Fluctuations and Response of Polymers

Klaus Kroy

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1 Introduction

Polymers are long threadlike molecules assembled from a very large number of identical units, the so-called monomers. In the 1920's, Hermann Staudinger first conjectured such a chain structure for very massive molecules that he termed "macromolecules"—against the prevailing view of a chemically less ordered, globular aggregate structure. Some classical examples are e.g. polyethylene, polybuthadine and polystyrene, which are industrially synthesized with their degree of polymerization N ranging up to millions of monomers per polymer, but countless other everyday materials from food and beauty products to plastics and synthetic tissues are just variations of the same basic theme.

Polymer physics has traditionally focussed on very *flexible polymers* that admit a highly coarse-grained description in terms of effective bead-spring models and exhibit universal physical behavior that can be explained using methods from statistical mechanics such as the renormalization group and scaling arguments [**?**]. Flexible polymers are characterized by small energetic barriers for rotations of their backbone bonds compared to the thermal energy k_BT, and entropy obliges them to attain a highly coiled equilibrium conformation if immersed in a solvent. The typical spatial extension of such a coil, estimated by the mean-square fluctuations $\langle R^2 \rangle$ of the end-to-end vector $\boldsymbol{R}$, is about

$$\mathcal{R} \equiv b\, N^{\nu} \ll L \, , \tag{1}$$

much smaller than its contour (or "chemical") length $L = bN$. Most interestingly, in the thermodynamic limit ($N \to \infty$) only three universal values of the exponent ν occur ($\nu \approx 3/5$ "swollen", $\nu = 1/2$ "ideal", $\nu = 1/3$ "collapsed"), depending on the solubility of the polymer, or the "solvent quality". Here, we encounter a first example of a profound statement that may be substantiated by a physical reasoning along the lines of thought pursued in these lecture notes, while being hard to grasp from—since essentially independent of—the chemistry of the sequence. In contrast to the universal exponent ν, the number N of effectively independent backbone sections of ("Kuhn") length b depends on chemistry; notably on the backbone stiffness. The scaling in Eq. (1) suggests a universal self-similar, or *fractal* spatial mass distribution on intermediate scales between the "microscopic" scale b and the "phenomenological" overall coil size

$\mathcal{R}$. Experimentally, this property is most naturally portrayed in reciprocal space as an intermediate asymptotic power-law form $I_q \propto q^{-1/\nu}$ of the scattering intensity I_q as a function of (the modulus q of) the scattering vector $\boldsymbol{q}$.

Recently, there is increasing interest into problems for which the successful but highly coarse-grained approach developed for flexible polymers fails, either because the polymers of interest are too stiff or because they are studied under conditions where they reveal structural properties not represented in the classical models. Many of these instances appear in applications involving biopolymers. Notorious examples are the nonlinear mechanical response of DNA, which has turned out to both participate in and allow to probe certain protein-DNA interactions [**?**]; or force transduction through the cellular scaffold structure known as the cytoskeleton, which is a major mechanism by which living cells explore their environment and react to external mechanical stimuli [**?**]. Biopolymers are, as a rule, substantially stouter than synthetic polymers. For example, with a mass of 43 kDa, the actin monomer is certainly of macromolecular size by itself, and under physiological conditions tens of thousands of these globular proteins can self-assemble into a plait rope of several nanometers thickness, the actin filament ("F-actin"). This model semiflexible polymer is the main building block of muscles and of the cytoskeleton of most animal and plant cells, contributing vitally to their remarkable passive and active elastic response. Microtubules have similar dimensions, while their bending stiffness is even higher, comparable to that of a human hair. They serve as stiff tracks for intermolecular transport by motor proteins and play a crucial role in cell division.

Yet, at finite temperature, none of these polymers should be imagined as a rigid rod. Even a very *stiff polymer* such as a microtubule exhibits small *self-affine* thermal contour fluctuations: if one end is clamped along a fixed spatial direction, the transverse excursions $\boldsymbol{R}_\perp$ of the other end have a typcial range

$$\mathcal{R}_\perp \equiv L^{3/2}\ell_p^{-1/2} \ll L \; . \tag{2}$$

A proper definition of the *persistence length* ℓ_p that controls this range, can be found in Section 2.2. An intuitive characterization is provided by recklessly evaluating Eq. (2) for $L \simeq \ell_p$. It then tells us that ℓ_p is on the order of the contour length that thermal fluctuations will typically bend into a roughly half-circular shape. The "thermal roughness" of the polymer contour implied by Eq. (2) is what distinguishes a stiff polymer from an infinitely rigid rod, i.e. a purely mechanical object. This equation plays a similarly important role for the physics of stiff polymers as Eq. (1) does for flexible polymers, despite its trivial rational exponent 3/2. The large persistence length keeps the amplitude of the transverse fluctuations extremely small compared to L for a microtubule and often smaller than the subsection of the contour that matters for actin and even for DNA. The detection of the anisotropic *self-affine* conformational correlations predicted by Eq. (2) is therefore somewhat less straightforward than for those implied by Eq. (1). They do not give rise to a very pronounced deviation of the end-to-end distance or the scattering function I_q from their stiff-rod limits. On the other hand, *dynamic* scattering experiments and real-space tracking techniques (e.g. using small attached tracer beads) reveal a characteristic sub-diffusive power-law growth $\delta\mathcal{R}_{\perp}^{2}(t) \propto t^{3/4}$, directly related[1] to Eq. (2). Moreover, in *semidilute* F-actin solutions, the same self-affine fluctuation spectrum has been identified as the origin of the scaling $G^0 \propto c^{7/5}$ of the rubber plateau in the frequency dependent shear modulus with actin concentration c. This relation ought to hold even better for the osmotic pressure—for concentrations at which both ideal rigid rods and flexible coils of identical backbone dimensions would behave as an ideal gas! In this way, cells might optimize their elasticity and osmotic resistance using a minimum amount of scaffold material compared to what would be required with either flexible chains or completely rigid rods. Additionally, by exploiting the highly anisotropic mechanical compliance of stiff polymers, which will be deduced from Eq. (2) in Section 2.3, the cytoskeleton can be strong and soft at the same time. Via a robust and redundant regulation of specific (actin binding/severing proteins) and unspecific (charge, hydrophobicity,...) molecular interactions, reversible polymer association and structural changes (such as local concentration fluctuations and bundling) can relatively quickly be induced in order to vary the mechanical strength by several orders of magnitude, whenever needed [**?**].

