Identifying *tube* in molecular simulations of polymer melt

**Abstract:**
Description of dynamics in a polymer melt is a difficult many-body problem. The tube theory suggests that this is equivalent to evolution of one polymer in a tube representing the effect of all the other polymers. The tube theory invokes phenomenological concepts of tube diameter and primitive path (axes of the tube). How these are connected to the full atomistic dynamics is not completely known. In this report we have used numerical simulations on a bead spring model to directly measure the primitive path, and the potential due to this tube. To compare our results to the tube model, we have also created a numerical model of one polymer in a tube and measured the monomer displacement.

We have underlined some differences between the tube theory and our model.

**Key word:** Polymere melt - tube model - primitive path - numerical simulation - bead-spring model

*Polymers and Complex Fluids Group,*  
*School of Physics and Astronomy,*  
*University of Leeds, LS2 9JT, UK.*  
[www.pcf.leeds.ac.uk](http://www.pcf.leeds.ac.uk)

*Directed by:*  
*Peter OLMSTED* (P.D.Olmsted@leeds.ac.uk)  
*Chinmay DAS* (C.Das@leeds.ac.uk)

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Introduction

The wide applicability of polymers make this field very important. Rubinstein and Colby[9] suggest that "in the twentieth century we entered in the polymer age." One of the useful properties of polymers is its mechanical properties. Polymer liquids have interesting mechanical properties between liquid and solid. But in order to use those amazing properties, we have to understand the link between rheological properties and microscopic structure.

Models, described by only a few parameters encoding the molecular informations, are valuable for both understanding the basic physics and for using in applications. The dynamics of dilute polymers is well understood. But when we increase the concentration, polymers begin to interact with each other and the problem is not completely solved. The De Gennes-Doi-Edwards model[1, 9], the so called tube model, suggest to reduce the many body problem by the simpler model of one polymer evolving in a tube. This model has been quite successful in explaining different experimental results. But some points still remain unclear. For example, how the tube diameter is connected to the molecular details, is not well defined.

Numerical simulation is a powerful method to study a many body system. It gives access to microscopic informations we can not get through experiments, such as the conformation of each of the molecules. In 1989 Kremer and Grest[6] have suggested a numerical model to simulate entangled polymers. 20 years after, computers are powerful enough to revisit the problem. Some recent study [2, 3, 10] has invented methods to measure the axes of the tube (called the primitive path). All those studies are based on the idea to minimise the path between the two ends of the polymer. Those studies considere the ends polymers as ends of the tube. But in an entangled polymer melt, the end monomers are the most mobile. Constraining the end monomers severely restricts the available conformations that the polymers could have explored in the absence of the constraints. In this report we present a new method to measure the primitive path from direct observation of unconstrained dynamics. We show that we can measure the primitive path and have access to the potential of the tube.

I. REVIEW OF DYNAMICS IN POLYMER MELT

In this section we present some theoretical aspects of the dynamic of polymers. To connect the theoretical models to experimental results, the rheological properties of polymers will be explained. Other experimental measures such as diffusion or X-ray scattering will not be explained.

A. Viscoelasticity of polymer melt

1. Polymer Liquid

Polymer solution exhibits properties which are intermediate between liquid and solid. This property is called viscoelastic property. Polymers solution can be divided into three kinds. Polymer solutions which are dilute enough so that they don’t feel other polymers, are called dilute polymers. If the concentration is increased, the polymers begin to feel other polymers, we call it semi-dilute solution. The concentration of semi-dilute polymers can remain very low but those solutions have very different rheological properties from the solvent. If there is no solvent, it is called a polymer melt. Polymer melt behave like a viscoelastic fluid above a temperature - called the glass transition temperature - which depends of the type of polymer. It has been found that one can describe the problem in terms of a few effective parameters determined by the detailed chemical composition. When described in terms of these effective parameters, the detailed chemical composition plays no further important role. The main parameters are:

- The structure: Polymer can have many different structures [Fig. 1], such as linear polymer, star polymer or H-comb... In this study we consider only linear polymers.
- The length and the distribution of length: Commercial polymer have a broad molar mass distribution. But one can synthesize polymers with a narrow distribution. So theoretical prediction on monodisperse polymer can be connected to experimental result.
- The flexibility: Depending on the flexibility, two limiting cases are rod-like polymers and fully flexible polymers. In this study we consider fully flexible polymer.

![Figure 1: The rheological properties depend on the structures of the polymers. Typical structures are a) linear polymer b) star polymer c) H-combs.](image)
To characterize the viscoelastic behavior we can deform a sample and measure the force we apply. In Figure 2, we represent a schematic experiment of a shear deformation.

The parameters characterizing the viscoelastic properties of the material should not depend on the size of the sample. So the good parameters are not the deformation $\Delta$ and $F$ but the shear rate $\gamma = \frac{\Delta}{L}$ and the shear stress $\sigma = \frac{F}{S}$.

![Figure 2: Example of a shear deformation: the sample (initially in red dashed lines) has a height $L$ and a surface perpendicular to the plane of the drawing $S$. This sample is deformed (to the black lines) by applying a force $+F$ on the upper part and keeping the lower part fixed with a force $-F$. The deformation is $\Delta$.](image)

At low deformation experimentally we have a linear relation between the shear rate and the shear stress:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\gamma(t')dt'$$  \hspace{1cm} (1)

$G(t)$ is called the shear modulus. For a purely elastic material we have $G(t) = constant$ and for Newtonian liquids $G(t) = \eta \cdot \delta(t)$.

