Polymer Physics Quiz 3 January 29, 2021

Habibi M, Adda-Bedia M, Bonn D, *Effect of the material properties on the crumpling of a thin sheet* Soft Matter **13** 4029 (2017) investigate the force-size relationship for crumpled sheets and find that there is a scaling relationship, $F \sim R^{-\beta}$.

- a) For a Gaussian polymer chain obtain the force-size scaling relationship from an expression for the energy of a single Gaussian coil.
- b) Habibi's measurement is based on a 3d force like pressure acting on a crumpled ball.



Fig. 2 (a) Experimental setup consisting of a net of wires distributed uniformly around a loosely crumpled sheet, which pass through a hole in the platform on which the crumpled sheet is placed. (b) By hanging weights at the bottom of the net one achieves higher degree of quasiisotronic compaction. The scales are 2 cm

Could this force still result in an expression for energy? $(V \sim R^3, P = F/A \sim F/R^2)$ From Habibi's force-size scaling relationship obtain an expression for the energy of a crumpled sheet as a function of size.

- c) Habibi finds a value for β of from 3 to 6 depending on the "plasticity" of the sheet with less plastic (moldable) sheets showing a larger β . With a value of β of 3 to 6 how does the energy change with size of the sheet? Does this make sense? (Compare this result with the function for a polymer coil. What is the equilibrium state in both cases?)
- d) How does the spring constant of the sheet change with size of the crumpled ball? Does this make sense? (Compare with a polymer coil.)
- e) Habibi finds that the number of folds of the sheet decreases with the size of the crumpled ball, less crumpled sheets have fewer folds. The behavior follows another power-law dependence, $N \sim D^{-\gamma}$. γ has a value from 1 to 2. It is found that β is proportional to γ such that $\beta = 3.44 \gamma$. Explain what the number of folds might have to do with the energy of a crumpled sheet and why β might reflect the same information as γ .



Fig. 4 Crumpling force (F) as a function of the average size of crumpled balls (D) for Mylar sheets crumpled for the first time ('virgin sheet') and one that has been crumpled before ('trained sheet'). The crumpling-force exponents for the virgin and trained sheets are 5.76 \pm 0.15 and 5.85 \pm 0.15, respectively. The thickness of the sheet is $h = 36 \ \mu m$.



Fig. 5 Variation of the mean number of layers N with the dimensionless size of crumpled balls (D/D₀) for rubber membrane and aluminum foil. Data points for Mylar and paper are not shown for sake of clarity. Dashed lines are power law fits of experimental data. The inset shows cross sections of crumpled sheets of rubber (top) and aluminum foil (bottom) and reveals different stacking behavior. While for aluminum foil the density of layers is larger near the outer surface, the compaction of rubber membrane is more homogeneous.



Fig. 7 Crumpling exponent β as a function of layering exponent γ for different materials. Circles are data obtained from the isotropic 3D compaction experiments of PDMS, Mylar, paper and aluminum foil as described here. Squares represent experimental results for quasi 1D compaction of Mylar, paper and aluminum foil in a cylinder. The experimental details for quasi 1D compaction are the same as described in ref. 8. The dashed line with slope 3.44 is the best fit to the data.

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a) For a Gaussian polymer chain obtain the force-size scaling relationship from an expression for the energy of a single Gaussian coil.

By equating the argument of the exponential for the Gaussian function for the probability of a given end-to-end distance R with the Boltzmann probability for a thermally activated process an expression for the energy of a single polymer chain can be obtained.

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right) \qquad \qquad P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

$$E = kT \frac{3R^2}{2nl_k^2}$$

Taking the derivative of this with respect to end-to-end distance an expression for the force can be obtained.

$$F = \frac{dE}{dR} = \frac{3kT}{nl_{\kappa}^2}R = k_{spr}R$$

b) Could this force still result in an expression for energy? $(V \sim R3, P = F/A \sim F/R2)$ From Habibi's force-size scaling relationship obtain an expression for the energy of a crumpled sheet as a function of size.

The Habibi's force is not subject to thermal equilibrium so it isn't possible to determine exactly an energy from it in the same context as the single coil chain, that is, it wouldn't depend on temperature (perhaps an analogy to temperature could be used like randomness of the structure or number of folds). However, force is still related to energy of the ball through an integral. So we could say that dE = FdR and we could still integrate the force to produce an energy, here $F \sim R^{-\beta}$, so, $E \sim R^{1-\beta}/(1-\beta)$.

You could get the same result if you said E = PV. $P = F/R^2 = R^{-\beta-2}$, and $V = R^3$, so $E = PV = R^{1-\beta}$.

c) Habibi finds a value for β of from 3 to 6 depending on the "plasticity" of the sheet with less plastic (moldable) sheets showing a larger β . With a value of β of 3 to 6 how does the energy change with size of the sheet? Does this make sense? (Compare this result with the function for a polymer coil. What is the equilibrium state in both cases?)

Energy decreases with the size of the sheet, so as the sheet is compressed it has less energy, it decreases with R^{-2} for moldable sheets to R^{-5} for more elastic sheets.

To see if this makes sense it could be compared with the polymer coil. For a polymer coil the energy is proportional to R^2 . This means that as the chain is extended the energy rapidly increases. For the crumpled sheet the energy decreases as the sheet is straightened because the crumpled state is not the equilibrium state, the sheet, to some extent, wants to return to a flat

sheet. The less elastic sheet there is a weaker drive to straighten out, with a more elastic sheet a stronger drive.

d) How does the spring constant of the sheet change with size of the crumpled ball? Does this make sense? (Compare with a polymer coil.)

The spring constant for a polymer coil is depends on n^{-1} (which is related to R^{-df} or R^{-2}). For Habibi's crumpled paper the spring constant is proportional to $R^{-\beta-1}$, so it decreases with R^{-4} for moldable sheets to R^{-7} for more elastic sheets. Larger sheets are more "floppy" and have a lower modulus, similar to a polymer coil but to a greater extent.

e) Habibi finds that the number of folds of the sheet decreases with the size of the crumpled ball, less crumpled sheets have fewer folds. The behavior follows another power-law dependence, $N \sim D^{-\gamma}$. γ has a value from 1 to 2. It is found that β is proportional to γ such that $\beta = 3.44 \gamma$. Explain what the number of folds might have to do with the energy of a crumpled sheet and why β might reflect the same information as γ .

If each fold contributes to the expansive force for the sheet to reach an extended state it makes sense that the force would be related to the number of folds. The exact relationship would depend on the geometry in 3d space of the contribution of each force to stretching out the sheet, similar to the analysis of a single coil force of extension to the stress on a rubber sheet. The relationship is fairly complicated.