In summary, what makes polymers interesting to physicists in the first place, is their dull chemical structure, which gives rise to *universal* static and dynamic conformational correlations. The relations deemed most significant and beautiful are those that would naturally appear to be the most useless to an experimental chemist. In particular, these lecture notes emphasize *intermediate asymptotic scaling laws*—such as those of Eqs. (1) and Eq. (2)—characteristic of whole classes of molecules of possibly very different microscopic chemical compositions. They act as a guiding theme in an attempt to provide an accessible first introduction to some basic elements of polymer physics that bridges over from the "classical" models for flexible chains [**?**] to more recent work concerned with stiff polymers. The classical models made polymer physics fashionable in the 1970's by linking it to the fascinating field of critical phenomena. They have since developed into both powerful practical tools for material scientists [**?**] and a formidable playground for sophisticated methods of theoretical physics [**?**]. The emerging theory of stiff polymers, which is the focus of these notes, has only just provided the first steps towards explaining the structure and mechanics of some of the most remarkable soft and biological materials, including our own bodies. In Sec. **??**, it is for example demonstrated, how a surprisingly rich bouquet of intermediate asymptotic power laws can be derived for the nonlinear dynamic response of a single polymer. Apart from the restriction to polymers with a (locally) rodlike structure, these laws are no less universal than those of classical polymer physics. They can moreover be derived in a very direct way, usually including exact prefactors by controlled approximations. And they can be tested directly and with unprecedented accuracy using some recently devel-

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[1] Just consider that the relaxation time of bendig modes scales with the fourth power of their wavelength and put this into Eq. (2) to see how the self-affine conformational correlations of Eq. (2) reveal themselves in the dynamic exponent 3/4.

oped biophysical methods collectively known as single-molecule spectroscopy.

The lecture notes are organized in three sections: *1. Basics*, which provides some basic notions and insights mostly from a back-door-entrance perspective before some general statistical-mechanics machinery is introduced that allows for a more systematic formulation of the theory in sections *2. Statics* and *3. Dynamics*, where the most salient predictions by the standard models for fluctuations and response of *flexible and stiff polymers* are reviewed. The mutual interdependence of thermal fluctuations and mechanical response serves as a unifying principle of the presentation. Knowing one of them immediately allows one to approximately (and sometimes exactly) deduce the other.

Exercise: The DNA packing problem

Each of your cells contains in its nucleus, which has a diameter of some microns about 2 meter of DNA. Estimate the swollen coil size of a polymer of length $L = 2$ m and Kuhn length $b = 0.1\ \mu$m in good solution. (Result: 2 mm, which compares to the size of the nucleus like a football to a grain of sand.)

2 Basics

2.1 Polymer models

2.1.1 "Microscopic" toy models and parametrizations

Depending on the microscopic structure, either discrete or continuous coarse-grained "microscopic" parametrizations of a polymer may be more appropriate. A discrete parametrization would consist in either the monomer positions $\boldsymbol{r}_n$ with $n = 1 \dots N$ or alternatively the *bond vectors* $\boldsymbol{b}_n \equiv \boldsymbol{r}_{n+1} - \boldsymbol{r}_n$ or normalized *tangent vectors* $\boldsymbol{t}_n \equiv \boldsymbol{b}_n / |\boldsymbol{b}_n|$ with $n = 1 \dots N$ (in wich case the degree of polymerization is strictly speaking $N + 1$, which we will not bother to distinguish). The natural continuous parametrization is the arc-length parameterization $\boldsymbol{r}_s$ of a continuous space curve with $s \in [0, L]$ and a tangent $\boldsymbol{t}_s \equiv \boldsymbol{r}'_s \equiv \mathrm{d}\boldsymbol{r}_s / \mathrm{d}s$ of unit length. Following the prescription

$$b\, n \leftrightarrow s, \qquad b \sum_{n=1}^{N} \leftrightarrow \int_0^L \mathrm{d}s \tag{3}$$

one may switch between these notations if needed. Fig. **??** illustrates the notation. To isolate the universal physical features from the specific chemical details, it is useful to introduce some simplistic polymer models. A caricature of a very flexible polymer is the so called *freely jointed chain* (FJC), a discrete chain of independently and freely rotating bonds. As far as its static conformation is concerned, it is formally equivalent to a finite one-dimensional classical paramagnet or to a discrete random walk, the bonds being identified with the spins or steps, respectively. As a natural extension, a minimalistic model of a *semiflexible chain* (SFC) is the *freely rotating chain* (FRC), where bonds are subject to steric constraints or an interaction energy favoring (small) prescribed angles between adjacent bonds. A particularly simple example is provided by a model that energetically favors aligned neighboring bonds, like e.g. in a ferromagnetic spin chain, which is known as the *wormlike chain* (WLC). An important special case of the general semiflexible chain and the wormlike chain occurs in the *weakly bending rod* (WBR) geomtry, where the tangent correlations persist over the whole length of the polymer, i.e., $L \ll \ell_p$. In this limit, where the polymer is almost straight, it is advantageous to parametrize the polymer in terms of small quantities $\boldsymbol{t}_\perp$ and $t_\parallel$ by writing

$$\boldsymbol{r} \equiv (\boldsymbol{r}_\perp, s - r_\parallel)^T \ , \qquad \boldsymbol{t} \equiv \boldsymbol{r}' = (\boldsymbol{t}_\perp, 1 - t_\parallel)^T \tag{4}$$

in a coordinate system that has its third axis aligned with the average orientation of the polymer as illustrated in Fig. **??**. In the continuum limit of vanishing bond length and diverging bond number, this model can be understood as the idealization of a stiff slender rod as an inextensible weakly bending space curve. For many biopolymers, this is indeed a very reasonable model to start with.