Usually we measure $G(t)$, we impose:

$$\gamma(t) = \gamma_0 \sin(\omega t)$$  \hspace{1cm} (2)

The shear stress at the stationary state is:

$$\sigma(t) = \gamma_0 G'(\omega) \sin(\omega t) + \gamma_0 G''(\omega) \cos(\omega t)$$  \hspace{1cm} (3)

and we measure $G'(\omega)$ and $G''(\omega)$. $G'$ and $G''$ can be connected to $G(t)$ by the equations:

$$G'(\omega) = G_{eq} + \omega \int_{0}^{+\infty} (G(t) - G_{eq}) \sin(\omega t)dt$$

and

$$G''(\omega) = \omega \int_{0}^{+\infty} (G(t) - G_{eq}) \cos(\omega t)dt$$

with $G_{eq} = G(t = +\infty)$  \hspace{1cm} (4)

For purely elastic material we have $G'(\omega) = constant$ and $G''(\omega) = 0$. For Newtonian fluid we have $G'(\omega) = 0$ and $G''(\omega) = \eta \cdot \omega$. $G'$ is related to the elastic behaviour and is called the storage modulus. $G''$ is related to the viscous behaviour and is called the loss modulus.

Now we can understand what we mean by polymers having a behaviour between a solid and an liquid. If we make experiments with a typical time scale $t_{exp}$ where $G(t_{exp}) \sim constant$ (that mean $G'(2\pi/t_{exp}) \sim constant \gg G''$) we can consider the material as elastic; if we do experiment at a bigger time scale, the material will have viscous behaviour.

The figure 3a and b represents the typical behavior $G(t)$, $G'$ and $G''$ for polymer melt. $G(t)$ decreases to reach a plateau at time $\tau_e$. We have $G(t) \sim constant = G_0$. $G_0$ is called the plateau modulus. For time $t > \tau_d$, $G(t)$ decreases. So for time $t < \tau_d$ the polymer melt has elastic behaviour and starts to flow for $t > \tau_d$. In figure 3c and d, we show experimental measure of $G'$ and $G''$ for narrow distribution of polystyrenes of different molecular weight. We see that the plateau modulus exists only for long polymers. So there is a transition between short and long chain. We say that long chains are entangled.

### B. Microscopic model of dilute polymers

In this report we study flexible polymers without taking into account their chemical structure. So polymers which have a well defined conformation, such as proteins, will not be well represented by this model. But many commercial polymers (polyethylene, PVC...) can be represented by this model. Before explaining the difficult problem of entangled polymers we will introduce some ideas on dilute polymer.
Figure 3: Typical behavior of the shear modulus $G(t)$ (fig. a) and of the storage and of the loss modulus $G'$ and $G''$ (fig. b) of polymer melt.


1. Conformation of a single polymer

The conformation of a single polymer is like a coil. We call it a “random coil”. It can be seen as a random walk where each monomer represents the step. This representation is really useful because random walk is well known model used, for example, in diffusion. A monomer is connected to the next one by chemical links which are not so flexible. So we can expect to keep correlation of the direction between two successive steps (two successive monomers). But we can expect that the correlation decreases with the number of steps. If it decreases faster than the length of the polymer, the polymer is called flexible. To quantify this let us introduce $b$ which is the distance between two monomers and $\cos \theta$ is the average of the cosine of the angle between two monomers. We can show that if $\vec{r}_k$ is the vector between $k$ successive steps, we have:

$$<r_k^2> = b^2 k \left( \frac{1 - <\cos \theta>}{1 - <\cos \theta>} + \frac{2 <\cos> (1 - <\cos \theta>^k)}{k(1 - <\cos \theta>^2)} \right)$$

(5)

Because the chains are flexible we find for the end to end vector $\vec{R}$.

$$<R^2> = N_k l_k^2$$

(6)

We find the same result as an uncorrelated random walk but with $N_k$ step of length $l_k$. $l_k$ is called the Kuhn length. So the polymer can be divided into Kuhn monomers with a new length $l_k$.

Moreover, with this model we can calculate the distribution of $\vec{R}$. We can show that $P(\vec{R}) \propto \exp(-R^2/(2l_k^2))$. So a polymer has an elastic behaviour - we call it entropic spring. The spring constant is $k_B T/l_k^2$. When we pull on the polymer, it tries to come back to its initial conformation.

In this model we have not considered interaction between monomers. The model can be corrected to take care of this interaction. We will not explain this point.

2. Rouse model

Now we will explain the dynamic of polymers. The first successful model was the Rouse model. It describes a polymer by a set of $N$ beads connected by spring. The average distance between two bead is $b$. $\{R_n\}$ are the
position of the beads. In this bead spring model, a bead represents the center of several monomers. The beads must contain enough monomers to neglect the correlation of the directions between two beads. To take account of the brownian motion we add a stochastic force and a viscous force (as in the Langevin equation.) The forces applied on one monomer are:

- an elastic force applied by the 2 neighbours in the chain. The spring constant is $k$.
- A viscous force $-\zeta \frac{d\vec{R}_n}{dt}$. We assume that the viscosity dominates the motion.
- Furthermore monomers feel force from solvent and other monomers: a random force $\vec{F}_n$. This force is an uncorrelated random noise characterized by:

$$< \vec{F}_n > = 0$$
$$< F_{n,\alpha}(t) F_{m,\beta}(0) > = \zeta k_B T \delta(t) \delta_{n,m} \delta_{\alpha,\beta}$$

Figure 4: The Rouse model describes polymers as beads connected by springs.

