z(0)$, and this for all the starting configurations $z(0)$. Practically, we will not weight the starting configurations with any thermodynamical factor. We are aware that this approach is quite different from the one taken in polymer physics [4] where, at $t = 0$, the chain is supposed to be in equilibrium with the environment at some finite temperature $T$. 
A_j and \theta_j being the area enclosed by the j^{th} particle and its winding angle around 0, our goal is to compute the joint probability distributions \( P(\{A_i\}) \) and \( P(\{\theta_i\}) \) for such trajectories. In order to make comparisons, we now recall some of the results concerning the planar Brownian motion.

We first quote the area and winding angle distributions, respectively \( P(A) \) (Lévy’s law [5]) and \( P(\theta) \) (Spitzer’s law [6]) for a particle allowed to wander everywhere in the plane:

\[
P(A) = \frac{\pi}{2t} \frac{1}{\cosh^2 \frac{\pi A}{t}}
\]

\[
P(\theta) = \frac{2}{\pi \ln t} \frac{1}{1 + \left( \frac{2 \theta}{\ln t} \right)^2}
\]

(the last one holds, in the limit \( t \to \infty \), for open curves, the final point being left unspecified).

Those two laws were obtained more than 40 years ago and since that time many refinements have been brought. For instance, in [7], the authors pointed out the importance of the small windings occurring when the particle is close to 0. Excluding an arbitrary small zone around 0, they showed that the variance \( \langle \theta^2 \rangle \) becomes finite in contrast with the Spitzer’s result, eq.(2).

On the other hand, for Brownian motion on bounded domains [8, 9], the scaling variables in the limit \( t \to \infty \), become, resp., \( A/\sqrt{t} \) and \( \theta/t \) with still an infinite variance \( \langle \theta^2 \rangle \). We close here this brief recall and start our chain study with the following set of coupled Langevin equations:

\[
\begin{align*}
\dot{z}_1 &= k(z_2 - 2z_1) + \eta_1 \\
\dot{z}_l &= k(z_{l+1} + z_{l-1} - 2z_l) + \eta_l, \quad 2 \leq l \leq n - 1 \\
\dot{z}_n &= k(z_{n-1} - z_n) + \eta_n
\end{align*}
\]

where \( k \) is the spring constant and \( \eta_m \equiv \eta_{mx} + i\eta_{my} \) a gaussian white noise:

\[
\begin{align*}
\langle \eta_m(t) \rangle &= 0 \\
\langle \eta_m(t) \eta_{m'}(t') \rangle &= 2 \delta_{mm'} \delta(t-t')
\end{align*}
\]

Introducing the complex \( n \)-vector \( \eta \), eq. (3) can be written in a matrix form:

\[
\dot{z} = -kMz + \eta
\]
where $M$ is the tridiagonal $(n \times n)$ matrix:

$$M = \begin{pmatrix}
2 & -1 & 0 & \cdots & 0 \\
-1 & 2 & -1 & \cdots & 0 \\
0 & -1 & 2 & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & 1
\end{pmatrix}$$

with an inverse given by:

$$M^{-1} = \begin{pmatrix}
1 & 1 & 1 & \cdots & 1 \\
1 & 2 & 2 & \cdots & 2 \\
1 & 2 & 3 & \cdots & 3 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
1 & 2 & 3 & \cdots & n
\end{pmatrix}$$

The eigenvalues of $M$ are:

$$\omega_j = 2 \left(1 - \cos \frac{\pi(2j-1)}{2n+1}\right), \quad 1 \leq j \leq n \quad (6)$$

With the matrix $\omega = \text{diag}(\omega_i)$, we can write:

$$\omega = R^{-1} M R \quad (7)$$
$$z = R Z \quad (8)$$

where $R$ is an orthogonal matrix and the components of $Z$ are the normal coordinates.

Let us call $P(z, z_0, t)$ the probability for the chain to go from $z_0$ at $t = 0$ to $z$ at time $t$. $P$ satisfies a Fokker-Planck equation [10]:

$$\partial_t P = \left( t \partial_z k M z + t \partial_{\bar{z}} k M \bar{z} + 2 t \partial_z \partial_{\bar{z}} \right) P \quad (9)$$

where $\partial_z$ (resp. $\partial_{\bar{z}}$) is a $n$-vector of components $\partial_{z_i}$ (resp. $\partial_{\bar{z}_i}$) and $t \partial_z$ (resp. $t \partial_{\bar{z}}$) is the transpose of $\partial_z$ (resp. $\partial_{\bar{z}}$). The solution can be written in terms of a path integral ($Dz D\bar{z} = \prod_{i=1}^n Dz_i D\bar{z}_i$):