2.1.2 Self-avoidance and solvent effects

Since the above toy models allow the polymer to cross through itself, which is not possible in the real world, they are often called "phantom models". *Self-avoidance* as well as the resulting topological constraints are notoriously hard to formalize, though, even on the computer. They become relevant for very flexible polymers with $L \gg \ell_p$. The so called self-avoiding random walk (SAW) problem has been studied in considerable detail as a challenging mathematical problem [**?**]. A seemingly crude physicist's approach is to replace the topological condition of self avoidance by a merely geometric excluded-volume penalty for self-intersections [**?**][2]. This captures the fact that self-contacts are entropically unfavorable and therefore somewhat suppressed in the equilibrium conformation, except if the polymer is too "sticky". This approach allows for a Hamiltonian description and has been very successful in the theoretical modelling of polymer melts and solutions. With some effort one can get from it the exponent

$$\nu \approx \nu_F = 3/(d+2) \tag{5}$$

for the fractal mass distribution of flexible polymers in a $d-$dimensional embedding space. The approximation ν_F, called the Flory exponent, follows immediately from the Hamiltonian, see Eq. (39) below, by simple dimensional analysis. It turns out to be exact for $d = 1, 2, 4$ and an excellent approximation for $d = 3$. To obtain truely quantitative results is generally somewhat tricky even in this effective excluded volume approach [**?**, ?], while all the qualitative information (including phase behavior, scaling and exponent relations) is easily obtained by

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[2] Theoretical physicists are not the only cheaters in the game. Nature has provided a special class of proteins called topoisomerases that can apparently very successfully release complicated non-local topological constraints in DNA by cutting and resealing the DNA backbone in the right places. Some classical anti-cancer drugs were designed to interfere with this action.

simple scaling arguments [?]; an odd discrepancy that has made scaling concepts very popular among polymer physicists.

In the following, the focus is on polymers that are immersed in a simple (i.e. low molecular weight) solvent. The fact that other cases, such as polymer *melts* and polymer *blends* will not be given much attention here, does however not imply that they are less important or less interesting. The solvent mainly affects flexible polymers in two ways. First, by its chemical composition, one can control the "solvent quality", or the *solubility* of the polymer. This allows one to tune the exponent ν to either of the three values 1/3, 1/2, and $\nu \approx 0.59$ (in $d = 3$ space dimensions). To achieve ideal behavior ($\nu = 1/2$) requires some fine-tuning to the so-called $\theta-$point, where the effective self-repulsion and self-attraction of the monomers in the solvent just balance, or "screen" each other (on the pair-interaction level). Secondly, the physical presence of the solvent affects the dynamics of the polymer via *hydrodynamic interactions* (HI). If one part of the polymer is set into motion, a diffusively spreading flow patern is induced in the solvent that acts back onto other parts of the polymer. The diffusing quantity is vorticity $\nabla \times \boldsymbol{v}$, since the velocity field in an incompressible solvent is divergence free. If the monomers or other relevant portions of the polymer are considerably larger than the solvent particles, they move slowly compared to the vorticity in equilibrium, and the dynamics of the latter can be integrated out. In this common approximation, HI "simply" provides another (quasi-static) long-ranged self-interaction of the polymer. To leading order in the reciprocal distance it takes the form of an anisotropic reciprocal distance law for the velocity $\boldsymbol{v}_i = \sum_j \boldsymbol{H}_{ij} \boldsymbol{f}_j$ of monomer i in terms of the forces $\boldsymbol{f}_j$ acting on all (other) monomers, with the *Oseen tensor* $\boldsymbol{H}$ given by

$$8\pi\eta \boldsymbol{H}_{i\neq j} = \mathbf{1} + \frac{\boldsymbol{r}_{ij}\boldsymbol{r}_{ij}}{r_{ij}^3} \ , \qquad \boldsymbol{r}_{ij} \equiv \boldsymbol{r}_i - \boldsymbol{r}_j \ , \qquad 6\pi\eta \boldsymbol{H}_{ii} = \mathbf{1} \ . \tag{6}$$

Similarly as the above mentioned long-ranged excluded volume interactions, it gives rise to serious complications in any attempt to honestly model flexible polymers, while stiff polymers are again much less affected. The results calculated for a weakly bending rod in the so called free-draining approximation, in which HI are dismissed, only acquire logarithmic corrections from HI.

2.2 Fluctuations: correlation functions

2.2.1 The persistence length ℓ_p

As empasized in the introduction, thermal fluctuations are a crucial ingredient if one wants to understand the static and dynamic conformational and mechanical properties of polymers[3]. A useful characterization of fluctuating quantities and their statistical correlations is provided by their thermal averages and correlation

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[3] Some aspects of stiff polymers are, however, well captured by mechanics alone. For example, some DNA-protein interactions involve electrostatic and mechanical energies on the order of many k_BT, so that conformational fluctuations play a negligible role and classical beam mechanics applies.

Table 1: Classification of polymers according their stiffness in terms of the three parameters a (microscopic scale, e.g. the monomer size), L (contour/chemical length), and ℓ_p (persistence length).

flexible	$\ell_p/a \simeq 1$ and $L/\ell_p \gg 1$	ℓ_p "microscopic"
semiflexible	$\ell_p/a \gg 1$ and $L/\ell_p \gtrsim 1$	ℓ_p "mesoscopic"
stiff, weakly-bending	$\ell_p/a \gg 1$ and $L/\ell_p \ll 1$	ℓ_p "macroscopic"
rigid rod	$L/\ell_p = 0$	ℓ_p "infinite"

functions. The simplest example is the canonical ensemble average of a variable, say the bond vector $\boldsymbol{b}_n$ or tangent $\boldsymbol{t}_n$, $\boldsymbol{t}_s$ of a polymer, or of its *end-to-end vector*

$$\boldsymbol{R} \equiv \boldsymbol{r}_N - \boldsymbol{r}_0 \equiv b \sum_n \boldsymbol{t}_n \qquad \text{or} \qquad \boldsymbol{R} \equiv \boldsymbol{r}_L - \boldsymbol{r}_0 = \int \mathrm{d}s \, \boldsymbol{t}_s \tag{7}$$