So the equation of motion is:

$$\zeta \frac{d\vec{R}_n}{dt} = -k(2\vec{R}_n - \vec{R}_{n+1} - \vec{R}_{n-1}) + \vec{F}_n$$

To solve this set of equations we introduce Rouse modes

$$\vec{X}_p = \frac{1}{N} \sum_n \cos(2\pi pn) \vec{R}_n$$

There are $N + 1$ Rouse modes. $\vec{X}_0$ corresponds to the position of the center of mass. For $p > 0$ the Rouse modes represent the Fourier transform with a wave length of $N/p$ monomers. We can calculate the evolution of the Rouse modes: // We show that

$$< (\vec{X}_0(t)^2 - \vec{X}_0(0))^2 > = D \cdot t \quad \text{with} \quad D = \frac{k_B T}{N}$$
$$< \vec{X}_n(t) \vec{X}_n(0) > = \exp\left( -\frac{t}{\tau_p} \right) \quad \text{with} \quad \tau_p = \frac{N^2}{p^2} \tau_0 = \frac{N^2}{p^2} \frac{\zeta b^2}{3\pi^2 k_B T}$$

So the center of mass diffuses with a diffusion coefficient $D$. The other modes relax exponentially. The correlation time increases with the wave length. The fastest modes is $p = N$ which corresponds to a wave length of one monomers. The slowest mode is $p = 1$, its correlation time is called the terminal time $\tau_r = \tau_0 N^2$.

3. Rheology of dilute polymers

When we apply a step strain on dilute polymers, we deform the molecules [fig. 5]. This deformation contributes to the the elastic behaviour. When polymers relax, the solution flows.

Figure 5: When we apply a shear the polymer is deformed. The polymer applies an elastic force. The polymer relaxes and releases this elastic force.

According to the equipartition principle, each degree of freedom has an energy $(1/2)k_B T$. After a step strain a chain stores an elastic energy about $Nk_B T$ stored on the N rouse modes (the mode $p = 0$ corresponds to the translation and is not involved). So the shear modulus of a dilute polymer of a volume fraction $\phi$ after a step strain is

$$G(t \to 0) = N \frac{k_B T \phi}{b^3}$$
When a mode relaxes, its elastic energy is released. The relaxation time of a mode $p$ is $\tau_p = \tau_0 \left( \frac{N}{p} \right)^2$. So for a time $\tau_0 < t < \tau_r$, the number of mode which have not yet relaxed is

$$N_{\text{mode}} = N \left( \frac{t}{\tau_0} \right)^{-1/2} \quad (12)$$

So for time $t < \tau_r$ the shear modulus is

$$G(t) = N \frac{k_B T \phi}{b^3} \left( \frac{t}{\tau_0} \right)^{-1/2} \quad (13)$$

for time $t > \tau_r$ we see the relaxation of the last mode $p = 1$

$$G(t) = N \frac{k_B T \phi}{b^3} e^{-t/\tau_r} \left( \frac{t}{\tau_0} \right)^{-1/2} \quad (14)$$

In figure 6, we plot $G'$ and $G''$ calculated from equation 14. There is a good correlation with experimental measurements. But some experimental result is not consistent with the rouse model. In section 4B2 we have shown that the diffusion coefficient is $D \propto N^{-1}$, experimentally one finds $D \propto N^{-1/2}$. Furthermore we predict that $\tau_r \propto N^2$, experimentally one has $\tau_r \propto N^{3/2}$. Zimm suggested correcting the Rouse model by taking account the hydrodynamic interactions between monomers. In this report we will not explain the Zimm model. In entangled polymers the viscosity is very important so hydrodynamic interactions are screened and can be neglected.

4. Monomer displacement

Another interesting experimental result is the mean square displacement of one monomer $g_1(t) = \left\langle (\vec{R}_j(t) - \vec{R}_j(0))^2 \right\rangle$. The result is hard to get experimentally but easy to get from numerical simulations. One can show that $g_1(t)$ has two different behaviours for $t \ll \tau_r$ and for $t \gg \tau_r$:

$$g_1(t) \propto \begin{cases} t^{1/2} & \text{for } t \ll \tau_r \\ t & \text{for } t \gg \tau_r \end{cases} \quad (15)$$

C. Entangled polymers : the tube model

1. Polymers melt and entanglement

In polymer melt, polymers interact strongly with each other. In figure 3 we have seen a transition of rheological properties of polymer melt between short chain and long chain. For long chains, main interactions are topological in nature : a polymer can not pass through another. The longer are the chains, the more important are the topological interactions.
In figure 7a, we have represented a polymer constrained by other polymers. Doi-Edwards suggests replacing those constraints by a tube of potential [fig. 7b]. To define the tube we have to define its axis - called the primitive path - and its potential. The potential is still unknown but we can define the typical tube diameter $a$. The polymer in the tube is composed of blobs of diameter $a$ [fig 7c]. The typical number of monomers in a blob called $N_e$ is:

$$N_e = \left( \frac{a}{l_k} \right)^2$$

(16)

The number of blobs $Z = N/N_e$ with $N$ the number of monomers. $Z$ can be seen as the number of entanglement, that means the typical number of chain which constrain the polymers. The average length of the primitive path is:

$$<L_e> = Z a = \frac{N}{N_e} a = N \frac{l_k}{a}$$

(17)

2. Modes of relaxation

To explain the rheology we have to explain the relaxation of the polymer [1, 4].

For small times the polymer will not move enough to feel the tube. So phenomena with a typical lengthscale smaller than the tube diameter $a$ should not be affected by the tube. The Rouse modes which involve less monomers than $N_e$ (that means modes with $p > N/N_e$) should not feel the tube and the dynamics has to be the same as for dilute polymer. At the opposite, modes which involve more monomers than $N_e$ (modes with $p < N/N_e$) are frozen by the tube. But the tube is not a static object. So those modes relax at the same time as the tube. We write $\vec{R}_{pp}$ the end to end vector of the primitive path. To quantify the relaxation of the tube let us introduce

$$\Psi(t) = \frac{<\vec{R}_{pp}(t)\vec{R}_{pp}(0)>}{<R_{pp}^2>}$$

(18)

The dynamic of the primitive path can be explain by three mechanisms.

- The reptation : (see figure 8)

- the fluctuation of the length of the primitive path : (see figure 9)

- the constraint release (see figure 10)

The calculation of $\Psi(t)$ is a key point of the theory. Even if this problem is not solved, we will be able to define a typical time of relaxation of the tube - called time of disentanglement $\tau_d$. 
Figure 9: Example of the mechanism of the length fluctuation.