$$P(z, z_0, t) = \text{det} \left( e^{tkM} \right) \int_{z(0)=z_0}^{z(t)=z} Dz D\bar{z} \exp \left( -\frac{1}{2} \int_0^t (\dot{z} + kM\bar{z})(\dot{\bar{z}} + kMz) d\tau \right) (10)$$

$$\equiv F(z, z_0, t).G(z, z_0, t)$$

with
\[ F(z, z_0, t) = \det \left( e^{tkM} \right) e^{-\frac{1}{2}(t^z kMz - t^z_0 kMz_0)} \]
\[ G(z, z_0, t) = \int_{z(0)=z_0}^{z(t)=z} \mathcal{D}z \mathcal{D}\bar{z} \exp \left( -\frac{1}{2} \int_0^t \left( \dot{z} \dot{\bar{z}} + \frac{1}{2} k^2 t \bar{z}M^2 z \right) d\tau \right) \]
\[ = \det \left( \frac{S}{2\pi} \right) \exp \left( -\frac{1}{2} \int_0^t \left( \dot{z} \bar{z} C z + \dot{z}_0 \bar{z}_0 C z_0 - \dot{z} \bar{z}_0 S z_0 - \dot{z}_0 \bar{z} S z \right) \right) \]
\[ H_0 = -2t \partial_\bar{z} \partial_z + \frac{1}{2} k^2 \bar{z}M^2 z \]

The matrices \( S \) and \( C \) appearing in (12) are defined as:
\[ S = kM \left( \sinh(tkM) \right)^{-1}, \quad C = kM \coth(tkM) \]

In fact, \( \mathcal{P} \), eq. (10), can be easily deduced from the gaussian distribution of \( \eta \) (use (5); \( \det(e^{tkM}) \) is simply the functional Jacobian for the change of variable \( \eta \rightarrow z \) [11]).

(12) is a generalization of the harmonic oscillator propagator [12]. It is obtained by using the normal coordinates. Furthermore, as can be easily checked, \( \mathcal{P} \) is properly normalized: \( \int d^2z d^2\bar{z} \mathcal{P}(z, z_0, t) = 1 \).

Remark that an effective measure can be built for a distinguished monomer of the chain [4]: this can be done by integrating the Wiener measure (10) over all the paths of the other monomers. The result is a complicated expression that contains, in particular, a non local part (in time) exhibiting the non-Markovian character of the process for this monomer. Nevertheless, we will show, in the sequel, that, despite this complication, we can compute some joint laws for several monomers (and \textit{a fortiori} for one monomer).

So, let us turn to the computation of the area distribution \( \mathcal{P}({\{ A_i \}}) \) for closed trajectories. Inserting the constraint
\[ \prod_{j=1}^n \delta \left( A_j - \frac{1}{4i} \int_0^t (\bar{z}_j \dot{z}_j - \dot{z}_j \bar{z}_j) d\tau \right) \]

in the Wiener measure and using \( \delta(x) = \frac{1}{2\pi} \int e^{iBx} dB \), we get the lagrangian for \( n \) particles submitted to uniform magnetic fields orthogonal to the motion plane (in addition to the harmonic interactions). Remark that, in principle, the magnetic fields are not the same for all the particles.

Introducing the \((n \times n)\) diagonal matrix \( B \) \( (B_{ij} = B_i \delta_{ij}) \), we obtain
\[ \mathcal{P}({\{ A_i \}}) = \int \left( \prod_{j=1}^n dB_j \right) \frac{e^{iB_j A_j}}{2\pi} \left( \frac{Z_B(t)}{Z_0(t)} \right) \]

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\[ \begin{align*}
Z_B(t) &= \text{Tr} e^{-tH_B} \\
H_B &= H_0 + V \\
V &= \frac{1}{2} \left(-t^2 B \partial_z + t \bar{z} B \partial_{\bar{z}}\right) + \frac{1}{8} t \bar{z} B^2 \bar{z} 
\end{align*} \]

(17)