Obviously, $\langle \boldsymbol{t}_n \rangle = \langle \boldsymbol{R} \rangle = 0$ for any free polymer, because of rotational symmetry, while $\langle \boldsymbol{t}^2 \rangle = 1$ and $\langle \boldsymbol{R}^2 \rangle = b^2 \sum_{nm} \langle \boldsymbol{t}_n \cdot \boldsymbol{t}_m \rangle \neq 0$. The last example naturally leads one to consider the somewhat richer construction of a thermal average of the scalar product of two tangents at chemical positions n and m, the static *correlation function* $\langle \boldsymbol{t}_n \cdot \boldsymbol{t}_m \rangle$. The latter is already sufficient for quantifying the important concept of stiffness (or flexibility) by the following reasonably general convention. The *bending stiffness of a polymer* is measured by comparing its total length L or any other relevant backbone subsection of interest with its *persistence length* ℓ_p defined as the correlation length of its tangent orientations via[4]

$$\langle \boldsymbol{t}_s \cdot \boldsymbol{t}_{s'} \rangle = \exp(-|s - s'|/\ell_p) = \exp(-|n - m|a/\ell_p) \; . \tag{8}$$

This enables us to propose a classification of polymers and polymer models into the four classes, "flexible", "semiflexible", "stiff" and "rigid" in terms of the three characteristic parameters a, $L \gg a$, and ℓ_p, see Tab. 1. Particularly important are the extreme cases "flexible" and "stiff", where we can expect simple intermediate asymptotic scaling laws to emerge as a consequence of dilation invariance between a lower and upper cutoff-wavelength. We reserved the notion "semiflexible" to the more complicated general situation, where one has to account for the crossover from a rod-like to a coiled conformation.

In the remainder of this section, we want to exemplify the notions of flexibility, stiffness, fractal and self-affine scaling by considering what can be deduced

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[4] This definition makes sense for distances $|s - s'|$ over which the exponential law applies (and if you wish you may maintain your personal little VIP lounge for the exceptions). Of course, not everybody can agree on the same definition. Some people prefer to define ℓ_p via $\langle \boldsymbol{t}_s \cdot \boldsymbol{t}_{s+\ell_p} \rangle = 1/2$ or even $1 - \langle \boldsymbol{\theta}^2 \rangle/2 = 1/2$, where θ is the angle between two tangents $\boldsymbol{t}_s$ and $\boldsymbol{t}_{s+\ell_p}$, and the like. This seems to be of tremendous help in communicating the concept to people who have never heard of e, scalar products, or cosines, but makes any effort to agree on absolute values of ℓ_p for particular polymers a nightmare. Once you have grasped the basic idea, you will certainly be able to invent your own definition to prove your originality and to add some sophistication to this otherwise somewhat banal subject.

from the phenomenological characterization in terms of the tangent correlations for stiff and flexible polymers. Only the later sections will introduce some machinery of statistical mechanics in order to give a more comprehensive quantitative characterization of the statistical mechanics and stochastic dynamics of polymers.

2.2.2 Ideal flexible chain (IFC)

According to our definitions, a flexible polymer is characterized by effectively independent bond orientations for "Kuhn" segments of length b on the order of the monomer size a, obtained after some moderate coarse-graining over some microscopically close correlated monomers $n \approx m$. This property is idealized in the FJC, which can formally be characterized by the property $\langle \boldsymbol{t}_n \cdot \boldsymbol{t}_m \rangle = \delta_{nm}$. Its mean-square end-to-end distance is then easily computed as

$$\langle \boldsymbol{R}^2 \rangle = b^2 \sum_{nm} \langle \boldsymbol{t}_n \cdot \boldsymbol{t}_m \rangle = b^2 N = b\, L \equiv \mathcal{R}_0^2 \,, \tag{9}$$

which is a special case of Eq. (1) with $\nu = 1/2$. Eq. (9) exemplifies what was said in the introduction about the fundamental self-similarity of the conformation. The power law $\langle R^2 \rangle \propto N^{2\nu}$, which identifies $1/\nu$ as the fractal dimension of a typical chain conformation, is the result of embedding the featureless (scale-free) chemical structure into an empty space. It is independent of the microscopic details and survives any local, finite-ranged modifictations of the model, which will only affect the value of the microscopic parameter b in Eq. (1). The latter is thus in practice to be understood as an *effective scale*, different from the microscopic chemical bond length, and is also known as the *"Kuhn length"*. On the other hand, as already mentioned above, the condition of self-avoidance induces correlations between chemically very distant parts of the chain, and therefore gives rise to a different ν.

2.2.3 Semiflexible chain (SFC)

With slightly more effort but along the same lines as for the FJC, you can as a useful exercise evaluate $\langle \boldsymbol{R}^2 \rangle$ for a semiflexible polymer of persistence length ℓ_p by using the exponentially decaying tangent correlations Eq. (8),

$$\langle \boldsymbol{R}^2 \rangle = 2\ell_p^2 \left(e^{-L/\ell_p} - 1 + L/\ell_p \right) \sim \begin{cases} L^2(1 - L/3\ell_p) & (L \ll \ell_p) \\ 2\ell_p L(1 - \ell_p/L) & (L \gg \ell_p) \end{cases} . \tag{10}$$

The notation $\sim$ stands for "asymptotically equal to". The SFC captures the crossover from a flexible phantom chain of Kuhn length $2\ell_p$ on large scales to a stiff rod on short scales.

2.2.4 Weakly-bending rod (WBR)

A major simplifaction occurs if the polymer has a weakly bending rod (WBR) conformation. In contrast to a general SFC, the WBR it can be parametrized by the small transverse excursions $\boldsymbol{r}_\perp$ alone to leading order in $\epsilon \equiv L/\ell_p \ll 1$. This is readily observed by rewriting the normalization condition for the tangent using the WBR parametrization Eq. (4) in terms of the small quantities $\boldsymbol{t}_\perp$ and $t_\|$,

$$\boldsymbol{t}^2 \equiv 1 \qquad \Rightarrow \qquad t_\| = 1 - \sqrt{1 - \boldsymbol{t}_\perp^2} = \boldsymbol{t}_\perp^2/2 + \mathcal{O}(\boldsymbol{t}_\perp^4)\ . \tag{11}$$

