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Polymerisation process and Brownian yet non Gaussian
diffusion

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Abstract

More and more single molecule experiments are reporting the observance of a Brownian-yet-non-Gaussian diffusion.

In numerous situations the evidence is that the presence of a complex environment "acts" on the probability density function, making it no more a Gaussian one. On the contrary, there is no alteration of the linear growth with time of the second moment of the diffusing particle displacement. A microscopic foundation mechanism for this phenomenon is presently lacking.

We start from a polymer immersed in a bath of monomers, that we claim to be an appropriate setting to show this evidence: so, the initial point is a polymerisation process which modifies the size of the initial molecule. We aim at solving the associated master equation for both the steady state and transient behaviour of this polymerisation process. For this part the main investigation tools employ mathematical methods. Indeed, the connection with queuing theory is critically important for the development of the solution that is presented.

By relying on the results of this analytic investigation, we go on with the analysis of the non-Gaussian characteristics by means of the kurtosis of the x coordinate of the centre of mass, κ_X : here we succeed in showing that its calculation can be simplified in terms of a specific stochastic process and so we take the first steps into that computation.

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Introduction

There is a growing number of single molecule experiments in soft matter and biological systems which find out that some anomalous behaviour is a common characteristic shared by many systems.

This behaviour [...] occurs quite robustly in a wide range of systems, including beads diffusing on lipid tubes or in networks, the motion of tracers in colloidal, polymeric or active suspensions and in biological cells, as well as the motion of individuals in heterogeneous populations such as nematodes. Similar effects on the PDF are also observed in the anomalous diffusion of labeled messenger RNA molecules in living *E.coli* and *S.cervisiae* cells. [7]

We claim that even a polymer in a chemostated monomer bath – that is actually undergoing polymerisation/depolymerisation – offers a natural and much easier setup to such peculiar diffusion if its centre of mass is under tracking. In this case, the mean square displacement of the molecule still grows linearly with time – as expected from a Brownian diffusion – but the associated probability density function is actually a non-Gaussian one. The latter is then a strange aspect of the dynamics that is of great interest. Existing theories are mesoscopic ones bringing up the subordination of diffusivities, but a “microscopic” description is currently lacking. So, we attempt at presenting one here, providing a view that encloses both water action in Brownian motion and polymerisation in a birth-death Markovian process.

The first section offers some general information on Brownian motion, stochastic processes and polymers, which are macro-molecules made up by monomers, that are all held together by covalent bonds. Their number represents the size of the polymer and varies from tens up to hundreds of thousands. This work focuses specifically on linear homopolymers, which are characterised by only one well defined type of sub-unit and form an open chain.

In our case, the polymerisation process (which happens when a three-unit initial polymer is immersed in a bath of monomers) is suitably addressed by a specific master equation. We solve it, both in the steady state and transient case: in this part mathematical methods are the primary instrument. In fact, queuing theory is crucial for the development of the solution presented in this thesis. It allows to compute explicitly the solution for the probability of the polymer size to be $N = n_0$ in the *time-dependent* case. A significant number of «properties of practical importance»[1] need the explicit form of the solution for transient behaviour: consequently, we present one of its equivalent rewriting in an integral “version”, as proposed by P. M. Morse in 1955.

From this point, we move to the non-Gaussian characteristics of the diffusion. As for this topic, the introduction of the kurtosis, κ , is the key to analyse and quantify the anomalous behaviour of those experimental data which show strong evidence of a significant deviation from the normal distribution if in presence of a complex environment. We end by rewriting the expression for κ along the x axis by means of $S(t)$, a new stochastic process, and start evaluating the first needed calculations for the expression of κ_X .

Polymer dynamics and polymerisation process

1.1 Stochastic processes

The mathematics underlying many physical processes is a generalisation of ordinary calculus, in which stochastic processes play a really relevant role [6].

A stochastic process¹ is denoted by $\{X(t), t \in T\}$ ² and consists of a set of random variables; the possible values assumed by $X(t)$ creates its state space. These random variables of $X(t)$ are themselves indexed by a set T , which is the parameter space of the process. $X(t)$ represents the state of the process at the time t . The set T could be either countable – in which case the process is a *discrete-time* one – or consisting of a collection of finite or infinite intervals on the time axis – referred as *continuous-time* one. Correspondingly, the behaviour of the state space causes the process to be a continuous process or a discrete one: the next sections will focus on both, analysing respectively Brownian motion and then Markov chains. Finally, we remind that a stochastic process is stationary if $(X(t_2 + s) - X(t_1 + s))$ has the same distribution as of $X(t_2) - X(t_1) \forall t_i \in T$ and $s > 0$ [5].

1.1.1 Brownian motion: Einstein’s and Langevin’s approaches

The discover of the Brownian motion dates back to 1827: botanist Robert Brown, while analysing microscopic life, observed very small particles of pollen moving in the liquid he was looking at in the microscope. But it was Einstein who firstly solved the issue of explaining it in 1905: he claimed that the peculiar pattern of motion of the particles was due to countless, constant collision with water molecules. Neither the force vector associated with water “bombardment”, nor the location of the pollen particle hit by water remained constant over time: this random characteristic implied “naturally” a stochastic description. In his approach, time is considered to increase in steps, Δt ; these, although being macroscopically small, are microscopically large enough to let the collision between many fluid molecules and the Brownian particle happen. Changes in the position of the Brownian particle evaluated during subsequent steps Δt turn out to be statistically independent.

Let $p(x, t)$ be a function of x -position and time, so that $p(x, t)dx$ is equal to the probability of finding a Brownian particle in $x \in [x, x + dx]$ at time t . The function $p(x, t)$ should satisfy the following, also referred as the “diffusion equation”

$$\frac{\partial p(x, t)}{\partial t} = D \frac{\partial^2 p(x, t)}{\partial x^2} \quad (1.1)$$

where D is a constant, called the “diffusion coefficient”, defined by means of the mean-square displacement of the particle in time Δt over $2\Delta t$. A phenomenological definition of D is

$$j_x(x, t) = -D \frac{\partial p(x, t)}{\partial x} \quad (1.2)$$

here $j_x(x, t)$ is the probability flux, straightforward related to the flux of Brownian particles in the x direction.

¹An example of this could be the number of customers in a queuing system at any time, or the value of the temperature recorded on different days of the same year.

²Usually, a function X of time t is addressed as a “process”.

The fundamental linker between these two equations is the equality

$$\frac{\partial p(x, t)}{\partial t} = -\frac{\partial j_x(x, t)}{\partial x}$$

also referred as the probability conservation equation (coming from particle conservation); it permits one to get Eq. (1.1) by using Eq. (1.2).

Einstein's solution of Eq. (1.1) resulted in a Gaussian distribution of the number of particles in the unit volume:

$$p(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (1.3)$$

with variance $\sigma^2 = 2Dt$. It follows that

$$\langle x^2 \rangle = \int_{\mathbb{R}} x^2 p(x, t) dx = 2D(t) \quad (1.4)$$

where t should be *large enough*: this restriction arises from Einstein's coarse-grained time assumption. A 3D analysis would – obviously – provide

$$\langle \vec{R}^2(t) \rangle = 6D(t). \quad (1.5)$$

This condition of linear dependence of $\langle x^2 \rangle$ – or $\vec{R}^2(t)$ – with respect of t permits to say that the pattern of motion is Brownian and the system is in a diffusive state.