In general, the matrices \( B \) and \( M \) do not commute and it is a difficult task to get the partition function \( Z_B(t) \). On the other hand, the distribution of the total area \( A = \sum_{i=1}^n A_i \) is obtained by taking \( B_j = B \) for all \( j \). In this case, \( B \) and \( M \) commute. Using normal coordinates and known results about the partition function of the “2D harmonic oscillator + uniform magnetic field” problem [13], we get the characteristic function of \( A \) (\( I_n \) is the \((n \times n)\) unit matrix):

\[ \frac{Z_B(t)}{Z_0(t)} = \prod_{j=1}^n \left( \frac{\cosh(tk\omega_j) - 1}{\cosh(t \sqrt{(k\omega_j)^2 + (\frac{B}{n})^2}) - \cosh(t \frac{B}{n})} \right) \]

(18)

\[ = \frac{\det \left( \cosh(tkM) - I_n \right)}{\det \left( \cosh(t \sqrt{(kM)^2 + (\frac{B}{n})^2}) - \cosh(t \frac{B}{n}) \right)} \]

(19)

(\( \omega_j \)'s are defined in (6)). By Fourier transformation, the above \( j^{th} \) factor gives:

\[ P_{\omega_j}(A) = 4 \frac{\alpha_j}{\pi} \sinh^2 \left( \frac{\alpha_j}{2} \right) \sum_{m,r=0}^\infty \left( \sqrt{\frac{\gamma_{jr}}{\beta_{jm}}} K_1(2 \sqrt{\beta_{jm} \gamma_{jr}}) + \sqrt{\frac{\beta_{jm}}{\gamma_{jr}}} K_{-1}(2 \sqrt{\beta_{jm} \gamma_{jr}}) \right) \]

(20)

where the \( K_{\pm 1} \) are modified Bessel functions.

Thus, in the general case, \( P(A) \) can be obtained by a \( n \)-convolution product of the \( P_{\omega_j} \)'s. However, we are afraid that the final result could be awkward! Nevertheless, if we consider the limit \( t \to \infty \), (18) leads to:

\[ \frac{Z_B(t)}{Z_0(t)} \sim \exp \left( -\frac{tB^2}{8k} \sum_{i=1}^n \frac{1}{\omega_i} \right) = \exp \left( -\frac{tB^2n(n + 1)}{16k} \right) \]

(21)

Then, Fourier transformation shows that, in the large \( t \) limit, \( A \) is gaussian and scales like \( \sqrt{t} \). Such a scaling is expected for all the areas \( A_i \). This is what we will demonstrate by perturbation theory. When \( t \to \infty \), we have

\[ Z_B(t) \sim e^{-tE_0(B)} \]

(22)

where \( E_0(B) \) is the ground state energy. Moreover, due to the large oscillations of the factor \( e^{iB_jA_j} \) in (16) when \( A_j \to \infty \), only small values of \( B_j \) will contribute. So, it is enough to compute \( E_0(B) \) at lowest order in \( B \). We will use the normal coordinates \( Z_i \).
The eigenstates of $H_0$ are given by [14]

$$\Psi\{m_j,n_j\}(Z_j) = \prod_{j=1}^{n} \left( \sqrt{\omega_j n_j!} \right) e^{i m_j \theta_j (\omega_j |Z_j|^2)m_j/2} L_{n_j}^{m_j} (\omega_j |Z_j|^2) e^{-i \omega_j |Z_j|^2} \right)$$

(23)

$$E_{\{m_j,n_j\}} = \sum_{j=1}^{n} (2n_j + |m_j| + 1) \omega_j$$

(24)

where $L_{n_j}^{m_j}$ is a Laguerre polynomial and the ground state is $\Psi\{0,0\}$. The perturbation $V$, (17), writes:

$$V = \frac{1}{2} \left( -i Z R^{-1} B R \partial Z + i \bar{Z} R^{-1} B R \partial \bar{Z} \right) + \frac{1}{8} t \bar{Z} R^{-1} B^2 Z$$

(25)

At first order in $V$, we get:

$$\Delta E^{(1)}_0 (B) = \int \Psi_{\{0,0\}}^* V \Psi_{\{0,0\}} = \frac{1}{8k} \text{Tr} (B^2 M^{-1}) = \frac{1}{8k} \sum_{m=1}^{n} m B_m^2$$

(26)

Quadratic terms in $B$ will also be produced at second order in $V$. The non-vanishing contributions will come out from the transitions from the ground-state to the states \{m_j = \pm 1, m_l = \mp 1, m_i = 0 if i \neq j, l\}, \{n_k = 0\}. The computation gives:

$$\Delta E^{(2)}_0 (B) = -\frac{1}{16k} \sum_{m,m'=1}^{n} B_mB_{m'} \sum_{j \neq l} R_{ml} R_{mj} R_{m'l} R_{m'j} \left( \frac{\omega_j + \omega_l}{\omega_l + \omega_j} \right)$$

$$= -\frac{1}{8k} \sum_{m=1}^{n} m B_m^2 + \frac{1}{2k} \sum_{m,m'=1}^{n} B_m D_{m,m'} B_{m'}$$

