Simple numerical techniques for mesoscale polymer models
Koopman, E.A.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 7

Polymer scaling behaviour in non-integer dimensions

7.1 Introduction

We are generally comfortable with the idea of different spatial dimensionalities, \(d\). For example, a one dimensional system lies on a line (described by one set of coordinates), a two dimensional system on a plane (described by two sets of coordinates) and a three dimensional system (described by three sets of coordinates) is that space that we commonly experience. Extending this to higher dimensionalities, described by an increasing number of coordinates, is mathematically (if not conceptually) straightforward. As an example, the integral \(I_d\) of some radially symmetric function \(f(r)\) over a hyperspace volume \(V\) of radius \(R\) is

\[
I_d = dC(d) \int_0^R f(r) r^{d-1} dr
\]

with

\[
C(d) = \frac{\pi^{d/2}}{\Gamma(1 + d/2)}
\]

Notice that in the above we could in principle treat \(d\) as a continuous variable. That is, also take non-integer values of \(d\). This would correspond to the odd concept of a system described by a fractional number of Cartesian coordinates. Nonetheless, several quantities when considered in hyperspace yield an expression that “advertises” such an extension to non-integer dimensions in this way [129]. The question is; does this extension to fractional dimensionalities have any physical meaning, or is it simply one of an infinite number of possible interpolation formulas between integer spatial dimensions? After all, we could always augment this type of procedure by introducing an additional function that vanished for integer dimensions and still recover the correct expression
for integer dimensions. With this in mind, Stillinger attempted to derive an axiomatic, rather than phenomenological, basis for non-integer dimensions.

The relevance of this to polymers is as follows. The Flory result for the scaling exponent, $\nu$, of a polymer with excluded volume (this is a chain where the monomers have a finite volume and cannot overlap, see Chapter 5) can be derived in general spatial dimensions yielding

$$\nu = \frac{3}{d + 2}$$

(7.3)

for $1 \leq d \leq 4$, and $\nu = 1/2$ for $d \geq 4$. In the one dimensional case the scaling of the end to end vector $\vec{R}_e$ is trivial ($\langle R_e^2 \rangle^{1/2} = N$) with $N$ the number of monomers and assuming the Kuhn length to be unity. The Flory model reproduces this correctly. Similarly, the two dimensional case can also be solved analytically ($\langle R_e^2 \rangle^{1/2} = N^{3/4}$ [130]). and agrees with the Flory result. It is also correct in its prediction that for $d \geq 4$ there is no "excluded volume" effect, because then $\nu = 1/2$ - the ideal chain result. One approach to improving the estimate of the exponent in three dimensions is to take advantage of this fact and write the exponent as a perturbation expansion from $d = 4$ in terms of a parameter $\epsilon = 4 - d$. Deriving this expansion involves generalizing integrals to non-integer dimensions using the form given in equation 7.1. This so called "epsilon expansion" yields to first order

$$\nu(\epsilon) = \frac{1}{2} - \frac{\epsilon}{16}$$

(7.4)

In fact, the first indication that the Flory result was not in general exact came from the observation that it yields an incorrect coefficient of $1/12$ for the second term in the $\epsilon$-expansion [131, 132]. Consequently, its prediction for the most practically important case of three dimensions, that $\nu = 3/5$ is incorrect. The best current numerical estimate is that $\nu = 0.5876$ [133].