**fig a**: The polymer (black line) is confined inside a tube (red line).  
**fig b**: By fluctuation the length of the primitive path is reduced. At the two ends, parts of the old tube disappear.  
**fig c**: When the length of the primitive path increases, new parts of the tube appear (blue line) which are not correlated to the part occupied in fig a.

Figure 10: Release and creation of the topological constraint: The topological constraint imposed by the chain C on A is released and recreated by the motion of the chain C. Reproduced from M. Doi and SF Edwards. The theory of polymer dynamics. Oxford University Press, USA, 1986.

3. Predictions of tube model for rheology

Using the dynamics we can [9] calculate the shear modulus of a polymer melt with a concentration of monomers $\rho_0$. For time $t < \tau_e$, the dynamics is mainly governed by the Rouse model and the entanglement has no effect. So rheology should be the same as that of an unentangled polymer. That means that for $t < \tau_e$ we have as eq [19]:

$$G(t) = k_B T \rho \left( \frac{t}{\tau_0} \right)^{-1/2}$$

For $t > \tau_e$, the dynamics is governed by the tube relaxation, we have $G(t) \propto \Psi(t)$. For time scale $\tau_e \ll t \ll \tau_d$, $\Psi(t) \sim \text{constant}$, so $G(t) \sim \text{constant}$. The shear modulus is the plateau modulus $G_0$. The value of the plateau modulus can be connected to the other parameters

$$G_0 = G(\tau_e) \approx \frac{\rho k_B T}{N_e^2}.$$  

(20)

In this model we have to take into account the deformation of the tube. One can show that the plateau modulus is:

$$G_0 = \frac{4 \rho k_B T}{5 N_e^2}.$$  

(21)

For times longer than $\tau_d$, the shear modulus decreases as fast as $\Psi(t)$:

$$G(t) = \Psi(t) G_0.$$  

(22)

We plot on figure 11 the typical evolution of $G(t)$ which can be compared to figure 3. In figure 3, the plateau modulus is not totally fixed but decreases slowly. In reality the tube should not be totally frozen for time $t \ll \tau_d$.

4. Monomer displacement in the tube model

As for dilute polymer we can calculate the mean square displacement of one polymer from the tube model [9] [fig. 12].
For $t \ll \tau_e$ the polymer is not affected by the tube: $g_1(t) \propto t^{1/2}$. For $\tau_e < t < \tau_d$ the polymer moves along the primitive path with the motion perpendicular to the primitive path restricted. The primitive path can be seen as a random walk. One can show that the subdiffusion along a primitive path is characterised by $g_1(t) \propto t^{1/4}$ for $\tau_e < t < \tau_r$. For $\tau_r < t < \tau_d$ $g_1(t) \propto t^{1/2}$. And finally for $\tau_d < t$, all the constraints are released and the monomer has a diffusive behaviour: $g_1(t) \propto t$.

The tube model has been quite useful in describing the dynamics of polymer melt. However, the microscopic basis of the tube theory parameters remains unclear. Because the tube is a dynamical concept, one needs to consider the dynamics of the tube itself. Heuristically one introduces “tube dilation”, wherein the tube diameter is assumed to increase with relaxation in a certain prescribed fashion to take account of the “constraint release”. But the tube diameter remains as an empirical parameter.

The length of the primitive path is calculated by assuming it to be a random walk with certain Kuhn length. But the Kuhn length is not known. Usually one makes the assumption that the Kuhn length is equal to the tube diameter.

A direct determination of the primitive path and the confining potential in a microscopic model can answer some of these questions.

**II. NUMERICAL SIMULATION**

**A. Model of simulation**

Kremers and Grest have demonstrated in 1989 that a numerical model, with only a few hundred polymers, can simulate entangled polymers.

To do such a simulation we have to forget atomistic details in order to keep the time of calculation feasible. The idea is to use a bead spring model where a bead represents several monomers.

In the simulations we have used the model introduced by Kremers and Grest. The beads have a diameter $\sigma$ and a mass $m$. The interaction between 2 monomers is represented by a purely repulsive Lennard-Jones potential:

$$U_{LJ}(r) = \begin{cases} 4\epsilon\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4} & \text{for } r < \sigma_c = 2^{1/6}\sigma \\ 0 & \text{for } r > \sigma_c \end{cases}$$

(23)

To connect two neighbours in the chain we add a non linear attractive potential - Finitely Extensible Non-linear Elastic bonds (FENE):

$$U_{FENE}(r) = -kR_0^2 \ln \left(1 - \frac{r^2}{R_0^2}\right)$$

with $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$

(24)
In this model the mean distance between two neighbours is 0.97σ. It is small enough to prevent a polymer from passing through another one and to maintain the topological constrains. In this model we can define a typical time scale \( \tau = \sigma (m/\epsilon)^{1/2} \) which corresponds to the typical time for a bead to move a distance of \( \sigma \).

The simulations have been done at volume, temperature and the number of beads fixed. The temperature was chosen as \( k_B T = \epsilon \) and the density \( \rho = 0.85\sigma^{-3} \). To control the temperature we have used a Nose-Hoover chain with 8 elements. will have a mass of \( 3^N - 3 \). To integrate the equation of motion we have used a velocity verlet-like algorithm with a time step of integration \( \Delta t = 0.01\tau \). One simulation has been studied with 256 polymers each containing 256 beads.