(27)

with:

$$D_{m,m'} = \frac{1}{4} \int_0^\infty \left( e^{-\gamma M} \right)_{m,m'}^2 d\tau + \frac{1}{8} \sum_{l=1}^{n} \frac{R_{ml}^2 R_{m'l}^2}{\omega_l}$$

(29)

So, to lowest order in $B$, we get:

$$\frac{Z_B(t)}{Z_0(t)} \sim \exp \left( -\frac{t}{2k} \sum_{m,m'=1}^{n} B_m D_{m,m'} B_{m'} \right)$$

(30)

As can be easily checked, (21) is recovered if we set $B_m = B$, $\forall m$.

With (16), we arrive at the probability distribution:
\[ P(\{A_i\}) = \left( \frac{k}{2\pi t} \right)^{n/2} \frac{1}{\sqrt{\det D}} \exp \left( -\frac{k}{2t} \sum_{m,m'=1}^{n} A_m(D^{-1})_{m,m'} A_{m'} \right) \] (31)

Thus, we observe that the areas \( A_i \) are correlated gaussian variables and that they scale like \( t^{1/2} \) as expected. For the special case \( n = 2 \), we have:

\[ P(A_1, A_2) = \sqrt{\frac{5}{3}} \frac{2k}{\pi t} \exp \left( -\frac{2k}{9t} \left( 23A_1^2 - 14A_1A_2 + 8A_2^2 \right) \right) \] (32)

The width of \( A_2 \) is larger than the one of \( A_1 \): this is related to the fact that the second particle is, in average, farther from 0 than the first one. So, it sweeps larger areas.

Now, going to the winding angles \( \{\theta_i\} \) around 0, we proceed as before and insert the constraint

\[ \prod_{j=1}^{n} \delta \left( \theta_j - \frac{1}{2i} \int_{0}^{t} \left( \frac{z_j \dot{z}_j - \bar{z}_j \dot{\bar{z}}_j}{z_j \bar{z}_j} \right) d\tau \right) \] (33)

in the Wiener measure. We are now faced to the problem of \( n \) harmonically bound particles submitted to the magnetic fields of point-like vortices located at the origin. The corresponding hamiltonian is:

\[ H_{\lambda} = H_0 + W \] (34)

\[ W = \sum_{i=1}^{n} \lambda_i \left( \frac{1}{z_i} \partial_{z_i} - \frac{1}{\bar{z}_i} \partial_{\bar{z}_i} \right) + \sum_{i=1}^{n} \frac{\lambda_i^2}{2z_i \bar{z}_i} \] (35)

and the distribution \( P(\{\theta_i\}) \) is given by:

\[ P(\{\theta_i\}) = \int \left( \prod_{j=1}^{n} \frac{d\lambda_j}{2\pi} e^{i\lambda_j \theta_j} \right) \left( \frac{Z_{\lambda}(t)}{Z_0(t)} \right) \] (36)

Studying the limit \( t \to \infty \), we cannot develop directly as before a perturbation theory with \( W \): this is because of the last term in \( W \) that leads to a singular perturbation [9]. Due to this term, all the eigenfunctions of \( H_{\lambda} \) must vanish in 0 at least as \( \prod_{i=1}^{n} (z_i \bar{z}_i)^{|\lambda_i|/2} \) (\( \equiv U \)). So we redefine those eigenfunctions [9]:

\[ \Psi = U \tilde{\Psi} \] (37)

The new hamiltonian acting on \( \tilde{\Psi} \) is:

7
\[ \vec{H} = H_0 + \vec{W} \]
\[ \vec{W} = \sum_{i=1}^{n} \left( (\lambda_i - |\lambda_i|) \frac{1}{z_i} \partial_{\bar{z}_i} - (\lambda_i + |\lambda_i|) \frac{1}{\bar{z}_i} \partial_{z_i} \right) \] (38)

That time, we can compute \( \Delta E_0(\lambda) \) perturbatively and it will appear that only first order is necessary. Integrals of the form

\[ \int e^{-\frac{1}{2} \xi M \xi} \frac{1}{z_i} \partial_{\bar{z}_i} e^{-\frac{1}{2} \xi M \xi} d\xi d\bar{\xi} \]

are involved. Integrating by parts and using \( \partial_{\bar{z}_i} \left( \frac{1}{z_i} \right) = \pi \delta (z_i) \), we get, after some algebra:

\[ \Delta E_0(\lambda) = k \sum_{j=1}^{n} \frac{|\lambda_j|}{(M^{-1})_{jj}} = k \sum_{j=1}^{n} \frac{|\lambda_j|}{j} \equiv \sum_{j=1}^{n} \mu_j |\lambda_j| \] (41)

