

## Chemistry C3102-2006: Polymers Section

### HOMEWORK #2

### SOLUTIONS

The aim of this short homework is to familiarise the student with the Gaussian probability distributions, which are central to the thermodynamics of polymer chains, and important in many areas of science

**Due Tuesday, May 2**

*We will have a problem solving session on Friday. April 28, 11AM-Noon, to address aspects of these homework problems.*

1. The size of an ideal chain is described by its mean square end-to-end distance,  $R \sim \sqrt{N}a$ . Name all assumption made in the ideal chain model and contrast them with assumptions made in the ideal gas model. Qualitatively describe how the size of the real chain would differ from the ideal chain if these assumptions were lifted.

The ideal chain model assumes:

- Assumes a linear chain of  $N$  statistical monomers, each of size or length  $a$  which have no orientational correlation in their successive placement. Or in other words, an ideal chain traces the trajectory of a random walker of  $N$  steps, each of size  $a$ .
- There are no interactions (attractive, repulsive, or volume excluding) between monomers of the chain such that the chain can self-intersect.

The analogous assumptions on an ideal gas are:

- An ideal gas comprised of  $N$  molecules in volume  $V$ , where each molecule has no positional correlation in its container of volume  $V$  (equally likely to be at any position within the container, with no correlation between molecules,
- There are no interactions (attractive, repulsive, or volume excluding) between gas molecules such that gas molecules can overlap each other.

If you were to lift assumption (1) and consider orientational correlation between successively-placed (but still inert and intersectable) monomers, then the size of the chain would increase, but the scaling law would remain unchanged. As explained in section, orientational correlation effectively increases the size of the statistical monomer, but the chain can still be modelled as an ideal chain, but one of fewer statistical monomers of larger size. Let  $N$  and  $a$  represent the chain of  $N$  correlated monomers of size  $a$ . Let  $a_{stat}$  be the size of a statistical monomer, or the smallest length along the chain backbone over which there is no orientational correlation and the chain can be considered again, freely jointed.  $a_{stat} > a$ . Then, the contour length of the chain is

$$Na = N_{stat}a_{stat}$$

or  $N_{stat} = Na/a_{stat}$ . Now the size of the correlation chain,  $R_{correlated}$  can still be written using the ideal chain scaling law if we use  $N_{stat}$  and  $a_{stat}$ .

$$\begin{aligned} R_{correlated} &\sim \sqrt{N_{stat}a_{stat}} \\ &\sim \sqrt{\frac{Na}{a_{stat}}}a_{stat} \\ &\sim R\sqrt{\frac{a_{stat}}{a}} \end{aligned}$$

and as  $\sqrt{a_{stat}/a} > 1$ , then  $R_{correlated} > R$ , *i.e.*, lifting the assumption of no orientational bias renders a chain with a larger mean end-to-end distance.

If you were to lift the assumption (2) and consider energetic interactions between monomers of the chain, you would get a change in chain size, as well as a different scaling expression. The scaling expression that you would get with attractive monomer-monomer interactions, repulsive monomer-monomer interactions, and excluded volume interactions is the topic of Chapter 3. Here we can qualitatively understand the size change as

- **attractive interactions** between monomers bring the monomers closer together, causing the chain to adopt configurations that are, on average, smaller;
- **repulsive interactions** push monomers apart, causing the chain to adopt configurations the are, on average, larger;
- **excluded volume interactions** prevent monomers from overlapping and the chain from self-intersecting. As chains are more likely to be self-intersecting when in compact configurations, the removal of excluded volume interactions causes the chain to increase in size.

2. A child builds a linear “sculpture” by randomly gluing together the ends of 120 identically sized sticks. For his first sculpture, the sticks are glued end-to-end, randomly onto paper (*i.e.*, the sculpture is 2-dimensional), but his later sculpture is 3-dimensional. Two thousand children Canberra-wide complete similar structures.. The probability distributions for the end-to-end distance for the 2- and 3- dimensional structures are said to be Gaussian. Provide formula for these distributions, making sure that you clearly state all assumptions necessary in constructing the Gaussian distribution from the sculpture exercise. How does the variance in the distribution depend upon the number of sticks in each sculpture and the total number of sculptures made by the children? AIM: to apply expressions for Gaussian distributions to an “experiment”

The Gaussian distribution of  $x$ , a  $d$ -dimensional measure is:

$$p(x) = \left(\frac{d}{2\pi\sigma^2}\right)^{d/2} \exp\left(-\frac{d(x - \langle x \rangle)^2}{2\sigma^2}\right)$$

where  $\langle x \rangle$  is the mean of  $x$  and  $\sigma^2$  is the variance which characterises the breadth of the distribution. The sculptures can be constructed a large number of ways and the distributions  $p_2(\mathbf{R})$ ,  $p_3(\mathbf{R})$  characterise the distribution of sculptures in terms of their end-to-end vector. In both two and three dimensions, we can assume

$$\langle \mathbf{R} \rangle = 0$$

in analogy with a random walker or simply by noting that the first and last sticks are indistinguishable (and the end to end vector can be measured as  $\mathbf{R} = \mathbf{a}$  or  $\mathbf{R} = -\mathbf{a}$ . (Note that the error in this assumption goes as  $n^{-1/2}$  where  $n$  is the number of experiments or sculptures ( $n = 2000$ ). The breadth of the distribution or variance depends upon the number of sticks in the sculpture,  $N = 120$  (if only 2 sticks were used, the distribution would not be very wide) and does not depend upon the number of sculptures, nor the dimension of the sculpture.