Clearly, the concept of non-integer dimensions is essential to this approach for deriving the scaling exponent. Numerical solutions to the problem provide predictions for the exponent in all dimensionalities, as do other closed expressions for the exponent based on alternative approaches to that of Flory [134, 135]. In lower dimensions the excluded volume affects is much stronger. That is short chains are more expanded and closer to the scaling limit, making it easier to determine the correct value of the exponent. An obvious way to test these predictions, rather than the brute force approach of simulating ever longer chains in three dimensions, is to develop a methodology for simulating them in fractional dimensions. For example, one could look for the lower critical dimensionality (the scaling exponent reaching unity for a dimensionality between $d = 1$ and $d = 2$) predicted by these theories.
The best known subject linked in a way to non-integer dimensional spaces is probably the group of objects known as fractals. These typically consist of subset of points from an integer dimensional space that is generated through some recursive rules. Trying to generate polymer chains in such spaces gives scaling exponents for even the most trivial case that are very different from the behaviour in the integer dimensional spaces in which the fractal is generated (See figures 7.1 and 7.2). This is related to the well studied phenomena of anomalous diffusion. We think that although this has its uses in fields of research such as diffusion in porous materials, it will not be of much use for problems related to theoretically predicted scaling exponents of polymers in fractional (as opposed to fractal) dimensions, because there is no demonstrable link to the mathematical procedures used when considering polymers in fractional spatial dimensionalities.

Figure 7.1: Fractal on which we generated random ideal chains.

Other people have already attempted to solve just this problem in non-
integer dimensions using re-normalization theory. We will approach it using a different method based on the proposal of Stillinger for the treatment of non-integer dimensional spaces [129].

7.2 Non-integer dimensional spaces

Stillinger starts by giving 5 axioms that should apply to a non-integer dimensional space $\int_D$. Most are very similar to the axioms relating to regular integer dimensional spaces, but we will list all of them here.

A1 $\int_D$ is a metric space.

A2 $\int_D$ is dense in itself.

A3 $\int_D$ is metrically unbounded.

A4 For any two points $y, z \in \int_D$ and any $\epsilon > 0$ there exists an $x \in \int_D$ such that:
(a) \( r(x, y) + r(x, z) = r(x, z) \);

(b) \( |r(x, y) - r(x, z)| < \epsilon r(y, z) \).

A5 The following equation holds:

\[
\int d\mathbf{x}_0 \exp\left(-\sum_{j=1}^{n} \alpha_j r_{0j}^2\right) = \left(\frac{\pi}{\tau}\right)^{D/2} \exp\left(-\frac{1}{\tau} \sum_{j<k=1}^{n} \alpha_j \alpha_k r_{jk}^2\right)
\]

with \( \tau = \sum_{j=1}^{n} \alpha_j \)

Here \( \alpha \) is some arbitrary variable, \( r_{ij} \) is the distance between point \( i \) and \( j \) and finally \( n \) is the number of points considered. The last axiom can be thought of as a more generalized version of the well known Gaussian integral

\[
\int d\mathbf{r} e^{-\alpha r^2} = \frac{\pi^{D/2}}{\alpha^{D/2}}.
\]

There are some consequences related to defining a space in this way. Most importantly, it does not allow us to write coordinates of a point in the regular vector way, we can only work with distances.

Stillinger then derives from axiom A5 an expression for integration weights. The easiest way to see where and how one needs those is from the volume of a sphere/circle in \( D \) dimensions. Knowing that we can only work with distances, we need a function that gives the amount of space at a distance \( R \) from a given point (the integration weight \( W_1 \)), if we then integrate this function from 0 to \( R \) we get the amount of space embedded in such a volume. Stillinger gives

\[ W_1 = \frac{2\pi^{D/2} R^{D-1}}{\Gamma(D/2)}. \]

Carrying out this integration, one gets

\[ V(R, D) = \int_0^R W_1(r) \, dr = \frac{\pi^{D/2} R^D}{\Gamma(1+D/2)}. \]

This indeed reduces to the well known results \( 2R \), \( \pi R^2 \) and \( \frac{4}{3} \pi R^3 \) for 1, 2 and 3 dimensions respectively. Similarly, one can use the other integration weights \( W_n \) for integrals involving \( n \) distances, the expressions for \( W_n \) with higher \( n \) do however get very tedious to calculate.