So, for the winding angle distribution, we obtain:

\[ P(\{\theta_i\}) = \int \left( \prod_{j=1}^{n} \frac{d\lambda_j}{2\pi} e^{\lambda_j \theta_j} \right) e^{-t \sum_{j=1}^{n} \mu_j |\lambda_j|} \]
\[ = \prod_{j=1}^{n} \left( \frac{1}{\pi \mu_j t} \right) \left( \frac{1}{1 + (\frac{\theta_j}{\mu_j t})^2} \right) \] (43)

At large times, the winding angles are uncorrelated, they scale like \( t \) and are distributed according to Cauchy laws. The variance \( \langle \theta_j^2 \rangle \) is infinite: this is, of course, due to the “small windings” occuring in the vicinity of the origin as will be seen explicitly at the end of this paper.

Moreover, we observe that \( \theta_j \) scales like \( \mu_j \), i.e. like \( 1/j \). This is reasonable because, when \( j \) increases, the considered particle is, in average, farther from 0 and, consequently, its winding angle must decrease. What is somewhat unexpected is such a simple dependence of \( \theta_j \) on \( j \).

We also addressed the problem of winding angles around \( n \) different points of complex coordinates \( b_l, l = 1, \ldots n \).

\( \theta_j' \) being the angle wound by the particle \( j \) around the point \( b_j \), we obtained for the set of variables \( \{\theta_j'\} \) the same joint law as (43) except for the change of \( \mu_j \) into \( \mu_j' \):

\[ \mu_j' = \mu_j e^{-\mu_j |b_j|^2} \] (44)
Owing to the rotationnal symmetry breaking when \( b_j \neq 0 \), the winding angles \( \theta'_j \) are statistically reduced by the factor \( e^{-\mu_j|b_j|^2} \). Nevertheless, even for large \( |b_j|'s \), the variance \( \langle (\theta'_j)^2 \rangle \) is infinite.

Setting all the \( b_j \)'s to zero, we recover (43). This is what we will consider now and assume that we count the winding angles \( \theta_j \) only when \( |z_j| > r_0 \) (i.e. the so-called “big windings” [7]). Still when \( t \to \infty \), the perturbation \( W \), eq.(35), can now be used because \( \lambda_j = 0 \) when \( |z_j| < r_0 \). At first order in \( W \), the linear contributions in \( \lambda_j \) will cancel. In the limit of a small, but finite \( r_0 \), we get, for the remaining contribution:

\[
\Delta E_0^{(1)}(\lambda) \sim k|\ln r_0| \sum_{j=1}^{n} \frac{\lambda^2_j}{j}
\]  

(45)

The quadratic contributions in the \( \lambda_j \)'s coming out from the second order in \( W \) will be finite (thus subleading) when \( r_0 \to 0^+ \). Finally, we get for the big winding angles asymptotic distribution:

\[
P(\{\theta_j\}) = \prod_{j=1}^{n} \sqrt{\frac{j}{4\pi tk|\ln r_0|}} \exp\left(-\frac{j}{4tk|\ln r_0|} \theta_j^2 \right)
\]  

(46)

In this limit, the variables \( \theta_j \) are uncorrelated: the correlations get smaller and smaller when \( r_0 \) decreases. They are now gaussian and scale like \( \sqrt{t|\ln r_0|/j} \). Their variance grows to infinity when \( r_0 \) goes to 0, showing the increasing contribution of the small windings around 0.

To summarize, we have computed explicitly the asymptotic joint laws for the areas (that scale like \( \sqrt{t} \)) and for the winding angles (that scale like \( t \) when no critical region is excluded). The scaling variables we have got compare well with those involved in the Brownian motion on finite domains: this is not so surprising since the chain is bound to a fixed point.

Moreover, we have shown that physical interactions between particles (harmonic interactions here) can lead to statistical correlations (case of the areas) or not (case of the winding angles): it depends on the quantity we consider.

In a forthcoming paper [15], we will study the statistical properties of the free Rouse chain. We will especially show that the areas and winding angles distributions are very different from those presented in this work. This is essentially due to the translation invariance that holds when the chain is free.

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