Hence, the density $t_\|$ of the contour length "stored" in transverse thermal undulations is of second order in the small transverse deflections $\boldsymbol{t}_\perp$ from the straight "ground state". Using a corresponding WBR-decomposition for the end-to-end vector

$$\boldsymbol{R} \equiv (\boldsymbol{R}_\perp, R_\|)^T \qquad \text{with} \qquad R_\| \equiv L - \delta R_\| \equiv L - \int_0^L \mathrm{d}s\ t_\|\ , \tag{12}$$

one deduces from Eq. (10) the leading order of the longitudinal thermal contraction $\delta R_\|$ of a polymer with

$$\text{hinged ends, } \boldsymbol{R}_\perp = 0\text{:} \qquad \langle \delta R_\| \rangle \sim L^2/6\ell_p\,. \tag{13}$$

(It is also customary to call $\delta R_\|$ the *"stored length"*, meaning the excess length needed to introduce undulations into a straight contour.) Similarly, for a so-called "grafted polymer" with one end clamped along the third axis, say, we have[5]

$$\text{grafted, } \boldsymbol{t}_0 = (0,1)^T\text{:} \qquad \langle \delta R_\| \rangle \sim L^2/2\ell_p\ , \quad \langle \boldsymbol{R}_\perp^2 \rangle \sim 2L^3/3\ell_p\ . \tag{14}$$

This establishes Eq. (2) as well as

$$\delta R_\|/L\,,\ t_{\|L} = \mathcal{O}(\epsilon) \qquad \text{and} \qquad R_\perp/L\,,\ \boldsymbol{t}_{\perp L} = \mathcal{O}(\sqrt{\epsilon})\ , \tag{15}$$

which will become of some importance in the following.

In summary, starting from a characterization of polymers by their tangent correlations we have without much effort already derived the two fundamental equations Eqs. (1) and (2) worth displaying in the introduction. The remainder should help to elucidate, why we put so much emphasis on them. Table **??** collects some structural information about a few common synthetic and natural polymers plus some common natural and artificial slender micro-rods (polyethylene, polystyrene, sugar, DNA, actin, microtubule, nanotube, fd-virus remark). It seems difficult to obtain accurate values for the persistence lengts of biopolymers. This might partly be related to the problem mentioned in the footnote to Eq. (8), partly it is due to the sometimes complex interactions with molecules in the "buffer" and the sometimes considerable number of available mutants or types of these molecules.

Exercise

Derive Eq. (10).

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[5] Asymptotically from Eq. (8), $1 - \langle t_{\|s} \rangle = \langle \boldsymbol{t}_s \cdot \boldsymbol{t}_0 \rangle \sim 1 - s/\ell_p$, i.e. $\langle t_{\|s} \rangle \sim s/\ell_p$ in the clamped case. The average contraction $\langle \delta R_\| \rangle$ follows by integration and $\langle \boldsymbol{R}_\perp^2 \rangle$ from Eq. (10).

2.3 Response: linear response and low moments

2.3.1 The fluctuation dissipation theorem

To linear order in an external perturbation $\boldsymbol{f}$, the response $\langle \Delta \boldsymbol{r} \rangle_{\boldsymbol{f}} \equiv \langle \boldsymbol{r} \rangle_{\boldsymbol{f}} - \langle \boldsymbol{r} \rangle$ of its conjugate variable $\boldsymbol{r}$ is proportional to the strength of its own equilibrium fluctuations. This is the content of the so-called fluctuation-response or fluctuation-dissipation theorem (FDT). Given that the response coefficient itself must be independent of the external perturbation, this result is certainly expected. On the other hand, given that the generally highly nonlinear microscopic dynamics of typcical systems of interest in statistical mechanics is extremely sensitive to perturbations, the practical usefullness of this connection is far from self-evident, and in this sense the FDT is rather to be understood as a phenomenological (not a mathematical) fact. The link between response coefficients (such as the compressibility or specific heat) to the strength of thermal fluctuations may be familiar to you from introductory text books, and the FDT is the generalization of this relation to dynamics. An early and elementary formulation of the dynamic FDT can be found in Einstein's paper on Brownian motion [**?**] published a century before the present lecture notes were written. There, he considers a colloidal sphere of radius a and position $\boldsymbol{r}$ subject to a stationary force $\boldsymbol{f} \equiv \hat{\boldsymbol{f}} f$. By an elegant argument, the Stokes friction coefficient $\zeta = 6\pi\eta a$, which controls the (average) velocity via $f = \zeta \langle \partial_t x \rangle_f$, is related to the thermal fluctuations of the coordinate $x = \boldsymbol{r} \cdot \hat{\boldsymbol{f}}$. This is accomplished in two steps. First, Einstein uses a macroscopic thermodynamic reasoning to establish the relation $D = k_B T/\zeta$ between the kinetic coefficients for the friction and for the diffusion of the particle density, respectively, which are phenomenologically defined via "macroscopic" hydrodynamic or thermodynamic relations[6]. More importantly, in the second step, he appeals to the great universality of these phenomenological laws, which hold irrespective of the specific realizations of the underlying microscopic details. As a consequence, so the idea, pertinent insights may be gained by studying a "toy model", i.e. a most simple representative of all those many microscopic processes that give rise to the same ubiquitous phenomenology. Thereby, he relates the phenomenological coefficients D and ζ to the microscopic stochastic (long-time) dynamics of his toy-model Brownian particle starting at $x \equiv x(t=0)$ by

$$\langle [x(t) - x]^2 \rangle / 2t \sim D = k_B T/\zeta \; . \qquad \text{(Einstein relation)} \qquad (16)$$

Slightly rephrased with help of a functional derivative (see appendix A for some technicalities), this takes the form of the very general result

$$\theta(t) \partial_t \langle x(t) x \rangle = -k_B T \frac{\delta \langle \Delta x(t) \rangle_f}{\delta f} \; , \qquad \text{(FDT)} \qquad (17)$$

called the fluctuation-dissipation theorem. It epresses the relation of the equilibrium fluctuations on the left to the response function on the right hand side as

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[6] Historically, it was very significant that it (surprisingly) involves the microscopic quantity k_B. If you do not yet know the derivation, you are urged to look up Einstein's original paper.

summarized at the beginning of this subsection. The step function $\theta(t)$ mediates between the fundamental time reversal symmetry of the equilibrium correlation function and the causality of the response. The physical content of the FDT was further explored by Onsager, Callen and Welton, Kubo, and others, who also generalized its derivation. In the same way as we are exploiting the featureless structure of polymers to arrive with the help of the law of large numbers at simple universal laws characterizing their macroscopic conformations, these developments exploited the presumed featureless structure of fluctuations in general thermodynamic systems. As long as the self-similar nature of the fluctuations is not substantially disturbed, forced deviations from equilibrium should relax in the same way as spontaneous equilibrium fluctuations: they could as well have been the result of an accidential equilibrium fluctuation. Further below, detailed examples shall illustrate this idea, known as Onsager's regression hypothesis, but for the time being we are simply exploiting Eq. (17) to derive the linear response of a polymer from the equilibrium moments obtained in Section 2.2.