In 1908 Paul **Langevin** offered a quite different perspective pursued by focusing on the velocity of the molecule instead of its position. He started from classical mechanics, arguing that the force to which the Brownian particle of mass m was subjected can be resolved into two components:

1. a drag, dissipative force of the form $-\gamma v_x(t)$ (γ is a positive drag coefficient and $v_x(t)$ is the time-dependent component of the velocity along the x axis);
2. a force $F(t)$ that is temporally uncorrelated, randomly fluctuating and with zero-mean, since the fluid is supposed to be homogeneous and isotropic.

Then he wrote Newton's second law:

$$m \frac{dv_x(t)}{dt} = -\gamma v_x(t) + F(t). \quad (1.6)$$

Under overdamped conditions, the drag term usually dominates the inertial one obtaining thus

$$\frac{dv_x(t)}{dt} = \frac{F(t)}{\gamma}$$

or

$$dx(t) = \frac{F(t)dt}{\gamma} = \sqrt{2D} dB(dt)$$

where $B(t) = \mathcal{N}(0, 1)$ is a Gaussian stochastic process with zero mean and unit variance, also called "Brownian motion".

1.1.2 Markovian chains and master equation

Whereas in the previous section we focused our attention on continuous stochastic processes in continuous time, here we shift to stochastic processes with a discrete state space, still addressing continuous time. In fact, these will be employed to describe polymerisation, which is proved to be one of this kind. From now on, we adopt this notation: a stochastic process will be addressed with $N(t) = n$ and we will refer to n_m as the value of N at time t_m , that is $n_m = N(t_m)$.

A discrete, stochastic process in continuous time is said to be a *Markovian* if it is stationary and satisfies

$$P(n_m|n_{m-1}; n_{m-2}; \dots; n_0) = P(n_m|n_{m-1}), \text{ with } : t_0 \leq t_1 \leq \dots \leq t_m \quad (1.7)$$

the latter expresses the memory-less property: the evolution just depends on the immediately prior condition. *Birth-death* processes are a subset of continuous time Markov process in which the transition takes place from a given state only to the nearest “neighbours”: the polymer size varies its size by finite “steps” of ± 1 sub-unit³. We refer to a *birth* as the addition of a sub-unit to the monomer and to a *death* as its the deletion. Lastly, the following

$$P(n, t|n_0, t_0) := \text{Probability}\{N(t) = n, N(t_0) = n_0\}, \forall t_0 < t \quad (1.8)$$

is the definition of the conditional distribution function.

If we have to deal with a system that is characterised by a probabilistic combination of states, master equations are especially helpful. A master equation outlines the continuous time evolution of the probability of a system to be in each one of the discrete states and generally consists of a set of first-order differential equations. The following is its the most general form

$$\partial_t P(n, t|n_0, t_0) = W(\nu|n - \nu, t)P(n - \nu, t|n_0, t_0) - W(-\nu|n, t)P(n, t|n_0, t_0). \quad (1.9)$$

W is a non-negative function called “stepping function”. It expresses the probability of a step ν , whose values can be $\nu = \pm 1$, and it has the dimension of the inverse of a time, that is: $[W_{\pm}] = \mathbf{T}^{-1}$.

1.2 Polymerisation and polymer dynamics

By establishing contact with queuing theory, we present a general description of the stochastic nature of the polymerisation process, since a simple idea to provide the so called “diffusion of diffusivities effects” with a microscopic foundation – which will be analysed in the second part – comes from polymer physics. In fact, for polymerisation, this peculiar diffusion is connected to the diffusion of the centre of mass of the macro-molecule.

Polymers are macro-molecules made up by several monomers, that are all held together by covalent bonds. The simplest model which describes these molecules is the Gaussian chain (see [10] and [4]). Considering a generic, linear polymer of size N – namely consisting of $N = n$ sub-units – we can change the length of its chain by adding or deleting monomers at each end.

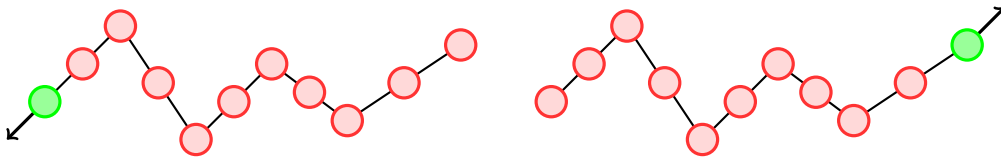


Figure 1.1: An elementary representation of the deletion of side-monomers for a homopolymer.

This process is governed by *association/dissociation* constants, k_+ and k_- , which in turn depend on the chemistry of the environment. The following equation

$$A_N \pm A_1 \rightleftharpoons A_{N\pm 1} \quad (1.10)$$

represents a chemical reaction where A_N is a chain of N sub-units. We choose an initial three-units-polymer ($N(t = 0) = n_0 = 3$): this mathematical “shifting” of N is not just a choice dictated by convenience, but has a physical reason for being; in fact, $N = 1, 2$ would create an asymmetric process which we do not like: the addition or deletion of sub-units during polymerisation should always include both ends of the macro-molecule.

³These stochastic processes are characterised by discrete random variables: the leap from the state n to a different state, n' , is instant and happens at a specific time t' : during all the time interval $\Delta t = (t' - t)$ the state remains n .

We now immerse it in a thermal, infinite monomer bath at temperature T . This bath also acts as a chemical reservoir and is thus characterised by a fixed number monomer concentration c . Finally, we define $\rho := \lambda/\mu = k_+c/k_-$, that is in “queuing language” the ratio of the “rate of input” λ and the “rate of service”, μ .

Polymerisation may be modelled as a Markovian birth-death stochastic process: “Markovian birth-death” due to the only possibilities for the polymer size N to remain unchanged ($N = n$) or increase/decrease by one unit ($N = n \pm 1$) whereas “stochastic” for the fact that there is no way to determine the exact moment in which two monomers are detached or added to the chain: there is no determinism, we compute only probabilities. But the Markovian nature of polymerisation implies that $W(\nu)$ satisfies

$$W(\nu|n, t) := W(\nu|n) = \begin{cases} W(1|n) = W_+(n) := \lambda = 2k_+c & n \geq 1 \\ W(-1|n) = W_-(n) := \mu = 2k_+ & n \geq 3 \end{cases}$$

where $W_{\pm}(n)dt$ represents the probability that a polymer being in the state $N(t) = n$ at time t jumps in the state with $N(t) = n \pm 1$ during the time interval $[t, t + dt)$; the factor “2” is due to addition/deletion of sub-units to both ends of the chain. Moreover, stepping functions satisfy the physical condition $W_+(0) = 0$, $W_-(0) = 1$, since we accept only non-negative physical states. Finally, there is also the constraint $W_-(1) = W_-(2) = 0 \forall t$.

All of this being considered, a master equation can be specifically derived in the case of polymerisation, using λ and μ (or equivalently, k_+ and k_-) instead of $W_{\pm}(n)$. Let $P(n, t) = P(N(t), t)$ with $N(t) = n$, then

$$\begin{cases} P(n, t + \Delta t) = \mu P(n + 1, t)\Delta t + \lambda P(n - 1, t)\Delta t + P(n, t)(1 - \lambda\Delta t - \mu\Delta t) + o(\Delta t), n > 1 \\ P(0, t + \Delta t) = \mu P(1, t)\Delta t + P(0, t)(1 - \lambda\Delta t - \mu\Delta t) + o(\Delta t), n = 1 \end{cases} \quad (1.11)$$

bringing $P(n, t)$ and $P(0, t)$ to the left, collecting and dividing both members by Δt , Eq. (1.11) can be written like this

$$\begin{cases} \frac{P(n, t + \Delta t) - P(n, t)}{\Delta t} = P(n, t)\mu + P(n - 1, t)\lambda - P(n, t)(\lambda + \mu) + \frac{o(t)}{\Delta t}, n > 1 \\ \frac{P(0, t + \Delta t) - P(0, t)}{\Delta t} = P(1, t)\mu - P(0, t)\lambda + \frac{o(t)}{\Delta t}, n = 1. \end{cases} \quad (1.12)$$

taking $\lim_{\Delta t \rightarrow 0}$ one obtains the time-derivative of $P(n, t)$ for the left side, considering that $\frac{o(t)}{\Delta t} = 0$

$$\begin{cases} \frac{dP(n, t)}{dt} = \mu P(n + 1, t) + \lambda P(n - 1, t) - P(n, t)(\lambda + \mu), n > 1 \\ \frac{dP(0, t)}{dt} = \mu P(1, t) - \lambda P(0, t), n = 1 \end{cases} \quad (1.13)$$

In Eq. (1.13) we have implicitly assumed the change of variables as: $n \rightarrow n - 3$ in order to maintain the – mathematically convenient – condition $n \geq 1$.