Stillinger suggest that we use the following "2 center weight":

\[ W_2(x_1, x_2 | r_{01}, r_{02}) = 2^{(D-3)} \sigma(D - 1) r_{01} r_{02} r_{12}^{(D-D)} \Delta^{D-3} (r_{01}, r_{02}, r_{12}) \]

with \( \Delta \) being the area of a triangle with sides \( r_{01}, r_{02} \) and \( r_{12} \) that can be calculated using a Cayley-Menger determinant [136]. A shorthand is used for \( \sigma \), defined as \( \sigma(D) = \frac{2\pi^{D/2}}{\Gamma(D/2)} \). This indeed seems to be the right expression for the area of the overlap between two circles/spheres shells separated a distance \( r_{12} \) and with an inner radius of \( r_{01} \) and \( r_{02} \) and an outer radius of \( r_{01} + \delta r_1 \) and \( r_{02} + \delta r_2 \).

Since our main interest in this work is with polymers, we will first attempt to interpret the weight functions such that they are useful for generating valid configurations in \( D \) dimensions. Consider a configuration with 3 points \( x_0, x_1 \)
and $x_2$ and only two known distances $r_{01}$ and $r_{12}$. In all integer dimensions the distribution for the 3rd one can be calculated, for example the simple case where $r_{01} = r_{12} = 1$. In 1 dimension there are two possible solutions, $r_{12} \in \{0, 2\}$. Both should be sampled with equal weight if we want to sample such configurations. For 2 dimensions we can derive the expression by realizing that the angle $\theta$ between the two known lines is uniform. The unknown distance is then $r_{12} = 2 \sin(\theta/2)$, solving for $\theta$ we get $\theta = 2 \sin^{-1} \frac{r_{12}}{2}$. If we then take the derivative with respect to $r_{12}$ we get $\frac{1}{\sqrt{1 - \frac{r_{12}^2}{4}}} = \frac{\partial \theta}{\partial r_{12}}$.

We can take a similar approach for the 3 dimensional case (which we will not use further on). The angle between the two known lengths is uniform in $\cos \Theta$, which in this case is equal to the dot-product ($\omega$). The resulting unknown distance $r_{12}$ is now $\sqrt{2 - 2\omega}$, solving for $\omega$ we get $\omega = 1 - \frac{r_{12}^2}{2}$. Again taking the derivative we get $\frac{\partial \omega}{\partial r_{12}} = r$. This implies that if we take $W_2$ in any dimension $d > 1$, we can use it to generate a distribution from which we need to sample.

Now the next problem is generating 4 point configurations. Stillinger mentions for $W_2$ that the Cayley-Menger determinant should be 0 if no triangle can be formed. This is equivalent to saying that it should be 0 if it is not real and positive. We should also assume that if a triangle can be formed in any dimension $D > 1$, we can also form a tetrahedron in $D > 2$ and an $n$-dimensional simplex in $n > (D - 1)$ dimensions.

There is a good argument for this that follows directly from Stillinger’s formalism. Remembering that the integral $\int_0^a x^n dx$ is only defined for $n \geq -1$ we can analyse $W_n$. $W_n$ needs to be integrable to be able to use it as a distribution of lengths. So we should check for which values of $D$ $W_n$ is integrable. For $W_1$ we have $W_1 = r^{(D-1)} * f(D)$, with $f$ being some irrelevant function. This is only integrable for $D > 0$. For the trimer case with bond-lengths 1 we can write $W_2 = r(4r^2 - b^4)^{\frac{D-3}{2}} f(D)$. This is only integrable on $0 \leq r$ for $D > 1$. Similarly for $W_3$ there is a multiplication with a Cayley-Menger determinant raised to the power $D - 4$. This determinant takes the form of a polynomial of at most order 4 in any of its variables. Using the same argument used for $W_2$ we come to the conclusion that $W_3$ can only be integrable for $D > 2$. Now our assumption is that any $W_n$ is only integrable for $D > (n - 1)$.