2.3.2 Flexible versus stiff polymers; Janus-faced entropy

For a stationary force $\boldsymbol{f}(t) \equiv \boldsymbol{f}$ pulling onto the end-to-end vector $\boldsymbol{R}$ of a polymer, the relation corresponding to Eq. (17) is readily integrated over time to yield the linear force-extension relation

$$\langle \Delta \boldsymbol{R} \rangle_{\boldsymbol{f}} \equiv \langle \boldsymbol{R} \rangle_f - \langle \boldsymbol{R} \rangle = \frac{\boldsymbol{f}}{k_B T} \left[\langle (\boldsymbol{R} \cdot \hat{\boldsymbol{f}})^2 \rangle - \langle \boldsymbol{R} \cdot \hat{\boldsymbol{f}} \rangle^2 \right] . \tag{18}$$

Here it has been used that Eq. (17) holds for the coordinate direction $\hat{\boldsymbol{f}}$ along which the force is acting, and it is understood that the stationary force is switched on "near the beginning" of the infinite time domain of integration.

For a flexible polymer, $\boldsymbol{R}$ is equally likely to point into any of the $d = 3$ space directions in equilibrium, so that $\langle \boldsymbol{R} \rangle = 0$ and

$$\langle \boldsymbol{R} \rangle_f = \langle \Delta \boldsymbol{R} \rangle_f = \frac{\langle \boldsymbol{R}^2 \rangle}{3 k_B T} \boldsymbol{f} = \frac{\mathcal{R}^2}{3 k_B T} \boldsymbol{f} , \tag{19}$$

where $\mathcal{R} = b N^{\nu}$ was introduced in Eq. (1). Note that this is a general, model-independent result.

For a stiff polymer (i.e. a WBR) clamped at one end, the response of the other end is highly anisotropic; just as its fluctuations, which we found to be smaller by a factor of ϵ along the direction of the grafted end than perpendicular to it. Perpendicular to the graft, Eq. (18) becomes

$$\langle \boldsymbol{R}_\perp \rangle_f = \langle \Delta \boldsymbol{R}_\perp \rangle_f = \frac{\langle \boldsymbol{R}_\perp^2 \rangle}{2 k_B T} \boldsymbol{f} = \frac{\mathcal{R}_\perp^2}{3 k_B T} \boldsymbol{f} = \frac{L^3}{3 k_B T \ell_p} \boldsymbol{f} , \tag{20}$$

which is again a general identity. Comparing the two results in Eqs. (19), (20), we observe that the response coefficient of the flexible polymer, Eq. (19), is determined solely by the (phenomenological) coil size and the temperature T. For the FJC, b and thus $\mathcal{R} = \mathcal{R}_0 = bN^{1/2}$ are temperature independent, which is what one typically expects for a flexible polymer. In other words, the spring stiffness is proportional to temperature: pulling on a flexible chain, we restrict its ability to attain all possible conformations, i.e., we work against its internal entropy. The same holds for a FRC, whereas one would naturally expect an enthalpic bending response of a slender rod. Hence, if one wants to recover the well-known force-law for mechanical beam bending via this thermodynamic detour, one might prefer to regard

$$\kappa \equiv k_B T \ell_p \qquad \text{in } d = 3 \tag{21}$$

as a (rather temperature-insensitive) material property of the rod. The limit $T \to 0$ ($\ell_p \to \infty$) can then be identified as the "mechanical limit", in which thermal fluctuations become negligible.

What about the stretching response? From our above experience with the equilibrium averages of $R_\parallel$, we may expect a sensitive dependence on the boundary conditions. Possible examples include a polymer with hinged ends where the force acts onto the distance of the hinges, or a grafted polymer where the external force is oriented along the graft direction. For a free polymer, one can imagine a pulling force with a fixed space direction, whereas a compressing force has to act precisely along the end-to-end distance to avoid rotations, which is then equivalent to the situation with hinged ends. One infers from Sec. 2.2.4 that what survives of the second term in the brackets in Eq. (18) evaluates to $\langle R_\parallel \rangle^2 \sim L^4/36\ell_p^2$ or $\langle R_\parallel \rangle^2 \sim L^4/4\ell_p^2$ for the hinged and the grafted case, respectively. However, since we have so far specified only a two-point correlation function of $\boldsymbol{t}$ in Eq. (8), we cannot evaluate the function $\langle \boldsymbol{t}_{\parallel s} \boldsymbol{t}_{\parallel s'} \rangle$ required for the first term, as this would require the four-point correlation function $\langle \boldsymbol{t}_{\perp s}^2 \boldsymbol{t}_{\perp s'}^2 \rangle$. (This indicates a shortcoming of our backdoor-entrance approach to polymer physics and may be taken as an incentive for swallowing some formalism to be introduced in the following section.) From our estimates of the orders of the various averages at the end of Section 2.2.4, we can merely infer that in the stiff limit $\langle \delta R_\parallel^2 \rangle \propto \langle \delta R_\parallel \rangle^2 \propto L^4/\ell_p^2$, hence, as long as the force acts along the average end-to-end distance,

$$\langle \Delta R_\parallel \rangle_f = \frac{\langle \delta R_\parallel^2 \rangle}{k_B T} \propto \frac{\epsilon \mathcal{R}_\perp^2}{k_B T} f \propto \frac{L^4}{\kappa \ell_p} f \; . \tag{22}$$