1.2.1 Rouse model for polymer dynamic

Among the variety of models which have been formulated both to describe the Brownian motion of the centre of mass of polymers immersed in a heat bath and to calculate its dynamical properties, we choose the so-called Rouse model.

The latter is as simple as possible in order to concentrate on physical concepts and not on mathematical issues and it is built on a Gaussian⁴ one; moreover, this model relies on the coarse graining of the polymer chain into subsections that are large enough to show rubber-like elastic behaviour, so the underlying physics it is quite easy.

⁴The Gaussian chain is used for the modelling of equilibrium properties of polymers, see [10] for details.

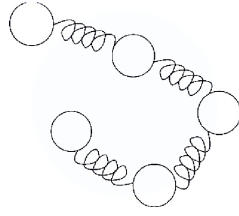


Figure 1.2: Stylised picture for the Rouse model of a polymer. Source [9].

A polymer immersed in a liquid moves and this motion causes a velocity field to emerge in the liquid, but to first order this can be neglected: water – or a different solvent – becomes an indifferent ether that is responsible only for the friction. Also, each bead (which could be either a monomer or a bigger portion of the chain) will be subjected both to a certain friction and to random forces. Now, let \vec{R}_i be the position vectors connecting the origin to the n -th monomer. Each monomer interacts with his “neighbours” *via* harmonic potential: let b be the rest length of the ideal springs connecting monomers one to each other. Defining $\vec{r}_n := \vec{R}_n - \vec{R}_{n-1}$, it holds true

$$\langle (r_i)^2 \rangle = b^2 \quad (1.14)$$

and the potential energy equals

$$U(\vec{R}_n) = \frac{3}{2b^2} k_B T \sum_{n=1}^N \left(\vec{R}_n - \vec{R}_{n-1} \right)^2. \quad (1.15)$$

Considering only one bead and keeping all the other fixed, we have a Gaussian equilibrium distribution for \vec{R}_n

$$G(\vec{R}_n) = C \exp \left(-\beta \frac{3k_B T}{2b^2} (\vec{R}_n - \vec{R}_{n-1})^2 - \beta \frac{3k_B T}{2b^2} (\vec{R}_{n+1} - \vec{R}_n)^2 \right). \quad (1.16)$$

Each degree of freedom of monomers contributes to energy with a factor $k_B T/2$, so in 3D, the Equipartition theorem implies that we would have $3k_B T/2$.

At this point, one could write the Langevin equation describing the motion of the bead⁵ [3] or derive the equation of motion for \vec{R}_{CM} by integrating

$$\frac{d\vec{R}_{CM}}{dt} = \frac{1}{N} \sum_{n=0}^{N-1} \vec{f}_n \quad (1.17)$$

where f_n is the statistical force [3], [10]. The result is

$$\vec{R}_{CM}(t) = \vec{R}_{CM}(0) + \int_0^t d\tau \frac{1}{N} \sum_n \vec{f}_n(\tau) \quad (1.18)$$

Bearing in mind that the probability density function of R_{CM} is a normal distribution that can be assumed to be a *zero mean* one⁶ with variance $\sigma^2 = 2Dt$, one gets the following result

$$\langle \left(\vec{R}_{CM}(t) - \vec{R}_{CM}(0) \right)^2 \rangle = \left\langle \int_0^t d\tau \int_0^t d\tau' \left(\frac{1}{N} \sum_n \vec{f}_n(\tau) \right) \cdot \left(\frac{1}{N} \sum_m \vec{f}_m(\tau') \right) \right\rangle = 6D_{CM}t \quad (1.19)$$

For the diffusion coefficient it holds true that $D_{CM}(N) = D_0/(N)^\alpha$ where D_0 is the diffusion coefficient of each sub-unit and α is a real parameter whose value depends on the chosen polymer model, that is $\alpha = 1$ for Rouse’s one. From now on, for sake of simplicity, we choose to refer to the x component of the random vector $\vec{R}_{CM}(t) := (X_{CM}, Y_{CM}, Z_{CM})$.

⁵We will not use them for this work, so they are not reported here.

⁶In $t = 0$ the centre of mass of the chain is located on the origin of the coordinate system.

Brownian non-Gaussian polymer diffusion

Brownian yet non Gaussian diffusion is one in which Eq. (1.1) does not hold: this kind of process is reported in experiments “following” the motion of the position of the centre of mass – \vec{R}_{CM} – of the macro-molecule in complex biological contexts. The following two sections will draw attention to the analysis of this peculiar diffusion on the basis of the details which were stressed out in the previous sections.

2.1 Solution of the master equation

Eq. (1.5) shows that $\langle(\vec{R}_{CM})^2\rangle$ is directly proportional to time t and D_{CM} . Moreover, under over-damped conditions, it is valid the following¹

$$d\vec{R}_{CM}(t) = \sqrt{2D(N)}d\mathbf{B}(dt) \quad (2.1)$$

where, as previously seen in section 1.1.1, $\mathbf{B}(t)$ is a Brownian motion. Specifically, if a polymer chain (its specific characteristic have been explained in section 1.2) undergoes a polymerisation process the size N becomes a random variable that changes over time: $N \rightarrow N(t)$ and, consequently, so does $D(N) \rightarrow D(N(t))$. By exploiting the connection with queuing theory, we aim here at finding both the *time-dependent* and *stationary* solutions for Eq.(1.13) that is we compute explicitly the solution for the probability of the polymer size to be $N = n_0$ in the stationary and *time-dependent* case of the Markov chain describing the polymerisation process.

Before we start, is relevant to mention that methods that will be exposed here are two out of many: one could apply different algorithms both for the stationary case (it could be the mathematical induction) and the *time-dependent* one (in this case see [5] for examples of other methods).

2.1.1 General approach

Eq.(1.13) is made up by differential-difference equations: differential equations in t and difference ones in n .

One possibility to manage the differential part is by using the Laplace transform: for this reason, it is useful to introduce a general notation, pointing out that we will refer to quantities that depend on the two couples (n, t) and (n_0, t_0) . The initial conditions $(n_0$ and $t_0)$ will not be made explicit in equations in order not to complicate notation.

Considering a sequence a_n with $n \in \mathbb{N}$ and $a_n \in \mathbb{R}$, the generating function of this sequence has the following definition²

$$G(z) := \sum_{n=0}^{\infty} (a_n z^n) \quad (2.2)$$

with $z \in \mathbb{C}$. If $\{a_n\}$ is the probability function of a non-negative, discrete random variable $N(t)$, then $G(z)$ is a *probability generating function*, that is analytic and converges $\forall |z| \leq 1$. For the polymerisation process we have

$$G(z, t) := \sum_{n=0}^{\infty} P(n, t) z^n \quad (2.3)$$

¹This form is the 3D one, in section 1.1.1 we also presented its one dimensional, “ x component” form.