Working from this assumption we see that all the higher order weights $W_n$ have relatively simple forms in dimensions $D \leq 2$, namely the values for which the Cayley-Menger determinant associated with the simplex in $n$ dimensions is exactly 0. If we then work only between 1 and 2 dimensions we can see that the actual equation for configurations with more than 3 points is irrelevant, they should only be chosen such that the volume of a simplex spanned by those points is 0.
7.3 Application

We will apply Stillinger’s approach to a single polymer chain in vacuum. To simplify matters we will only consider two models of such a chain, the ideal chain with fixed bond-lengths and an excluded volume chain where the fixed bond-length is equal to the monomer diameter. The reason for this is mostly computational efficiency later on.

Now let us first consider a trimer. We can place the first monomer $x_0$ anywhere we want in our fractional dimensional space. The second one is then added at a random point on the spherical shell with radius 1 having $x_0$ as centre point. The last monomer is now randomly put on the spherical shell with radius 1 having $x_1$ as centre point taking care that for multiple configurations the distribution $W_2$ is correctly sampled. An easy way to do this is simply construct a distance matrix $r_{ij}$, set the diagonal to 0, the first off diagonal to 1 and the second off diagonal to a random number sample from the distribution $W_2$. Working only with distances also avoids explicitly constructing a position, for which we have no clear definition in a fractional dimensional space.

Generating a random number from $W_2$ can be done by integrating $W_2$ between 0 and 2, inverting it and applying that function to random numbers from a uniform distribution between 0 and 1. This procedure can be extended to chains of arbitrary lengths. There is however some subtlety involved that is not directly clear from Stillinger’s formalism. All the weights $W_n$ he mentions contain a multiplication with a Cayley-Menger determinant. The problem is that this restricts the domain for which $W_n$ is valid in dimension $d \leq n - 1$ because the volume of a $d$ dimensional object in $d-1$ dimensions or less should be 0. If we interpret this as constraints on the system, we can generate longer chains.

For the ideal chain in $1 < d \leq 2$ dimensions we use the following two constraints: $C_2$ for a configuration with 4 points and 5 known distances, the 6th and last one then has 2 possible values, and $C_1$ for a configuration with 5 points and 9 known distances, the 10th and last one then has one single unique value. When applying $C_2$, we pick one of the two solutions at random with equal probability.

To summarize, we generate a single chain configuration by calculating every element in a distance matrix $r_{ij}$ in this way:

$$r_{ij} = \begin{cases} 0 & |i - j| = 0 \\ 1 & |i - j| = 1 \\ \hat{W}_2 & |i - j| = 2 \\ C_2(r_{i,i+1}, r_{i,i+2}, r_{i+1,i+2}, r_{i+1,i+3}, r_{i+2,i+3}) & |i - j| = 3 \\ C_1() & |i - j| > 3 \end{cases}$$
where $\hat{W}_2$ is a random number generated from the distribution $W_2$, $C_2$ is the constraint using all the known distances between $x_i$, $x_{i+1}$, $x_{i+2}$ and $x_j$ (assuming $i < j$) and $C_1$ is the constraint using all the known distances between $x_i, x_{j-3}, x_{j-2}, x_{j-1}$ and $x_j$ (assuming $i < j$).

![Figure 7.3: C2 constraint. For a 4 points configuration the last distance can be one of two values (or one degenerate). The thick line represents the configuration, 4 can be placed on either of the two given locations. The thin straight lines are distances we already fixed. The large circle represents the distance we have generated between 2 and 4, the small circle represents the (unit) distance between 3 and 4.](image)

![Figure 7.4: C1 constraint. For a 5 points configuration the last distance can be only one unique value. The thick line represents the configuration, the thin lines are the distances we have already generated.](image)

There are at least two approaches for applying the constraints $C_1$ and $C_2$. One is finding the roots for the 4th and 3rd order polynomials resulting from the Cayley Menger determinants for a 4 and 3 dimensional volume respectively. The roots for $C_2$ always consist of 2 positive roots (possibly degenerate).
and the solution to $C_1$ always has just one positive degenerate solution (see figure 7.4). Another approach is constructing actual vector coordinates in 2 dimensions for all the points and using circle intersections for finding the solutions to $C_2$ and $C_1$ (see figure 7.3).