B. Some numerical result about this model

Likhtman et al. \[7\] have measured the shear modulus of this model [fig. 15]. They show a deviation from the Rouse model, for polymers with a length 200 and 350 beads. But the length of chains we can simulate is not big enough to separate \( \tau_e \) and \( \tau_d \). So there is not a well defined plateau modulus. To calculate the plateau modulus, they proposed a model called slip-spring model. From this model they predict \( G(t) \) for \( N = 750 \) and \( N = \infty \). They calculated a modulus plateau \( G_0 = 0.013 \epsilon/\sigma^4 \). With this result they determined the entanglement time \( \tau_e = 5800\tau \) and the number of beads contained in one entanglement \( N_e = 72 \). They measured the distentanglement times : for \( N = 200 \), \( \tau_d = 60 \cdot 10^3\tau \) and for \( N = 350 \), \( \tau_d = 303 \cdot 10^3\tau \).

Kremers and Grest \[6\] have measured the monomer displacement \( g_1(t) \). The results are consistent with the measurements of \( G(t) \). They find that at short times \( g_1(t) \propto t^{1/2} \). For long chains \( (N > 100) \) they find the entangled behaviour \( g_1(t) \propto t^{1/4} \). They measure a time of entanglement \( \tau_e = 1800\tau \) smaller than the time measured by Likhtman et al. In the next parts, we will use the Likhtman’s entanglement time \( \tau_e = 5800\tau \) as reference.

C. First determination of the primitive path

Doy and Edward defined the primitive path as the shortest path which connects the two ends of the polymer and respects the topological constraints. Everaers et al. [2] suggests a way to measure the primitive path using this definition. They fix the ends of the polymers, remove repulsive interactions between beads of the same chain and reduce the temperature. When they cool the melt the distance between two monomers goes to zero and so they minimize the path of all the polymers at the same time. They can measure the Kuhn length of the primitive path: \( L_{k,pp} = 10.5 \sigma \). They identify the Kuhn length with the radius of the tube, so that they can calculate the plateau modulus. They find \( G_{ppa}^0 = 0.0103 \epsilon/\sigma^4 \) which can be compared to the modulus measured from the shear modulus \( G_0 = 0.013 \epsilon/\sigma^4 \).

Other methods based on the minimization of the path between the two ends have been suggested. Zhou et al. [10] use a different way to cool polymer melt. They find the same mean length for the primitive path, but a different distribution of length. Foteinopoulou et al. [3] suggest a direct minimization of the length, called Z-code.

III. HOW TO MEASURE THE PRIMITIVE PATH?

A. Idea of Kremer and Grest

Kremer and Grest have suggested a way to measure the tube. They have done a simulation of polymer melt during a time \( t = 24000 \tau \) and taken the conformation of the polymer each \( t_{t,c} = 600 \tau \). Because they do simulation at time scale smaller than \( \tau_d \), the evolution of a polymer is governed by the tube. The figure 16 represents 40 configurations of one polymer. We can see a tube which governed the dynamic.

Zhou et al. [10] have done a similar work. They simulate for a long time with the ends of the polymers fixed to stop tube relaxation. From this simulation, they have measured the density of beads. The isosurfaces of density [fig. refkremertube.b] are like a tube. In the center of the tube we find the primitive path measured from cooling methods.

B. Tube of density.

We have done many simulations (1024) starting from the same initial position but with different initial velocities to get all possible trajectories which are accessible from the starting configuration. We save the positions of all the beads after a time \( \Delta t \). To see tube effects we have chosen 5 different time intervals: \( \Delta t = 0.2 \tau_c, 0.4 \tau_c, 0.6 \tau_c, 0.8 \tau_c \) and \( 1.0 \tau_c \).

We have calculated the density of beads at each of these time intervals. In figure 17 we plot the isosurface of density of the same polymer for two different times (\( \Delta t = 0.2 \tau_c \) to \( \Delta t = \tau_c \)). Isosurfaces show a well defined tube with slow evolution. The axis of the tube is conserved but its length seems to decrease. Furthermore the diameter increases slowly.

C. Mean position of the beads

When the polymer evolves in the tube, each monomer is constrained by the tube [fig. 18]. So the mean position of a bead should be on the primitive path for \( t \sim \tau_c \). The mean positions of all the beads make a path [fig. 19]. We call it mean path. This mean path seems to converge to the center of the the tube of density. To show this
Figure 16: (left) 40 configurations of a same polymer each separated by 600\(\tau\). In this plot we can guess the tube which governs the evolution of the polymer.


(right) Black and white lines are two measures of the primitive path using the Zhou’s method or the Everaers’ method. The surfaces are isosurfaces of density of beads. The isosurface of density creates a tube. We see that the primitive pathes follow this tube of density.


Figure 17: Isosurfaces of the density calculated at two different time intervals \(\Delta t = 0.2\tau_e\) (left) \(\Delta t = 1.0\tau_e\) (right) (blue surface \(d = 0.03\sigma^{-3}\) red surface \(d = 0.09\sigma^{-3}\)). White dots correspond to the initial position of the polymer.

convergence we plot the correlation of the length of the mean path for two different times [fig.20.a and b]. The correlation increases with the time and is very good between 0.8\(\tau_e\) and 1.0\(\tau_e\). While we have not explored the behaviour at times longer that \(\tau_e\), we expect that the mean path continue to shrink as a function of time (see fig. 18.c). For this report, we define the mean path at \(t = \tau_e\) as the primitive path which appear in the tube theory.

D. Reproducibility of the measure of the primitive path

We plot in figure 20.c the correlation of the length of the primitive path calculated from the same initial state but with two independent sets of 512 simulations. We have a very good correlation between the two measures and so a high reproducibility.

IV. ANALYSIS OF THE PRIMITIVE PATH

A. Length of the primitive path

Length of the primitive path, \(L_{pp}\) is an important parameter in the model. The relaxation by reptation depends on the length of the primitive path. Furthermore if we know the distribution of \(L_{pp}\) we can also measure the impact of the relaxation by fluctuation of the primitive path length. The distribution is plot on figure 21. The distribution is well approximated by a gaussian distribution. The mean length is \(< L_{pp} > = 33.9\sigma\) and the variance \(\Delta L_{pp} = 6.5\sigma\).
Figure 18: Evolution of the position of a monomer in a tube. The initial position of the monomer is the black dot. Its diffusion is represented by the blue circle.