²Here the notation $G(z)$ is used in a general way, for the definition (and comes from the word “generating”).

it is easy to obtain, for example that

$$1 = \langle N^0(t) \rangle = \sum_{n=0}^{\infty} P(n, t) n^0 = \lim_{z \rightarrow 1} G(z, t)$$

or

$$\langle N^1(t) \rangle = \sum_{n=0}^{\infty} P(n, t) n^1 = \lim_{z \rightarrow 1} \left(z \frac{\partial G(z, t)}{\partial z} \right)$$

since repeated differentiation of $G(z, t)$ yields the factorial moments of $N(t)$. All these relations are also valid for $G^*(z) := \sum_{n=0}^{\infty} P^*(n) z^n$ where $\lim_{t \rightarrow \infty} P(n, t) := P^*(n)$ is the stationary distribution³.

Finally, we define what follows

$$\begin{aligned} \tilde{G}(z, \theta) &:= \int_0^{\infty} e^{-\theta t} G(z, t) dt; \\ \tilde{P}(n, \theta) &:= \int_0^{\infty} e^{-\theta t} P(n, t) dt \end{aligned} \tag{2.4}$$

where the tilde indicates the application of the Laplace transform. We make here two assumptions:

- There are initially i monomers;
- $P(n, t)$ is one of bounded exponential growth⁴.

We now wish to obtain the equation for the time evolution of $G(z, t)$. Let's start by considering the left member of the first equation in (1.13), multiply it by z^n and sum from $n = 1$ to ∞

$$\sum_{n=1}^{\infty} \frac{dP(n, t)}{dt} z^n. \tag{2.5}$$

To this we add and subtract $dP(0, t)/dt$:

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{dP(n, t)}{dt} z^n &= \sum_{n=0}^{\infty} \frac{dP(n, t)}{dt} z^n - \frac{dP(0, t)}{dt} = \\ &= \frac{\partial G(z, t)}{\partial t} - \frac{dP(0, t)}{dt} = \\ &= \frac{\partial G(z, t)}{\partial t} + \lambda P(0, t) - \mu P(1, t). \end{aligned} \tag{2.6}$$

Multiplying the latter once again by z we get

$$z \left(\sum_{n=1}^{\infty} \frac{dP(n, t)}{dt} z^n \right) = z \frac{\partial G(z, t)}{\partial t} + z (\lambda P(0, t) - \mu P(1, t)). \tag{2.7}$$

We want now to rewrite the left hand side of Eq. (2.7) in a new form. Using again Eq. (1.13) we have

$$z \left[\sum_{n=1}^{\infty} \mu P(n+1, t) z^n + \lambda P(n-1, t) z^n - (\lambda + \mu) P(n, t) z^n \right]. \tag{2.8}$$

³This definition means also that a different way to express $G^*(z)$ is

$$\lim_{t \rightarrow \infty} G(z, t) := G^*(z).$$

⁴The Laplace Transform of a generic function $f(t)$ is:

$$\tilde{f}(s) := \int_0^{\infty} e^{-st} f(t) dt$$

and a sufficient condition for its existence is that $f(t)$ has a bounded exponential growth, meaning that there exists numbers μ and γ , such that for all $t > 0$, $|f(t)| < \mu e^{\gamma t}$.

Let us define A , B and C as the quantities below

$$\begin{aligned} A &:= \sum_{n=1}^{\infty} \mu P(n+1, t) z^{n+1} = \mu \left[\sum_{n=-1}^{\infty} P(n+1, t) z^{n+1} - P(1, t) z - P(0, t) \right] = \\ &= \mu G(z, t) - \mu P(1, t) z - \mu P(0, t), \end{aligned}$$

$$B := \sum_{n=1}^{\infty} \lambda P(n-1, t) z^{n+1} = \lambda \left[\sum_{m=0}^{\infty} P(m, t) z^{m+2} \right] = \lambda z^2 G(z, t), \text{ in which we define } m := n-1,$$

$$\begin{aligned} C &:= - \sum_{n=1}^{\infty} (\lambda + \mu) P(n, t) z^{n+1} = -z \left[\sum_{n=0}^{\infty} (\lambda + \mu) P(n, t) z^n - (\lambda + \mu) P(0, t) \right] = \\ &= z(\lambda + \mu) P(0, t) - z(\lambda + \mu) G(z, t), \end{aligned}$$

so that Eq. (2.8) simplifies to $(A+B+C)$, that equals

$$A + B + C = \mu G(z, t) - \mu P(1, t) z - \mu P_0(t) + \lambda z^2 G(z, t) + z(\lambda + \mu) P(0, t) - z(\lambda + \mu) G(z, t). \quad (2.9)$$

For the first equation of (1.13) we have obtained (2.7) = (2.8) that is

$$z \frac{\partial G(z, t)}{\partial t} + z(\lambda P(0, t) - \mu P(1, t)) = A + B + C. \quad (2.10)$$

Rearranging and simplifying Eq. (2.10) we have

$$z \frac{\partial G(z, t)}{\partial t} = G(z, t) [\lambda z^2 - z(\lambda + \mu) + \mu] + \mu P(0, t)(1 - z). \quad (2.11)$$

Now we compute the roots for the polynomial and rearrange: $\lambda z^2 - z(\lambda + \mu) + \mu = (1 - z)(\mu - \lambda z)$, so (2.11) becomes

$$z \frac{\partial G(z, t)}{\partial t} = (1 - z) [(\mu - \lambda z) G(z, t) - \mu P(0, t)]. \quad (2.12)$$

Equation (2.12) contains the equation we aimed at the beginning.

2.1.2 Steady state behaviour with the generating function method

We want to evaluate now $\lim_{t \rightarrow \infty} P(n, t) := P^*(n)$. This follows directly from the general approach presented above: one takes the limit of both sides of (2.12) to get to

$$0 = (\mu - \lambda z) G^*(z) - \mu P^*(0). \quad (2.13)$$

From (2.13)

$$G^*(z) = \frac{\mu P^*(0)}{\mu - \lambda z} = \frac{P^*(0)}{1 - \rho z}. \quad (2.14)$$

Since $\lim_{z \rightarrow 1} G^*(z) = 1$, we can obtain an expression for $P^*(0)$: $P^*(0) = 1 - \rho$, so that $G^*(z) = 1 - \rho / (1 - \rho z)$.

Lastly, applying ‘‘backwards’’ the geometric series formula

$$G^*(z) = \frac{1 - \rho}{(1 - \rho z)} = (1 - \rho) \left(\sum_{n=0}^{\infty} \rho^n z^n \right). \quad (2.15)$$

Remembering the definition of $G^*(z)$:

$$\sum_{n=0}^{\infty} P^*(n) z^n = \left(\sum_{n=0}^{\infty} (1 - \rho) \rho^n z^n \right) \quad (2.16)$$

we get to the final solution for the stationary case:

$$P^*(n) = U(n)(1 - \rho)\rho^n \quad (2.17)$$

note that we replaced the condition ($n \geq 1$) by multiplying by $U(n)$, the discrete unit step function. The sequence $P^*(n)$ is a probability distribution only for $\rho < 1$, since

$$\sum_{n=0}^{\infty} (1 - \rho)\rho^n = \infty$$

if $\rho \geq 1$. The mathematical condition $\rho < 1$ is intuitively confirmed: if it weren't so, the size of the polymer could grow to excess with time and there would not be a time independent solution.