The longitudinal response and fluctuations of a WBR are by a factor of $\epsilon = L/\ell_p$ smaller than the transverse response and fluctuations, respectively. If one sticks to the mechanical interpretation and assumes that $\kappa = k_B T \ell_p$ is an essentially temperature independent material constant, the longitudinal response turns out to be propotional to temperature T. In contrast to the "typical" flexible polymer, where according to Eq. (19) the force coefficient is proportional to T, it is now inversely proportional to T. Again, one can interprete this as a sign that the linear response is ruled by entropy. However, in Eq. (22) the deformation is not restrained but facilitated by entropy, or more precisely, it is solely due to thermal fluctuations, since it vanishes in the mechanical limit. The vanishing of the longitudinal linear response of an inextensible rigid rod with finite bending stiffness (hence finite transverse linear response) is due to the *Euler buckling instability*: longitudinal forces less than a critical force called the

$$\text{Euler buckling force} \qquad f_c \propto \kappa / L^2 \tag{23}$$

do not deform the rod at all, for $f \geq f_c$ the response is undetermined in linear elasticity. The critical force f_c provides a natural scale for the expected domain of validity of linear response. Its absolute value is sensitive to the boundary conditions [**?**]. So is the omitted prefactor in Eq. (22), which may be interpreted intuitively as weighing the equilibrium thermal contraction $\delta R_{\|} \propto L^2/\ell_p$ of the chain with the ratio f/f_c of the applied force to the critical Euler force f_c.

Exercise

Derive Eq. (18).

3 Statics

In this section we introduce some concepts from statistical mechanics that allow (at least formally) for a complete statistical characterization of the polymer conformation in terms of a conformational distrubution function $\psi\big(\{\boldsymbol{r}_n\}\big)$. The latter is a function of all degrees of freedom of the chain, i.e. a function of all joint positions $\{\boldsymbol{r}_n\}$ in the case of a discrete chain or a functional of the whole conformation $\boldsymbol{r}_s$ for a continuous chain. This dependence is usually expressed in canonical form as an exponential of a Hamiltonian $\mathcal{H}\big(\{\boldsymbol{r}_n\}\big)$. In practice, one is rarley interested in this complete *microscopic* information. As common in statistical mechanics, *reduced distribution functions* and *propagators*, in which all but a few pertinent (collective, mesoscopic) degrees of freedom have been integrated out via a so called *constrained partition sum*, are more practical. In these functions only the information of interest—for example the probability distribution $Z(\boldsymbol{R}) \propto e^{-\beta F(\boldsymbol{R})}$ of the end-to-end vector $\boldsymbol{R}$ of a polymer (with $\beta = 1/k_B T$)—is retained. In these reduced distribution functions *free energys* such as $F(\boldsymbol{R})$ play the role of the Hamiltonian. Free energies or reduced distribution functions of some pertinent and easily observable "phenomenological" variables thus give the most complete *macroscopic or phenomenological* characterization of the polymer, generalizing and extending the preliminary characterization in terms of low moments or correlation functions of such variables in the previous section.

3.1 Polymers: Hamiltonians and distribution functions

3.1.1 "Two-parameter" models (FJC, WLC)

Starting with the distribution function $\psi_1(\boldsymbol{r}) = \delta(|\boldsymbol{r}| - b)/4\pi b^2$ for the tip of a freely rotating rod, it is easy to write down the microscopic distribution function

$\psi_N(\{\boldsymbol{b}_n\})$ of a FJC in terms of its bond vectors b_n

$$\psi_N(\{\boldsymbol{b}_n\}) = \prod_n \psi_1(\boldsymbol{b}_n)\ . \tag{24}$$

This can be rewritten in terms of the monomer positions by using $\boldsymbol{b}_n = \boldsymbol{r}_n - \boldsymbol{r}_{n-1}$. An additional prefactor V^{-1} then serves as normalization for the center of mass of the polymer, which is assumed to be located somewhere in a prescribed region of volume V. (It may be omitted if one considers a conditional distribution function instead, e.g. if it is understood that the first monomer is fixed at the origin.) If the model is not (entirely) described by steric constraints but involves energetics, it is more convenient to specify a Hamiltonian $\mathcal{H}$, from which the canonical distribution function in thermal equilibrium is (up to possible steric restrictions) obtained as

$$\psi \propto e^{-\beta\mathcal{H}}\ . \tag{25}$$

One advantage of $\mathcal{H}$ over ψ is antropomorphic (most physicists find an energy more intuitive than a distribution function), another that the omitted normalization in Eq. (25) may be formally divergent in the case of infinitely many degrees of freedom.

As an example, consider the particularly simple realization of a SFC by a classical Heisenberg chain (freely rotating joints with some resistance to bending),

$$\mathcal{H} = -J\sum_n^N \boldsymbol{t}_n \cdot \boldsymbol{t}_{n+1}\ . \tag{26}$$

Thermal fluctuations excite conformational undulations around the straight ("fully magnetized") ground state, so that the bond orientations decorrelate exponentially along the contour at any finite temperature as familiar from other one-dimensional systems with short ranged interactions.

The standard model of a polymer that is rod-like on the monomer scale is the *wormlike chain* (WLC), which is obtained from a chain with Hamiltonian Eq. (26) and segments $\boldsymbol{b}_n = b\,\boldsymbol{t}_n$ upon taking the continuum limit

$$N \to \infty,\ b \to 0 \qquad \text{with } L = b\,N \text{ and } \kappa \equiv b\,J \text{ both finite,} \tag{27}$$

which yields the continuum WLC Hamiltonian

$$\mathcal{H} = \frac{\kappa}{2}\int_0^L \mathrm{d}s\,\left(\boldsymbol{r}_s''\right)^2\ , \qquad \left|\boldsymbol{r}_s'\right| = 1 \tag{28}$$

Via this renormalization of the model the microstructure is wiped out and the specific content is reduced to the two phenomenological parameters κ and L. By comparison of Eq. (8) with the textbook result for the magnetization fluctuations of a (classical) ferromagnetic Heisenberg chain one can immediately check that our new definition of κ is consistent with Eq. (21), while the relation

$$2\kappa = (d-1)\ell_p\,k_BT \tag{29}$$

for general space dimension d may be rationalzed by a physical reasoning: ℓ_p must diverge for $d = 1$ (no space for turning) and decrease as d^{-1} with the space dimensions to turn into for $d \to \infty$. Note that the spin coupling J has to diverge proportional to N in the WLC continuum limit to keep the bending rigidity κ and the persistence length ℓ_p finite. In the magnetic language: the Heisenberg chain with finite J does not exhibit a spontaneous magnetization in the thermodynamic limit. Alternatively, starting from the continuum mechanical description of an elastic rod, the WLC Hamiltonian is obtained (disregarding torsion) by idealizing the low resistance of the backbone to bending as compared to stretching in taking the limit of an "infinitely slender rod". Indeed, Eq. (28) is easily recognized as the total bending energy of a slender rod, expressed as an integral over the square of the local curvature.