**fig. a:** at short time the evolution is not constrained by the tube. The mean position (red cross) is at the initial position of the monomer.

**fig. b:** for $t \approx \tau_e$ the evolution is constrained by the tube, the mean position is on the primitive path.

**fig. c:** at long times, it diffuses along the tube with its mean position remaining on the primitive path till the disentanglement time.

Figure 19: Mean path at different times : $0.2\tau_e$ (blue), $0.4\tau_e$ (white), $0.6\tau_e$ (green), $0.8\tau_e$ (yellow), $\tau_e$ (red)

### B. Kuhn length of the primitive path

The primitive path calculated from the mean path can be seen as a random walk with 256 steps with correlation between successive steps. Primitive path are too small to lose all correlation between the first and the last step. So we can not measure the Kuhn length as $<\vec{R}^2>/<L_p^p>$ with $\vec{R}$ the end to end vector. However we can calculate $<\vec{r}_k^2>$ with $\vec{r}_k$ the vector between two points separated by k steps. For random walk with constant step length $b$, we can show that $<\vec{r}_k^2>$ obeys equation $\ref{eq:random_walk_stats}$. But the primitive path does not follow to this statistics [fig 22.a]. We have measured [fig. 22] the mean cosine of the angle between two step as a function of the distance along the primitive path between the two steps (and not as a function of the number of steps). We find that it obeys an exponential law $<\cos \theta> = \exp(-L/L_p)$ with a persistence length $L_p = 4.7\sigma$.

To define the Kuhn length, we can compare our result to a random walk with constant step length. In such a random walk the angle between two successive steps obeys $<\cos \theta> = \exp(-L_{step}/L_p)$ furthermore we have:

$$l_k = L_{step} \frac{1 + <\cos \theta>}{1 - <\cos \theta>} = L_{step} \frac{1 + e^{-L_{step}/L_p}}{1 - e^{-L_{step}/L_p}}$$

So we can approximate the Kuhn length of the primitive path by the equation $\ref{eq:kuhn_length}$ using the mean step length $<L_{step}> = 0.13\sigma$. We find $l_k = 9.5 \pm 0.5\sigma$

### C. Effective potential

From the mean density $\rho(r)$ of the beads at a distance $r$ from the tube, we can calculate the effective potential of the tube: $U_{eff}(r) = -k_BT \ln (\rho(r)/\rho(r = 0))$

The effective potential are quadratic for distances smaller than $6\sigma$. Assuming a functional form $U_{eff}(r) = k_BT r^2/(2R_{eff}^2)$, the measures of $R_{eff}$ are reported table $\ref{table:effective_radius}$. For distances larger than $6\sigma$, the potential is softer.
V. FROM THE POLYMER MELT TO THE TUBE MODEL

A. Model of one polymer in a tube

To be able to compare the result on a polymer melt to the tube model, we have constructed a model of one polymer in a tube. With this model we can try to answer two main questions. Firstly by calculating the effective potential can we measure a tube diameter. Secondly we would be able to compare our method for calculating the primitive path to the imposed primitive path.

The model is based on the molecular dynamics using the Kremer Grest model. Interactions between beads are the same that in paragraph II A. We do a simulation with one polymer of 256 beads.

1. Tube potential

To constrain the polymer in a tube we apply a tube potential which is a function of the orthogonal distance $r_\perp$ from a curve. This curve is the axis of the tube and so it is the primitive path. This primitive path is constructed by a random walk with a Kuhn length $L_{k,tube} = 11\sigma$. We have generated points with a step length of $0.2\sigma$. We have done simulation only with one primitive path.

To measure the orthogonal distance, we look for the closest point on the primitive path. The resolution of the primitive path is $0.2\sigma$ so we can expect an error of $0.2$ on $r_\perp$. To avoid the polymer jump from one part of the primitive path to another one, we have used a primitive path which has no loop. Furthermore when we look for the minimum distance we only consider the portion of the primitive path of length $2\sigma$ on both sides of the point we used at the last time step.

To avoid problem at the end of the primitive path we use a tube with a length of $L = 600\sigma$ and started with a polymer in the middle of the tube. Times of simulation are small enough to prevent the polymer from reaching the end of the tube.
Figure 22: **fig. a:** $<\vec{r}_2^2>/k$ as a function of $k$, the number of steps. We compare the result to equation 5 (black line for $b = L_{step} = 1.5$ and $<\cos \theta >= 0.95$). **fig. b:** Mean cosine of the angle between two steps as a function of the distance along the chain between those two steps. Line is a fit using $\exp(-l/L_p)$: $L_p = 4.7\sigma$ as a function of the distance along the chain.

Figure 23: **Effective potential** as a function of the distance from the tube calculated for two different times $0.2\tau_e$ and $1.0\tau_e$. Lines are fit using $U(r) = k_BT r_\perp^2/(2R_{eff}^2)$: $R_{eff} = 2.23\sigma$ (fit $0.2\tau_e$) and $R_{eff} = 2.49\sigma$ (fit $1.0\tau_e$).

We have considered two potentials.
- The first one is an harmonic potential $U = k_BT r_\perp^2/(2R_0)$.
- The second one is constant for $r_\perp < R_0$ and diverges for bigger distance. To simulate such a potential we have used:

$$U(r) = \begin{cases} 
0 & \text{if } r_\perp < R_0 \\
 k_BT (r_\perp - R_0)^2 / 2R_{wall} & \text{if } r_\perp \geq R_0 
\end{cases}$$  \hspace{1cm} (26)

We call it hardwall potential. $R_{wall}$ controls the hardness of the wall. For small $R_{wall}$, the beads will rarely visit the part with $r_\perp > R_0$. So for small enough $R_{wall}$, the exact value of $R_{wall}$ should have little impact on the simulation. We have done a simulation with $R_{wall} = 0.1\sigma$.