2.1.3 Transient behaviour

Equation (2.12) contains $P(0, t)$, which makes it unsolvable in a "direct" way: here we exploit the possibilities of the Laplace transform, applying it on both its sides⁵ to obtain

$$z \left(\theta \tilde{G}(z, \theta) - z^i \right) = (1 - z) \left[(\mu - \lambda z) \tilde{G}(z, \theta) - \mu \tilde{P}(n, \theta) \right] \quad (2.18)$$

where i is the initial number of monomers; it follows easily that

$$\tilde{G}(z, \theta) = \frac{z^{i+1} - \mu(1 - z)\tilde{P}(0, \theta)}{-\lambda z^2 + z(\lambda + \mu + \theta) - \mu}. \quad (2.19)$$

Before assessing the situation, a brief analysis on the denominator of (2.19), that has two zeroes:

$$z_{1,2} = \frac{\mu + \lambda + \theta \mp \sqrt{(\mu + \lambda + \theta)^2 - 4\lambda\mu}}{2\lambda}. \quad (2.20)$$

By easy computation, one can show that

$$(-\lambda z^2 + z(\lambda + \mu + \theta) - \mu) = \lambda(z - z_1)(z_2 - z) \quad (2.21)$$

Using the obvious inequality, $|z_1| < |z_2|$, together with simple computation one gets that

$$(z_1 + z_2) = \frac{\mu + \lambda + \theta}{\lambda}, (z_1 z_2) = \frac{\mu}{\lambda}. \quad (2.22)$$

Since we started, we have obtained a great result that is Eq. (2.19). Now we want to get an explicit expression for $\tilde{P}(0, \theta)$ from Eq. (2.19): Rouché's Theorem is one of great help in this case.

It states "Let $f(z)$ and $g(z)$ be analytic inside a region C and $|g(z)| < |f(z)|$ in each point on the boundary of C . Then $f(z)$ and $f(z) \pm g(z)$ have the same number of zeroes inside C ".

We choose contour $C : |z| = 1$ that has no self-intersections and identify the functions needed by the hypotheses $f(z) = +z(\lambda + \mu + \theta)$ and $g(z) = -\lambda z^2 - \mu$. So, we consider the region $R : |z| < 1$ in the complex plan and check for the validity of assumptions:

⁵This in turn is obtained using

$$\int_0^{\infty} e^{-\theta t} \left(\frac{\partial G(z, t)}{\partial t} \right) dt = \theta \tilde{G}(z, \theta) - z^i$$

which is proved *via* integration by parts:

$$\begin{aligned} \int_0^{\infty} e^{-\theta t} \left(\frac{\partial G(z, t)}{\partial t} \right) dt &= \left[G(z, t) e^{-\theta t} \right]_0^{\infty} - \int_0^{\infty} (-\theta) e^{-\theta t} G(z, t) dt = \\ &= 0 - (z^i) + \int_0^{\infty} (\theta) e^{-\theta t} G(z, t) dt = \\ &= \theta \tilde{G}(z, \theta) - z^i, i, \text{ is the initial number of monomers. } \square \end{aligned}$$

- $f(z) = +z(\lambda + \mu + \theta)$ and $g(z) = -\lambda z^2 - \mu$ are holomorphic in R ;
- $|-\lambda z^2 - \mu| < |z(\lambda + \mu + \theta)|$ in each point of the boundary of R .

The first one is easily proved by using the Cauchy–Riemann equations⁶. The second point requires different considerations:

$$|g(z)| = |-\mu - \lambda z^2| \geq |-\mu| + |\lambda z^2| = \mu + \lambda |z|^2 \quad (2.23)$$

which, if evaluated in $C : |z| = 1$ equals $\mu + \lambda$. For $|f(z)|$ the same passages are repeated to get $|f(z)| = \lambda + \mu + \theta$.

Now, θ is a complex number, so it has a real part and an imaginary one. The inequality we wanted to solve has become

$$\mu + \lambda < \mu + \lambda + \theta$$

which holds true if $(\Re(\theta) > 0)$ ⁷. So, Rouché's Theorem allows us to state that the denominator of (2.19) has only one zero inside R and, since $|z_1| < |z_2|$, this is z_1 .

Lastly, $\tilde{G}(z, \theta)$ converges⁸ in R . The denominator of $\tilde{G}(z, \theta)$ diverges if $z = z_1$ but this can be avoided if the numerator goes to zero: $N(z_1) = 0$; this turns out to be $\left[z^{i+1} - \mu(1-z)\tilde{P}(0, \theta) \right]_{z=z_1} = 0$. The latter permits us to get

$$\tilde{P}(0, \theta) = \frac{z_1^{i+1}}{\mu(1-z_1)}. \quad (2.24)$$

Now we go on by searching for an explicit expression of $\tilde{G}(z, \theta)$. Putting together Eq. (2.19) with Eq. (2.25) we get to

$$\tilde{G}(z, \theta) = \frac{z^{i+1} - \mu(1-z) \left(\frac{z_1^{i+1}}{\mu(1-z_1)} \right)}{\lambda(z-z_1)(z_2-z)} = \frac{z^{i+1}(1-z_1) - (1-z)z_1^{i+1}}{\lambda(z-z_1)(z_2-z)(1-z_1)}. \quad (2.25)$$

The right member can be expressed in a different way which will serve us later, that is

$$\begin{aligned} \frac{z^{i+1}}{\lambda(z-z_1)(z_2-z)} - \frac{(1-z)z_1^{i+1}}{\lambda(z-z_1)(z_2-z)(1-z_1)} &= \frac{1}{\lambda(z_2-z)} \left[\frac{z^{i+1}}{(z-z_1)} - \frac{(1-z_1+z_1-z)z_1^{i+1}}{(z-z_1)(1-z_1)} \right] = \\ &= \frac{1}{\lambda(z_2-z)} \left[\frac{z^{i+1}}{(z-z_1)} - \frac{z_1^{i+1}}{(z-z_1)} + \frac{z_1^{i+1}}{(1-z_1)} \right]. \end{aligned} \quad (2.26)$$

Now (2.26) can be written as

$$\frac{1}{\lambda(z_2-z)} \left[\frac{z^{i+1}}{z(1-z_1/z)} - \frac{(z_1/z)^{i+1}z^{i+1}}{z(1-z_1/z)} + \frac{z_1^{i+1}}{(1-z_1)} \right] = \frac{1}{\lambda(z_2-z)} \left[z^i \left(\frac{1-(z_1/z)^{i+1}}{1-(z_1/z)} \right) + \frac{z_1^{i+1}}{(1-z_1)} \right]$$

where we have recognised the sum of the first $i+1$ terms of a geometric series ($|z_1/z| < 1$). Finally, we get to

$$\tilde{G}(z, \theta) = \frac{1}{\lambda(z_2-z)} \left[z^i \sum_{k=0}^i (z_1/z)^k + \frac{z_1^{i+1}}{(1-z_1)} \right]. \quad (2.27)$$

⁶The Cauchy–Riemann theorem states that a function of $z \in \mathbb{C}$, $f(z) = u(x) + iv(y)$ is holomorphic if and only if the equations $\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y}$ and $\frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x}$ are satisfied; if one writes z as $z = x + iy$, where i is the imaginary unit, it is trivial to verify that these equations hold true both for $f(z)$ and $g(z)$.

⁷A complex number θ is positive by definition if $\Re(\theta) > 0$.

⁸In fact, one has:

$$\tilde{G}(z, \theta) := \int_0^\infty e^{-\theta t} G(z, t) dt = \int_0^\infty e^{-\theta t} \sum_{n=0}^\infty P(n, t) z^n dt = \sum_{n=0}^\infty z^n \int_0^\infty e^{-\theta t} P(n, t) dt = \sum_{n=0}^\infty z^n \tilde{P}(n, \theta)$$

here $\sum_{n=0}^\infty z^n \tilde{P}(n, \theta)$ converges if $P(n, t)$ is characterised by bounded exponential growth; we assumed that $P(n, t)$ was one of bounded exponential growth and found now that this is consistent with what we obtained. Moreover, $|z| < 1$ ensures the convergence of the geometric-series component.