### 7.4 Experimental details

As in all the chapters in this work, the actual experiments are computer simulations. For our setup to generate non-integer dimensional polymer chains there is no reference code or even similar code available, so we will attempt to describe through some code snippets the full procedure.

We start with some helper functions and definitions.

```c
double d; // Dimensionality of the system

double sigma()
{
    return 2 * pow(PI, d/2)/exp(gamma(d/2));
}

double vol(double a, double b, double c)
{
    return 0.25 * sqrt(2 * (a*a*b*b + a*a*c*c+b*b*c*c)
        - (a*a*a*a) - (b*b*b*b) - (c*c*c*c));
}

double w2(double r01, double r02, double r12)
{
    return pow(2.0, d-3) * sigma(d-1) * r01 * r02
        * pow(r12,2-d) * pow(vol(r01,r02,r12),d-3);
}

double randf()
{
    return (double)rand() / (double)RAND_MAX;
}

double c2(double r02, double r13)
{
    // Randomly pick on of the two options
    if(rand() \%2 == 0)
    {
    
```
return (sqrt(2 + r02 * r02 * r13 * r13 - r02 *
    sqrt(4 - r02 * r02) * r13 *
    sqrt(4 - r13 * r13)) /
    (sqrt(2.0)));
}
else
{
    return sqrt(1 + (0.5 * r02 * r02 * r13 * r13)
        + 0.5 * r02 * r13 * sqrt(4 - r02 * r02)
        * sqrt(4 - r13 * r13));
}
}

double rw2()
{
    // Look-up on a pre-calculated table.
    // Table is calculated by integrating \( w_2 \) with fixed
    // values \( r_{01}=1 \) and \( r_{12}=1 \), normalizing it and then
    // doing an inverse look-up from a uniform random number.
}

This calculates the unique missing distance if we have a 5x5 symmetric
distance matrix with only (0,4) and (4,0) missing. We tried to do this directly
by explicitly putting in the 0 value solution to a Cayley-Menger determinant
with those two values as unknowns. However the expression we retrieved for
this from Mathematica was over 130 lines of obfuscated c code that proved to
be unstable due to round-off errors.

double c1(double y01, double y02, double y03,
    double y12, double y13, double y14,
    double y23, double y24, double y34)
{
    double r04[4], dr[4], min;
    int i, mini;
    double a, b, dz, e, f;
    // This one tries to find 0-4, do two sub problems and result
    // common solution:
    // first 0 2 3 4
    a = y02*y02;
    b = y03*y03;
    dz = y23*y23;
    e = y24*y24;
    f = y34*y34;
    r04[0] = (b*dz-dz*dz+b*e+dz*e-b*f+dz*f+a*(dz-e+f)
And the actual program that we abbreviated by not doing self-avoiding walks and generating just a single configuration, such functionality will be left as an exercise to the reader. When doing self-avoiding walks, keep in mind that a very easy optimization is by only generating values from \( \text{rw2()} \) that fall
in the \([d..2]\) range when using spheres with diameter \(d\).

```c
int main(int argc, char **argv)
{
    // dimensionality, not checked for <1..2] range.
    d = atof(argv[1]);

    // \(r\) is a square matrix of size np, where
    // np[i][j] is the distance between particle i and j.

    // Distances to self
    for(i=0;i<np;i++)
    {
        r[i][i]=0;
    }

    // Rigid chain
    for(i=0;i<(np-1);i++)
    {
        r[i][i+1]=1;
    }

    // Stillinger's expression for 3 point distance
    // with 2 knowns (1,1)
    for(i=0;i<(np-2);i++)
    {
        r[i][i+2]=rw2();
    }

    // Get one of the (at most ) two allowed
    // distances in 1 < d <= 2
    for(i=0;i<(np-3);i++)
    {
        r[i][i+3]=c2(r[i][i+2],r[i+1][i+3]);
    }

    // All remaining points in the distance matrix are
    // now uniquely determined. Calculate each of them,
    // diagonal by diagonal, inward out.
    for(i=4;i<np;i++)
    {
        for(j=0;(j+i)<np;j++)
        {
            // Code continues...
        }
    }
}
```
7.5 Results