2. **Thermal stretch at the end of the polymer**

In a real polymer melt, the two ends of a polymer are not constrained by the tube [fig 24]. In our model, this freedom is missing. Doi and Edward have calculated that this freedom conducts to a force at the two ends of the polymer. In our model we apply a force on the two last beads of the chain. Those forces are along the primitive path in opposite directions and depend on one parameter $R_{end}$ with the magnitude:

$$F_{end} = \frac{3k_BT}{2R_{end}}$$  \hspace{1cm} (27)
3. Friction

In a polymer melt, a monomer feels interactions from other polymers. Those interactions can be assimilated to friction. Kremer and Grest [6] have measured the relaxation of the last Rouse modes \((p > N/N_e)\). Those modes should not be affected by topological constraints. From this relaxation, they have calculated a friction coefficient \(\zeta = 24 \pm 3 \tau^{-1}\). So simulations have been realized with a Langevin bath with the same friction coefficient.

4. Parameters of the simulation

We have done two simulations with an harmonic potential with 2 different parameters for \(R_0\) (6σ and 10σ). We have done the simulations with \(R_{end} = 6\sigma\) which correspond to the tube diameter calculated from the measurement of \(G(t)\). To test the impact of this force we have also done a simulation without force at the end \((F_{end} = 0)\). Two other simulations have been done with the hardwall potential with the parameters \(R_0 = R_{end} = 5\sigma\) and 7σ. The equations of motion are integrated with a verlet algorithm with a time step \(t_{step} = 0.01 \tau\).

<table>
<thead>
<tr>
<th>Type of potential</th>
<th>(R_0/\sigma)</th>
<th>(R_{tube}/\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harmonique</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>(F_{end} = 0)</td>
</tr>
<tr>
<td>Hardwall</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Table II: Parameters of the tube we have simulated

B. Monomer displacement

1. Harmonic potential

On figure 25 we have plot the monomer displacement, \(g_1(t) = \langle (\vec{r}(t) - \vec{r}(0))^2 \rangle\) measured for the different parameters.

The monomer displacement for the harmonic potential with \(R_0 = 6\sigma\) [fig. 25a] has 3 different power laws \((g_1(t) \propto t^\alpha)\) as a function of the time . Those three behaviours are consistent with the predictions of the tube model [I C.4]: at small times the beads do not feel the tube and so we have a Rouse like behaviour with an exponent \(\alpha_1 = 0.63\) not far from the coefficient 0.5 predicted by the Rouse theory. At intermediate times the beads feel the tube and we have \(\alpha_2 = 0.32 = \alpha_1/2\). At long times \(\alpha_3 = 0.69\) (the theory predicts 0.5). With these 3 power laws we can define \(\tau_e\) and \(\tau_r\) as the the time when respectively fit1 crosses fit2 and fit2 crosses fit3. We find \(\tau_e = 660 \tau\) and \(\tau_r = 25400 \tau\). The number of entanglement is given by \(Z = \sqrt{\tau_r/\tau_e} = 6.2\). Furthermore, we have measured the mean square displacement along the primitive path [fig. 25c]: \(\langle \Delta s^2 \rangle = \langle (s(t) - s(0))^2 \rangle\) with \(s(t)\) being the cuvilinear displacement along the primitive path of one monomer. We
find two power laws and the time of transition is $\tau_r$ measured above. For $t > \tau_r$, the exponent is $\alpha_1 = 0.48$ (prediction is $1/2$) and for $t > \tau_r$, $\alpha_2 = 0.88$ (prediction is 1). The monomer displacement for $R_0 = 10\sigma$ [fig. 25b and d], has the same behaviour. We can measure $\tau_e = 1085\tau$ and $\tau_r = 79000\tau$.

In figure 26 we compare the mean square displacement with and without a force at the end. We see few difference consistent with the incertitude.

**Figure 25:** Fig. a and b : $g_1$ as a function of time with $R_0 = 6\sigma$ (fig. a) and $R_0 = 10\sigma$ (fig. b). Fig. c and d : $\langle \Delta s^2 \rangle$ as a function of time with $R_0 = 6\sigma$ (fig. c) and $R_0 = 10\sigma$ (fig. d). All are averaged over all the monomer and are simulated with $R_{end} = 6\sigma$. The lines are fit using a power law $f(t) \propto t^\alpha$ : (fig a) fit1 $\alpha = 0.60$ fit2 $\alpha = 0.32$ fit3 $\alpha = 0.69$ (fig. b) fit4 $\alpha = 0.62$ fit5 $\alpha = 0.34$ fit6 $\alpha = 0.82$ (fig c.) fit7 $\alpha = 0.48$ fit8 $\alpha = 0.88$ (fig. d) fit9 $\alpha = 0.43$ fit10 $\alpha = 1.09$.

**Figure 26:** $g_1$ (fig. a) and $\langle \Delta s^2 \rangle$ (fig. b) averaged over all the monomers as a function of the time for an harmonic potential with $R_0 = 6\sigma$ with and without force at the end.
<table>
<thead>
<tr>
<th>type of potential</th>
<th>$R_0/\sigma$</th>
<th>$R_{end}/\sigma$</th>
<th>$&lt; L_{pp} &gt; /\sigma$</th>
<th>$\sqrt{\Delta L_{pp}^2}/\sigma$</th>
<th>$\tau_e/\tau$</th>
<th>$\tau_r/\tau$</th>
<th>$Z = \sqrt{\tau_e/\tau_r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harmonic</td>
<td>6</td>
<td>6</td>
<td>104.5 ± 0.5</td>
<td>12.8</td>
<td>660</td>
<td>25000</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$F_{end} = 0$</td>
<td>92.4 ± 0.5</td>
<td>12.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hardwall</td>
<td>5</td>
<td>5</td>
<td>102.7 ± 0.5</td>
<td>19.3</td>
<td>200</td>
<td>17000</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>7</td>
<td>104.1 ± 0.5</td>
<td>11.4</td>
<td>410</td>
<td>33500</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table III: Mean and variance of the length of the primitive path, $\tau_e$, and $\tau_r$ calculated from the monomer displacement for the different parameters.