$$\sigma^2 = Na^2.$$

3. Consider three linear, freely-jointed chains having the same number of steps,  $N$ , with monomers of the same size  $a$ , but in different dimensions. One chain is 1-dimensional, another is 2-dimensional, and the last is in 3 dimensions. Order the chains of different dimension in terms of increasing
  - (a) mean end-to-end distance, and
  - (b) probability of finding the largest end-to-end distance.

Make sure you justify your answers with plots of probability distributions (using Maple for maximum efficiency). Does your answer agree or contravene your intuition?

First it is useful to express each of the distributions

- (a) The distribution in 1-D is

$$p_1(R) = \left( \frac{1}{2\pi Na^2} \right)^{1/2} \exp \left( - \frac{R^2}{2Na^2} \right)$$

where you can check that this distribution is normalised by showing  $1 = \int_{-\infty}^{+\infty} p_1(R) d\mathbf{R}$ . You can change the integration variable to a scalar  $R$  and integrating the scalar distance from 0 to  $\infty$ .

- (b) The distribution in 2-D is

$$p_2(R) = \left( \frac{2}{2\pi Na^2} \right)^{2/2} \exp \left( - \frac{2R^2}{2Na^2} \right)$$

where you can check that this distribution is normalised by showing  $1 = \int_{-\infty}^{+\infty} p_2(R) d\mathbf{R}$ , where you are integrating over all 2-D vectors  $\mathbf{R}$ . You can change the integration variable to a scalar  $R$  using  $d\mathbf{R} = 2\pi R dR$  and integrating the scalar distance from 0 to  $\infty$ , so that the normalisation check is  $1 = \int_0^{\infty} p_2(R) 2\pi R dR$

- (c) The distribution in 3-D is

$$p(R) = \left( \frac{3}{2\pi Na^2} \right)^{3/2} \exp \left( - \frac{3R^2}{2Na^2} \right)$$

where you can check that this distribution is normalised by showing  $1 = \int_{-\infty}^{+\infty} p_3(R) d\mathbf{R}$ , where you are integrating over all 3-D vectors  $\mathbf{R}$ . You can change the integration variable to a scalar  $R$  using  $d\mathbf{R} = 4\pi R^2 dR$  and integrating the scalar distance from 0 to  $\infty$ , so that the normalisation check is  $1 = \int_0^{\infty} p_3(R) 4\pi R^2 dR$

Now, if I am going to compare the probabilities of finding a scalar  $R$  in a 1, 2, and 3-dimensions, I must ensure that I compare “apples” with “apples”. To achieve this I will do 2 things. First (purely for convenience), I will rewrite  $R$  in a dimensionless form, using  $x = R/(\sqrt{N}a)$  or relating  $R$  with  $x\sqrt{N}a$ . The normalisation conditions for each of the distributions is then, for 1-d:

$$\begin{aligned} 1 &= \int_0^\infty 2p_1(R)dR \\ &= \int_0^\infty 2\left(\frac{1}{2\pi Na^2}\right)^{1/2} \exp\left(-\frac{x^2}{2}\right)(\sqrt{N}adx) \\ &= \int_0^\infty \frac{2}{\sqrt{2}} \exp\left(-\frac{x^2}{2}\right)dx \end{aligned}$$

for 2-d:

$$\begin{aligned} 1 &= \int_0^\infty p_2(R)2\pi R dR \\ &= \int_0^\infty \left(\frac{2}{2\pi Na^2}\right)^{2/2} \exp\left(-\frac{2R^2}{2Na^2}\right)2\pi R(\sqrt{N}adx) \\ &= \int_0^\infty 2x \exp\left(-x^2\right)dx, \end{aligned}$$

and for 3-d:

$$\begin{aligned} 1 &= \int_0^\infty p_3(R)4\pi R^2 dR \\ &= \int_0^\infty \left(\frac{3}{2\pi Na^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2Na^2}\right)4\pi R^2(\sqrt{N}adx) \\ &= \int_0^\infty 6\sqrt{\frac{3}{2\pi}}x^2 \exp\left(-\frac{3x^2}{2}\right)dx. \end{aligned}$$

Second, recognise that you want to plot the quantity  $y$  of  $1 = \int_0^\infty ydx$  versus  $x$  for each dimension. This will ensure that the area under the curves that you plot is equivalent. This is important because it amounts to ensuring that you are considering all scalar distance  $R$  in each of the dimensions, and that the probability, integrated over all possible dimensionless distances  $x$  is unity. So what I have done is plotted each of these using Maple using (blue,green,red) = (1, 2, 3 dimensions). Moreover, I also checked to ensure that the areas under the three curves is unity (plus a small error when I approximate  $\pi$  with 3.14159) when integrated out to infinity.