We finish by doing a *two-stage* inversion, so that we have $\tilde{P}(n, \theta)$ and then we can get to $P(n, t)$. In fact, one notices that

$$\tilde{G}(z, \theta) := \int_0^\infty e^{-\theta t} G(z, t) dt = \int_0^\infty e^{-\theta t} \sum_{n=0}^\infty P(n, t) z^n dt = \sum_{n=0}^\infty z^n \int_0^\infty e^{-\theta t} P(n, t) dt = \sum_{n=0}^\infty z^n \tilde{P}(n, \theta) \quad (2.28)$$

and so, from the equality Eq. (2.27) = Eq. (2.28), that is

$$\frac{1}{\lambda(z_2 - z)} \left[z^i \sum_{k=0}^i (z_1/z)^k + \frac{z_1^{i+1}}{(1 - z_1)} \right] = \sum_{n=0}^\infty z^n \tilde{P}(n, \theta)$$

some standard calculation exploiting relations between z_1 and z_2 of Eq. (2.22) leads to:

$$\tilde{P}(n, \theta) = \frac{1}{\lambda} \left[z_2^{i-n-1}(\rho)^0 + z_2^{i-n-3}(\rho)^{-1} + \dots + z_2^{-i-n-1}(\rho)^{-i} + \rho^{n+1} \sum_{j=n+1+2}^\infty (\rho z_2)^{-j} \right]. \quad (2.29)$$

The final step is to invert (2.29). We get through this apparently-hard-analytic computation thank to:

1. The following relation for the inverse Laplace Transform of z_2^{-n}

$$\left[\widetilde{(z_2^{-n})} \right]^{-1} = \frac{e^{-(\lambda+\mu)t} \cdot (n) \cdot (\rho)^{n/2} \cdot (I_n(2\sqrt{\lambda\mu}t))}{t}; \quad (2.30)$$

2. the *Bessel differential equation* ([2],[8])

$$z^2 \frac{d^2 u}{dz^2} + z \frac{du}{dz} + (z^2 - n^2)u = 0, n > 0 \quad (2.31)$$

has a set of solution, $J_n(z)$, called *Bessel function of the first kind* of order n . The values assumed on the imaginary axis $z = iy$ by J_n in the case $J_n(z)$ define a new family of real-valued functions, $I_n(y) = (i^{-n})J_n(iy)$, namely the *modified Bessel function* of order n . These have a power series representation

$$I_n(y) = \sum_{k=0}^\infty \frac{(y/2)^{n+2k}}{k!(n+k)!}. \quad (2.32)$$

Moreover, a generating function of $I_n(y)$ is given by a specific Laurent series. Some useful properties are

- $I_n(y) = I_{-n}(y)$ for all non negative integers n ;
- $I_n(0) = \delta_{0n}$ for $y = 0$ where δ_{0n} is the Kronecker delta;
- $I_{n-1}(y) - I_{n+1}(y) = \frac{2n}{y} I_n(y)$, the recurrence relation.

Hence:

$$P(n, t|n_0) = U(n)U(n_0) \cdot (e^{-(\lambda+\mu)t}) \left[\rho^{\frac{n-n_0}{2}} E + \rho^{\frac{n-n_0-1}{2}} F + (1 - \rho)\rho^n G \right] \quad (2.33)$$

where

$$E := I_{n-n_0}(2\mu t\sqrt{\rho}) \quad (2.34)$$

$$F := I_{n+n_0+1}(2\mu t\sqrt{\rho}) \quad (2.35)$$

$$G := \sum_{m=n+n_0+2}^\infty (\rho^{-m/2}) \cdot (I_m(2\mu t\sqrt{\rho})) \quad (2.36)$$

The behaviour of I_n as $t \rightarrow \infty$ proves the fact that $\lim_{t \rightarrow \infty} (2.33) = P^*(n)$ and this confirms the correctness of the result obtained in (2.17).

2.1.4 Integral representation

We report now the main result of [1].

Eq. (2.33) could be even presented in a more versatile form which makes use of integrals, “leaving” the transform space. The solution (see [1] for details) is

$$P_{n|n_0}(t) = U(n)\delta_{n,n_0} - U(n)U(n_0) \left(\frac{\mu}{\pi} \rho^{\frac{n-n_0}{2}} \int_0^{2\pi} d\theta f(\theta) \right) \quad (2.37)$$

where

$$f(\theta) = [\sin(n_0\theta) - \sqrt{\rho} \sin((n_0 + 1)(\theta))] \cdot [\sin(n\theta) - \sqrt{\rho} \sin((n + 1)(\theta))] \cdot \left[\frac{1 - e^{-\mu t[(1+\rho) - 2\sqrt{\rho} \cos(\theta)]}}{\mu[(1 + \rho) - 2\sqrt{\rho} \cos(\theta)]} \right]. \quad (2.38)$$

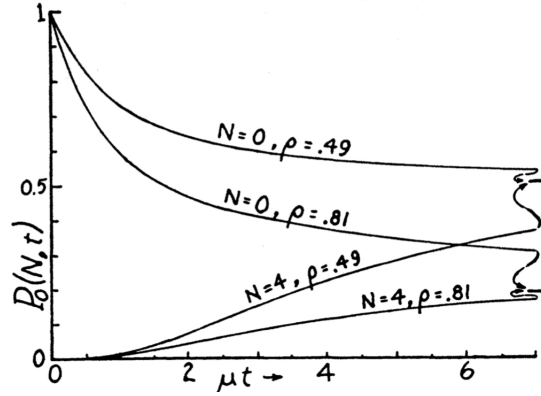


Figure 2.1: This plot has been taken from Morse’s article of 1955 [1]. In this picture, $n_0 := N = (0 \vee 4)$ and $n = 0$. Arrows point at the stationary solution, that is expressed by Eq. (2.17).

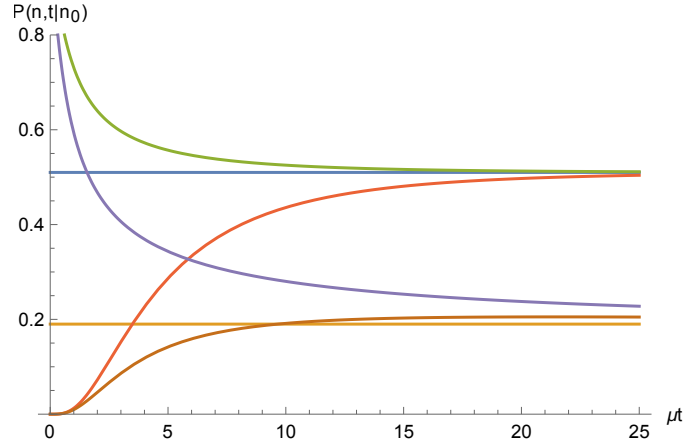


Figure 2.2: This image has been obtained using Eq. (2.33) and contains all four cases covered by figure 2.1: the same two values for ρ , 0.49 and 0.81 have been used.

The green and the red curves, respectively $P_{\rho=0.49}(0, t|0)$ and $P_{\rho=0.49}(0, t|4)$, tend to the equilibrium solution in light blue, that is $P^*(0) = (1 - 0.49)(0.49)^0 = 0.51$.

The purple and the dark orange functions are $P_{\rho=0.81}(0, t|0)$ and $P_{\rho=0.81}(0, t|4)$ and tend to the stationary solution in yellow, which equals to $P^*(0) = (1 - 0.81)(0.81)^0 = 0.19$.