2. Hard wall

We carry out the same analysis on results from the hardwall potential. In figure 27 we have plot $g_1(t)$ and $< \Delta s^2 >$ for simulation with an hardwall potential with $R_0 = 7\sigma$. $g_1(t)$ has three different power laws. But the transitions are not as clear as for the harmonic potential and the exponents are far from the theoretical predictions. However, we can measure $\tau_e$ and $\tau_r$ from those results [table III].

**Figure 27:** $g_1$ (fig. a) and $< \Delta s^2 >$ (fig. b) averaged over all the monomers as a function of time for the hardwall potential ($R_0 = 7\sigma$). The lines are fit using a power law $f(t) \propto t^\alpha$ with (fig. a) fit 1 $\alpha = 0.63$ fit 2 $\alpha = 0.50$ fit 3 $\alpha = 1.45$ (fig. ) fit 4 $\alpha = 0.47$ fit 5 $\alpha = 1.38$. 

C. Effective potential

When we apply a potential to a set of independent particle, the density obeys $\rho \propto \exp(-V/(k_B T))$. In a polymer the problem is different, a monomere feels also attraction from the two neighbours. Because there are more monomers in the center this attraction is directed to the center of the potential and so we get a narrower distribution. In the simulation we have calculated the distribution of beads as a function of distance $r_\perp$ from the primitive path. The distribution is calculated with 1000 configurations from 10 independent simulations. In each simulation the polymer is allowed to relax for times longer than 1000 $\tau$ and we consider subsequent configurations at intervals of 1000 $\tau$. This time is long enough to consider the configurations to be independent. From this distribution we can calculate the effective potential [fig. 28] using the equation : $U_{eff}(r) = k_B T \ln (\rho(r_\perp) / \rho(r = 0))$ where $\rho(r_\perp)$ is the density at a distance $r_\perp$.

The effective potential from simulations with an harmonic potential is an harmonic potential : $U_{eff} = k_B T r_\perp^2 / (2 R_{eff}^2)$. But $R_{eff}$ is smaller than $R_0$ which is consistent with the prediction of a narrower distribution. The potential is not affected by the force $F_{end}$.

Effective potentials from hardwall simulations are also narrower than applied potentials. They are not constant for $r_\perp < R_0$ but increase slowly to diverge at $r_\perp = R_0$.

D. Analysis of the primitive path

In this model, the primitive path is known. The two ends of the polymer defines the two ends of the primitive path. So it is easy to measure the length of the primitive path of one polymer. We have measured the
distribution of the length for the different parameter for 1000 polymers. The mean length and the variance are reported on Table III.

For the harmonic potential the mean length decreases with the radius of the tube. Furthermore, the force applied at the end increases the tube length of the tube. For the hardwall potential, the mean length stays nearly constant between $R_0 = 5$ and $7 \sigma$. This result is against the prediction. We have measured the primitive path by calculating the mean path. We have realized 100 simulations from the same initial state with an harmonic potential, $R_0 = 10 \sigma$ and $R_{end} = 6 \sigma$. We have measured the mean position of the monomers [fig. 29] after 1000$\tau$ which correspond to $\tau_c$ measured for those parameters. The mean position follows the axes of the tube. But the mean path is smoother than the tube. The initial length of the tube is $109 \sigma$ the length of the mean path is only $85 \sigma$.

**VI. DISCUSSION**

In this report we have suggested a way to visualize the tube by constructing isosurfaces of density. It could be interesting to compare our result to simulation where polymers can cross each other to see if the tube of density is really due to entanglement. Using this tube of density, we have proposed a new way to measure the primitive path with the mean path. If we compare our results to the simulation of one polymer in a tube, we see that mean path is a good approximation of the primitive path. But the mean path is smoother than the primitive path.

We have measured the effective potential of the tube and found an harmonic potential. This potential becomes softer with the time, which corresponds to relaxation. We have proved that one part of this potential is due to interaction with other polymers of the chain. The part only due to the tube is also an harmonic but with
a typical length $R_0$ bigger than the parameters $R_{eff}$. The result from the tube melt agrees quite well with the simulation of the tube model with a harmonic potential with $R_0 = 10\sigma$.

We have shown that the tube diameter is not something obvious to be defined from the potential. The mean square displacement seems to obey the tube theory, but the terminal time depends on the tube diameters. So the entanglement number cannot be measured from $Z = \sqrt{\tau_r/\tau_e}$. Furthermore we have seen [table III] that $\sqrt{\tau_r/\tau_e}$ increases with the tube diameter whereas it should decrease. Another way to get the tube diameter should be to measure the length of the primitive path. But the length of the primitive path depends on the force at the end. We are able to measure $\tau_e$ and $\tau_r$ from simulations, and we have underlined differences with the tube model. Those differences are more important for the hardwall potential.

**Conclusion**

During my internship, I have used a model of polymer melt to measure the primitive path. This measure is the first step to improve the tube model. Not only have we measured the primitive path but we have also measured the effective potential of the tube. I have also created a numerical model for one entangled polymer by considering the tube potential as an externally applied potential.

This internship has been for me a way to learn many interesting things. I have improved my skills in computer and in using programming languages such as C++. I have also learnt the true problems of simulation as time of calculation.

**Acknowledgment**

I would like to thanks all the polymer group of the university of Leeds who reserved me a warm welcome and took time to answer my questions. I would like to thanks Peter Olmsted and Chimnay Das who guided me and trusted me.