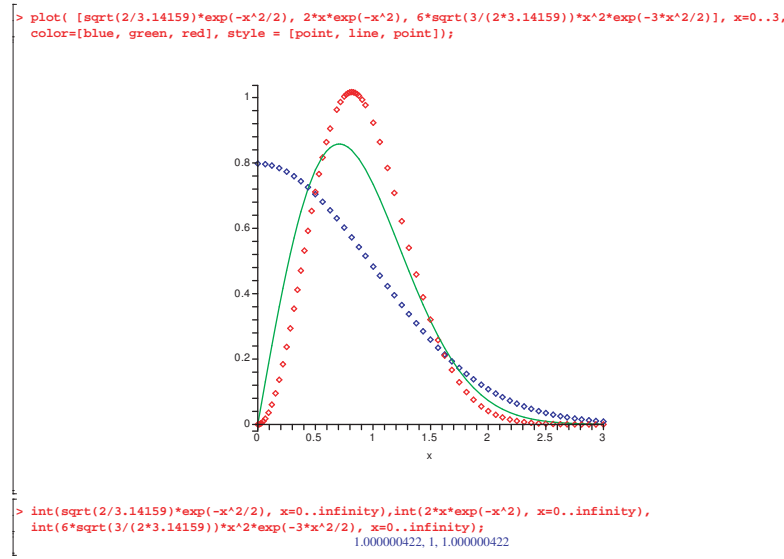


Figure 1: Maple 9.5 output.

From these distributions you can order the chains:

- (a) the mean end-to-end distance ( $\sqrt{\langle R^2 \rangle}$  and not  $\langle \mathbf{R} \rangle$  as that is 0!) is roughly the same,  $\sqrt{N}a$ , to within order 1. That is  $\langle x \rangle \sim 1$ . However, you can check this by integrating  $x$  over the distributions:

For 1-D:

$$\text{int}(x * \text{sqrt}(2/3.14159) * \exp(-x^2/2), x = 0..infinity) = 0.79$$

For 2-D:

$$\text{int}(2 * x^2 * \exp(-x^2), x = 0..infinity) = 0.89$$

For 3-D:

$$\text{int}(6 * \text{sqrt}(3/(2 * 3.14159)) * x^3 * \exp(-3 * x^2/2), x = 0..infinity) = 0.92$$

So you see that as the dimension increases, the mean increases slightly. But again, the mean is still  $\langle x \rangle \sim \mathcal{O}(1)$

- (b) the probability of finding the largest end-to-end distance increases with smaller dimension. (You can see this particularly well for values  $3 < x < 4$ ).

This does agree with intuition. Consider a drunken walker. If the walker were confined to a line (1 -D) as opposed to 2-D, then it would be more likely that she would return to her original starting position. In higher dimension, it is less likely to find your way back to the starting condition. Moreover, it is also likely that the walker will venture furthest away from the origin in 1-D whereas in higher dimension you are less likely to venture. From the distributions you see that a walker becomes more “localised” about  $x = 1$  as dimension is increased.

4. What is the probability of observing a chain in three dimensions whose end-to-end distance,  $R$ , is within one standard deviation of the mean end-to-end distance? AIM: Constructing and extracting information from a probability distribution, using Maple for maximum efficiency.

The mean end-to-end distance is  $\sqrt{\langle R^2 \rangle} = \sqrt{N}a$  and the standard deviation,  $\sigma$  (or the square root of the variance  $\sigma^2$ ) is  $\sqrt{N}a$ . So we seek the probability of observing a chain with end-to-end distance between 0 and  $2\sqrt{N}a$ . Following from page 13 of Chapter 2 where we solve the integral,

$$P(R)d\mathbf{R} = \int_0^{2\sqrt{N}a} 4\pi R^2 \left(\frac{3}{2\pi N a^2}\right) \exp\left(-\frac{3R^2}{2N a^2}\right) dR$$

but first express it in the variable  $x$ ,

$$4\pi\left(\frac{3}{2\pi}\right)^{3/2} \int_0^2 x^2 \exp\left(-\frac{3x^2}{2}\right) dx,$$

which, in Maple is input as:

$$4 * pi * (3/2/pi)^{(3/2)} * (int(x^2 * exp(-3 * x^2/2), x = 0..2));$$

output as:

$$3\pi\sqrt{3}\sqrt{2}\left(\frac{1}{\pi}\right)^{3/2}\left(-\frac{2}{3}e^{-6} + \frac{1}{18}\sqrt{\pi}\sqrt{6}erf(\sqrt{6})\right)$$

which is after evaluating this using “evalf(%)”, yields the answer

$$I = 0.9926172590.$$