To be exact, $n = 0$ is not possible for a polymer, since it has no sense from a physical point of view: we consider images 2.1 and 2.2 as a mathematical, graphical proof of the equivalence between (2.33) and (2.37).

We made a plot of Eq. (2.33): we set $n = 4$, $n_0 = 3$ and $\rho = 0.49$. We also used the fact that $\lambda = \rho\mu$, so that $\lambda + \mu = (\mu(1 + \rho))$. So the function resulted in:

$$P(4, t|3) = U(4)U(3) \cdot (e^{-(1+\rho)\mu t}) \left[\rho^{\frac{1}{2}}(I_1(2\mu t\sqrt{\rho})) + I_8(2\mu t\sqrt{\rho}) + (1 - \rho)\rho^4 \left(\sum_{m=9}^{\infty} (\rho^{-m/2}) \cdot (I_m(2\mu t\sqrt{\rho})) \right) \right]$$

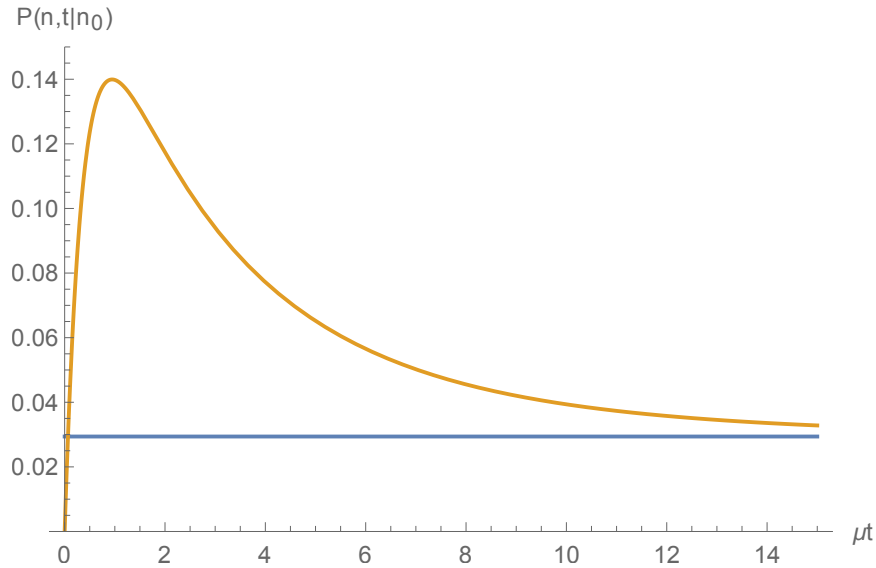


Figure 2.3: Example plot that proves $\lim_{t \rightarrow \infty} (2.33) = P^*(n)$. Here $n = 4$, $n_0 = 3$ and $\rho = 0.49$. The yellow line is the non-equilibrium curve, whereas the blue is the stationary solution. Graphically, the asymptotic behaviour is evident for $\mu t \rightarrow \infty$.

2.2 Diffusion of diffusivities effects

As previously seen, since the polymerisation process is a stochastic one, it is clear that during it its size N becomes a random variable that changes over time. This entails the diffusion coefficient D being a random variable too, due to its dependence on $N(t)$. In section 1.1.1 we have found that the probability density function of X_{CM} is a normal distribution that can be assumed to be a *zero mean* one with variance $\sigma^2 = 2Dt$.

However, the variance itself should be treated as a random variable whenever short times are concerned. This results in a specific probability density function for the position of the centre of mass, that is actually a weighted mean of Gaussian distributions. The following formula shows clearly the last concept: a mean over all normal-distribution-determined positions with reference to the probability density function of the variance σ

$$p_{X_{CM}}(x) = \sum_i p_\sigma(\sigma_i) \frac{e^{-\frac{x^2}{2\sigma_i^2}}}{\sqrt{2\pi\sigma_i^2}}. \quad (2.39)$$

With Eq. (2.39), we clearly see that if the probability density function $p_\sigma(\sigma_i)$ is a Kronecker delta, the distribution along the x axis for the position of the centre of mass remains Gaussian.

In this case, the *anomalous-to-Gaussian* shift could be linked to temporal fluctuations of D . As a consequence,

models in which the diffusion varies with time by obeying a stochastic equation have been introduced and solved both analytically than numerically. These models are referred in the literature as “diffusing diffusivity”⁹. [7]

Starting from Eq. (2.1), one could rewrite its x component as

$$X_{CM}(t + dt) = X_{CM}(t) + \sqrt{2D(t)}\mathbb{N}(0, 1)\sqrt{dt} \quad (2.40)$$

and, if N were fixed, assuming $x = 0$ at $t = 0$ we would have

$$p_{X_{CM}}(x, t|N) = \frac{e^{-\frac{x^2}{4D(N)t}}}{\sqrt{4\pi D(N)t}}. \quad (2.41)$$

However, N does not remain constant over time. The diffusing path is then reparametrised using a new coordinate related to a different and convenient stochastic process:

$$S(t) := \int_0^t dt' [2D(N(t'))] \quad (2.42)$$

with $s \geq 0$ and, directly from (2.42)

$$ds = 2[D(N(t))]dt. \quad (2.43)$$

We thus have that the x component of Eq.(2.1) and Eq. (2.40) become

$$dX_{CM}(s) = dB_X(ds) \quad (2.44)$$

$$X_{CM}(s + ds) = X_{CM}(s) + \mathbb{N}(0, 1)\sqrt{ds}. \quad (2.45)$$

$S(t)$ is nothing but a stochastic process, so we have the subordination formula:

$$p_{X_{CM}}(x, t) = \int_0^\infty ds [p_{X_{CM}}(x, t|s)p_S(s, t)] = \int_0^\infty ds \left[\frac{e^{-\frac{x^2}{2s}}}{\sqrt{2\pi s}} p_S(s, t) \right]$$

⁹In this case the diffusion coefficient diffuses itself: this is the reason why this phenomenon is referred to as “diffusing diffusivity”.

where we exploited the formula for the conditional probability¹⁰. For a polymer of size $N = n_0$ at time t_0 more precisely we get

$$p_{X_{CM}}(x, t|n_0) = \int_0^\infty ds \left[\frac{e^{-\frac{x^2}{2s}}}{\sqrt{2\pi s}} p_S(s, t|n_0) \right] \quad (2.46)$$

This result shows us expressly the non-Gaussian nature of the CM diffusion. However, that is not all: from Eq. (2.46) we now note that

$$\begin{aligned} \langle [X_{CM}^k(t)|n_0] \rangle &= \int_{-\infty}^\infty dx \left[x^k p_{X_{CM}}(x, t|n_0) \right] = \int_{-\infty}^\infty dx \left[x^k \int_0^\infty ds \left(\frac{e^{-\frac{x^2}{2s}}}{\sqrt{2\pi s}} p_S(s, t|n_0) \right) \right] = \\ &= \int_0^\infty ds p_S(s, t|n_0) \int_{-\infty}^\infty dx \left[x^k \left(\frac{e^{-\frac{x^2}{2s}}}{\sqrt{2\pi s}} \right) \right] = \int_0^\infty ds p_S(s, t|n_0) \langle (X^k) \rangle_{\mathbb{N}(0,s)} \end{aligned} \quad (2.47)$$

Now we perform a change of variables such that: $x' = x/\sqrt{s}$. It follows that $dx = (s^{\frac{1}{2}})dx'$ (with both the lower and the upper limit of the dx integral remaining unchanged) one gets

$$\begin{aligned} \langle (X_{CM}^k(t)|n_0) \rangle &= \int_0^\infty ds p_S(s, t|N) \int_{-\infty}^\infty dx' \frac{s^{k/2}}{\sqrt{2\pi}} (x')^k e^{-\frac{(x')^2}{2}} = \\ &= \int_0^\infty ds p_S(s, t|N) \left(s^{k/2} \langle (X^k) \rangle_{\mathbb{N}(0,1)} \right) = \langle (X^k) \rangle_{\mathbb{N}(0,1)} \left(\langle (S^{k/2}) \rangle \right) \end{aligned} \quad (2.48)$$

where $\langle (X^k) \rangle_{\mathbb{N}(0,1)}$ is the zero-mean, unit-variance Gaussian moment of order k .