Using the method described in the previous section we can generate two types of chains, ideal chains and excluded volume chains. Every generated configuration can be accepted as an ideal chain, while only chains where each distance is larger than 1 is a valid excluded volume chain.

In all integer dimensions we know that the following relation for the end to end distance $R_e$ of an ideal chain holds:

$$\langle R_e^2 \rangle = N$$

We tested this for different dimensionalities between 1 and 2 and found that this relation holds very accurately.

It is interesting to note again that for the same problem on fractals, this relation does not hold (this is known as “anomalous diffusion”). Some end to end vector distributions can be found in figure 7.2.

If we consider excluded volume chains, the probability of generating a valid configuration is extremely small even for relatively short chains. One easy way to generate much longer chains is by generating random numbers from $w_2$ but only ones that are between 1 and 2. This way we can generate quite long chains for dimensionalities close to 1. Doing this we discover that the scaling of the end to end vector is different from the predictions of both Dreischor and Lowe and re-normalization group theory. For all dimensionalities $2 > d > 1$ the scaling seems to go to the two dimensional result $\langle R_e^2 \rangle \sim N^{3/d}$, only the “length-scale” where this happens gets longer for lower dimensionalities (Fig 7.5). Only in the limit of $d \rightarrow 1$ do we recover the 1 dimensional scaling $\langle R_e^2 \rangle \sim N$. 

\[\]
7. POLYMER SCALING BEHAVIOUR IN NON-INTEGER DIMENSIONS

![Graph showing d log(R^2)/d log(N) vs N for different values of d.](image)

Figure 7.5: Scaling exponent of d-dimensional chains.

7.6 Conclusion

It seems that within Stillinger’s framework it is possible to model polymer chains in non-integer dimensions. Interestingly enough the results do not agree with known predictions for scaling behaviour in these cases. One slightly disturbing observation is that the behaviour of both an ideal and an excluded volume chain approach that of a 2-dimensional chain for all dimensionalities between 1 and 2. Stillinger already notes something similar when he says “It leads to the striking conclusion that the number of mutually perpendicular lines can exceed the dimension of space, specifically when $2 > D > 1$”. This can lead to two different conclusions. The first might be that the method is flawed. We assumed that, as Stillinger implies, a triangle “fits” in any dimensionality larger than 1, a tetrahedron only fits in a dimensionality larger than 2 etc. This assumption basically gives the method an integer number of independent degrees of freedom leading to integer dimensional behaviour.

The other conclusion (which we think is the relevant one) is that non-integer dimensionality is not “naturally” defined. We believe though, that this is the right approach for dealing with non-integer dimensional problems. As Stillinger shows, the formalism allows one to reproduce many results that
have the dimensionality as a continuous variable in the solution. Under the presumption that the formalism itself is correct, we now claim that at least for polymer physics, all physics in non-integer dimensions are equal to those in the next-highest integer dimension. While this might be a slightly disappointing conclusion, the computational effort required to get a certain degree of accuracy is less for certain non-integer dimensional cases. It might also open the door to new and more efficient Monte-Carlo schemes, since there are multiple ways of choosing a valid 3 particle pair configuration that we have shown are equivalent when you are only concerned with the scaling behaviour.