

Statistical Mechanics Assignment 5 Solutions

I used Excel for these simulations. To generate, the polymers, I first generated random θ and ϕ values. If r_1 and r_2 are random numbers (produced by the Excel `RAND()` function), then $\theta = \pi r_1$ and $\phi = 2\pi r_2$. I then generated random unit vectors using the formulas

$$\begin{aligned}\Delta x &= \sin \theta \cos \phi, \\ \Delta y &= \sin \theta \sin \phi, \\ \Delta z &= \cos \theta.\end{aligned}$$

I placed the first monomer at $(0, 0, 0)$. Subsequent monomers were placed by adding random vectors generated as described above to the previous monomer's coordinates. I generated 1000 monomers in this fashion. To study the dependence of the radius of gyration (r_g) on the number of monomers (n), I performed the calculations described below for the first n monomers, for different values of n . Because of the automatic recalculation in Excel everytime any cell value is changed, each value of n represents a statistically independent sample.

The calculation of the radius of gyration of a monomer proceeded in three steps. First, I calculated the centre of mass (CM) by

$$x_{\text{CM}} = \frac{1}{n} \sum_{i=1}^n x_i,$$

and similarly for the y and z coordinates. I then calculated, for each monomer, the relative displacement from the CM:

$$s_{x,i} = x_i - x_{\text{CM}},$$

again with similar calculations for the y and z coordinates. The radius of gyration is then

$$r_g = \sqrt{\frac{1}{n} \sum_{i=1}^n (s_{x,i}^2 + s_{y,i}^2 + s_{z,i}^2)}.$$

A few Excel implementation details: Most of the calculations described thus far were carried out in a straightforward way. An ensemble of 122 polymers was generated by putting one polymer on each worksheet. To allow easy subsetting, the `INDIRECT()` function was used, with ranges required for various operations stored in the first worksheet (`Sheet1`). The value of n was calculated by

`COUNT(INDIRECT(A1004))`

Cell A1004 held the range of x values to be used in the calculations, e.g. A2:A101 for $n = 100$, or A2:1001 for $n = 1000$. Similarly, the centre of mass was found using the formulas

```
SUM(INDIRECT(A1004))/B1005
SUM(INDIRECT(B1004))/B1005
SUM(INDIRECT(C1004))/B1005
```

where B1004 and C1004 held the ranges of y and z values, and B1005 held the value of n . Similarly, the ranges of cells which held the values of $s_{x,i}$, $s_{y,i}$ and $s_{z,i}$ were described in the entries of cells F1004, G1004 and H1004, respectively. The radius of gyration was calculated by

```
SQRT((SUMSQ(INDIRECT(F1004))+SUMSQ(INDIRECT(G1004))
+SUMSQ(INDIRECT(H1004)))/B1005)
```

In the second and subsequent worksheets, similar calculations were performed except that references to cells A1004, B1004, . . . H1004 were replaced by `Sheet1!A1004`, etc.

Finally, the ensemble average and standard deviation of the radius of gyration were calculated using the following Excel formulas:¹

```
AVERAGE(Sheet1:Sheet3!A1010)
STDEVA(Sheet1:Sheet3!A1010)
```

Note that, despite its name, `Sheet3` was my last worksheet. I just made sure that I inserted my worksheet copies before `Sheet3` when I created my ensemble.

By changing the ranges in cells A1004, B1004, . . . H1004, I calculated the radius of gyration and its standard deviation for ensembles corresponding to various values of n . Theoretically, we should have

$$r_g = \sqrt{n\ell^2/6}.$$

Figure 1 shows my computational results, along with the theoretical curve. The theoretical curve is well within the error bars of the calculation. Interestingly, every single point is below the theoretical curve. Although this is a small effect, it seems like a systematic error, either in the simulation, or in the theory, since this event would only be expected to occur by chance once in 2^{10} (1024) times. Given the number of approximations required to obtain the radius of gyration, I would suspect that the theory is at fault, but for the moment I have no idea which approximation would be responsible for this systematic error. That being said, the agreement between our computational experiment and theory is still excellent.

¹STDEVA() gives the sample standard deviation, while STDEV() gives the population standard deviation. We have a sample (i.e. a random subset of a group, in this case the group of all possible freely jointed polymers) rather than a population (i.e. all members of a particular group). The difference between the two kinds of standard deviation is small unless you have a very small sample, so this isn't an issue you need to worry about much.

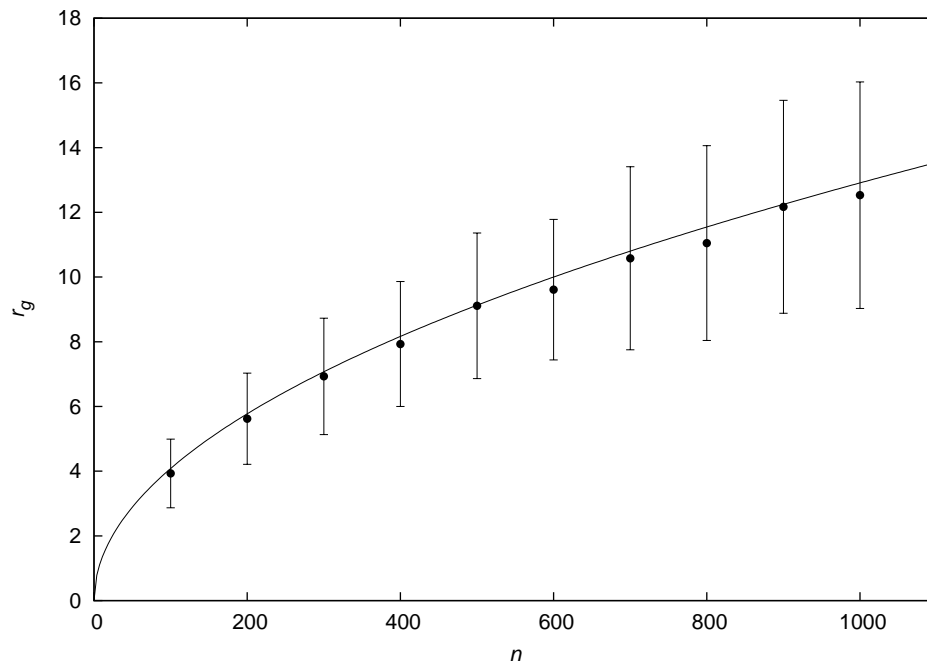


Figure 1: Radius of gyration vs n . The error bars show the standard deviations of the simulation averages. The curve is the theoretical relationship $r_g = \sqrt{n/6}$.