2.2.1 The kurtosis

The introduction of the kurtosis, κ , is the key to analyse and quantify the anomalous (equivalently, non-Gaussian) behaviour of those experimental data which show strong evidence of a significant deviation from the normal distribution of the probability density function if in presence of a complex environment (such as the polymerisation one). $\kappa_X = 3$ only for Gaussian variables.

The kurtosis, κ , is defined as follows:

$$\kappa_X := \frac{\langle [(X - \langle X \rangle)^4] \rangle}{(\langle [(X - \langle X \rangle)^2] \rangle)^2} \quad (2.49)$$

The concept and the consequent definition of kurtosis is of general validity in statistics and probability theory and it is strongly connected to the already-addressed *subordination* of stochastic processes. The subordination process involves a subordinant one, whose statistics directly influences the subordinated (here the latter is the motion of the centre of mass). Each of these two processes follows its own distribution, whose moments determine the statistics.

In this case, the equation describing the subordination process holds for at least two reasons:

- The diffusion coefficient depends on the size of the polymer $N(t)$ (that is, in fact, due to Rouse's model);
- $N(t)$ itself is a stochastic process.

From the subordination formula – Eq.(2.46) – thanks to what we saw in Eq.(2.48), the latter expression simplifies to:

$$\kappa_X := 3 \frac{\langle S^2(t)|n_0 \rangle}{(\langle S(t)|n_0 \rangle)^2} \quad (2.50)$$

One could investigate the behaviour of κ when the probability density function coincides either with the stationary solution for $P(n, t|n_0)$ or with the non-equilibrium solution.

¹⁰That is $P(B|A) = P(A, B)/P(A)$.

From Eq.(2.50) we deduce that, given n_0 , we need to calculate $\langle S(t)|n_0\rangle$ and $\langle S^2(t)|n_0\rangle$ if we want to study the kurtosis of X_{CM} .

Calculation of $\langle S(t)|n_0\rangle$:

Here there are a few simple steps:

$$\langle S(t)|n_0\rangle = \left\langle \left[\int_0^t dt' (N(t')|n_0) \right] \right\rangle = \int_0^t dt' \langle [2D(N(t')|n_0)] \rangle = \sum_{n=0}^{\infty} \frac{2D_0}{(n+3)} \int_0^t dt' P(n, t'|n_0). \quad (2.51)$$

Calculation of and $\langle S^2(t)|n_0\rangle$:

This computation requires many more passages (and some will be omitted in order not to overshadow the basic subject with mathematical tricks)

$$\begin{aligned} \langle S^2(t)|n_0\rangle &= \left\langle \left[\int_0^t dt' D(N(t')|n_0) \int_0^t dt'' D(N(t'')|n_0) \right] \right\rangle = \\ &= \int_0^t dt' \int_0^t dt'' \langle [D(N(t')|n_0)D(N(t'')|n_0)] \rangle = \\ &= \int_0^t dt' \int_0^t dt'' \sum_{n'=0}^{\infty} \frac{2D_0}{(n'+3)} \sum_{n''=0}^{\infty} \frac{2D_0}{(n''+3)} P(n', t'; n'', t''|n_0) = \\ &= \sum_{n', n''|n_0}^{\infty} \left(\frac{2D_0}{(n'+3)} \frac{2D_0}{(n''+3)} \right) \int_0^t dt' \int_0^t dt'' P(n', t'; n'', t''|n_0). \end{aligned}$$

For $t'' \geq t' \geq 0$

$$\begin{aligned} &= \sum_{n', n''|n_0}^{\infty} \left(\frac{2D_0}{(n'+3)} \frac{2D_0}{(n''+3)} \right) \int_0^t dt' \int_0^t dt'' P(n', t'; n'', t''|n_0) = \\ &= \sum_{n, n''|n_0}^{\infty} \left(\frac{2D_0}{(n'+3)} \frac{2D_0}{(n''+3)} \right) \left[\int_0^t dt'' \int_0^{t''} dt' P(n', t'; n'', t''|n_0) + \int_0^t dt' \int_0^{t'} dt'' P(n', t'; n'', t''|n_0) \right] \end{aligned}$$

Referring to

$$\star := \int_0^t dt'' \int_0^{t''} dt' P(n', t'; n'', t''|n_0)$$

and to

$$\star\star := \int_0^t dt' \int_0^{t'} dt'' P(n', t'; n'', t''|n_0)$$

and applying to both \star and $\star\star$ Bayes' theorem and the Markov-memoryless property¹¹, we see that actually \star and $\star\star$ are the same integral, hence

$$\langle S^2(t)\rangle = 2 \left(\sum_{n, n''}^{\infty} \left(\frac{2D_0}{(n'+3)} \frac{2D_0}{(n''+3)} \right) \left[\int_0^t dt'' \int_0^{t''} dt' P(n', t'; n'', t''|n_0) \right] \right). \quad (2.52)$$

¹¹That is the equation: $P(n', t'; n'', t''|n_0) = P(n', t'; n'', t'')$.

Conclusions and Outlook

To sum up, we have presented here a microscopic model for Brownian yet non-Gaussian diffusion: this depicts the diffusion dynamics of the centre of mass of a polymer molecule undergoing a specific polymerisation process.

As for the initial part of section **2**, we solved the master equation in both the stationary and non-equilibrium cases. In fact, equations (2.17) and (2.33) together constitute the solution of Eq. (1.13), being the key result of this work. Eq. (2.17) and Eq. (2.33) are self-consistent, since $\lim_{t \rightarrow \infty} (2.33) = (2.17)$. In particular, the transient solution is often involved in further applications. One first example could be the evaluation of the auto-correlation coefficient (see [1] and [11]); moreover, its integral rewriting, combined with the identity

$$\pi \delta_{n,n_0} U(n_0 - 1) = \int_0^{2\pi} d\theta \sin(n_0\theta) \sin(n\theta)$$

where $U(n)$ is the discrete unit step function, shall be used to provide a convenient short-time expansion to apply to calculations or approximations in a much deeper study of kurtosis (some of these have been partially treated in [11]).

Taking into account the “diffusion diffusivity”, what has been analytically computed in **2.2.1** offers several developments, since both $\langle S(t)|n_0 \rangle$ and $\langle S^2(t)|n_0 \rangle$ could be evaluated by means of the transient solution of the master equation (more likely in its integral rewriting); this may lead to an exact expression for κ , which might be studied with classic mathematical analysis tools; for example, one could check its possible convergence or divergence, expecting it not to have a monotonic trend but, instead, to have a stationary point at some time.

Another possible aspect would be the study of the dynamics of the centre of mass of the polymer to varying of the initial conditions, so that $P(n, 0|n_0)$ is either a Kroneker delta or coincides with the stationary solution of Eq. (2.17).

Lastly, a possible and interesting evolution of what was made with queuing theory would be the search for complex polymer topologies, such as branched polymers (as has been proposed in [11]).

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