Exercise: WLC continuum limit

Derive Eqs. (8), (21) by taking the continuum limit of the corresponding results for a Heisenberg chain.

3.1.2 One-parameter models (CGC, WBR)

So far, we have introduced what one might call two- (FJC, WLC) and three-parameter (FRC) models, since in the (dynamically relevant) parametrization in terms of monomer positions they are uniquely characterized by two or three of the material parameters b, κ/k_BT and L, respectively. These names are somewhat euphemistic, however, since these models involve rigid contraints that fix a very large or even continuously infinite number of bond or tangent lengths, respectively. Although one may still derive some useful analytical results such as an infinite series representation of the radial distribution function of the FJC [**?**] or the linear response of a grafted WLC of arbitrary stiffness [**?**], **remark: 2d-t,r-propagator**, the constraints make any more ambitious calculations quite tedious in general. It goes without saying that the clear-cut fractal and self-affine scaling limits already mentioned in the introduction require extreme parameter ratios, for which one can effectively describe the polymer by much simpler *one-parameter models.*

Continuous Gaussian chain (CGC)

For example, the FJC and the Heisenberg chain with a fixed finite interaction energy J are both plausible coarse-grained models of a flexible polymer, and they both reduce to the same one-parameter model in the *self-similar or fractal scaling limit*, which is the continuum limit

$$N\,, L \to \infty,\ b \to 0 \qquad \text{with } b^2 N = b\,L \equiv \mathcal{R}_0^2 \text{ finite.} \tag{30}$$

For flexible polymers, $\kappa = bJ \to 0$ is thus treated as a microscopic parameter on the same footing with b, and the renormalization in Eq. (30) wipes out the whole structural information except for the single macroscopic phenomenological parameter $\mathcal{R}_0$. This may sound a bit bold but makes perfect sense, given that the whole business relies on the major physical properties being independent of microscopic details, which are only very schematically represented in the toy models, anyway. In the continuum limit, Eq. (30), any one-dimensional chain with finite interactions reduces to the same universal phenomenology. The resulting *one-parameter model*, which is representative of the whole class of flexible polymers, is called the *continuous Gaussian chain* (CGC). Its Hamiltonian in $d = 3$ space dimensions reads

$$\beta\mathcal{H} = \frac{3}{2b}\int_0^L \mathrm{d}s\,\left(\boldsymbol{r}'_s\right)^2 = \frac{3}{2\mathcal{R}_0^2}\int_0^1 \mathrm{d}\eta\,\left(\boldsymbol{r}'_\eta\right)^2\,, \tag{31}$$

where the derivative is understood to be taken with respect to s in the first expression and to η, which is a dimensionless contour parameter, in the second expression, respectively. As apparent from the second expression, the CGC has only a single phenomenological mesoscale parameter $\mathcal{R}_0^2$, and not two microscopic paramters b, L, as one might be mislead to believe by the first expression, which is more commonly found in text books. The CGC exhibits so called “fractal” self-similar or scale-free spatial correlations for distances less than $\mathcal{R}_0$. Because of this somewhat unintuitive property, it is often visualized by its closest relative among the two-parameter models, the *discrete Gaussian chain* (DGC),

$$\beta\mathcal{H} = \frac{3}{2b^2}\sum_n^N \boldsymbol{b}_n^2 = \frac{3}{2b^2}\sum_n^N \left(\boldsymbol{r}_{n+1} - \boldsymbol{r}_n\right)^2\,. \tag{32}$$

which is nothing but the CGC–Hamiltonian discretized according to the rule in Eq. (3).

The DGC–Hamiltonian is indeed quite helpful in illustrating the physical content of the CGC by physical analogies. The Boltzmann factor $e^{-\beta H}$ corresponding to this Hamiltonian may (after normalization) be recognized as the factorized joint probability density for a Brownian particle starting at $\boldsymbol{r} = \boldsymbol{r}_0$ at time $t = 0$ to diffuse to $\boldsymbol{r}_N$ in time $t = L = bN$ via the intermediate positions $\boldsymbol{r}_n$ reached at times $t = bn$,

$$G(\{\boldsymbol{r}_n, bn\}|\boldsymbol{r}_0, t = 0) = \prod_n \left(e^{3(\boldsymbol{r}_{n+1}-\boldsymbol{r}_n)^2/2b^2}\, 2\pi b^2/3\right)^{-3/2}\,. \tag{33}$$

One easily checks that each term in this product is a solution to the diffusion equation,

$$\partial_t G(\boldsymbol{r}, t|0, 0) - D\nabla^2 G(\boldsymbol{r}, t|0, 0) = \delta(\boldsymbol{r})\delta(t)\,, \qquad D = b/6 \tag{34}$$

for time $t = b$. Hence, by the identification of arclength s with time t, the CGC–Hamiltonian in Eq. (31) can be read as the free energy functional for a particle diffusing along the path $\boldsymbol{r}_t$.

Alternatively, the DGC can be interpreted as the “elastic” energy of a collection of N entropic springs of spring stiffness $3k_BT/b^2$. According to the equipartition theorem each spring has a thermal mean-square end-to-end distance $\langle (r_{n+1} - r_n)^2 \rangle = b^2$. With regard to Eq. (19), each of these springs may thus be understood as a coarse-grained representation (valid in linear response) of any mesoscopic subsection of an *arbitrary*[7] flexible polymer chain with a mean square end-to-end distance b^2. The DGC therefore provides a universal coarse-grained description for all possible microscopic flexible polymer models, valid unless the polymer is more than mildly deformed. Therefore, the DGC Hamiltonian should be understood as a phenomenological effective free energy rather than a Hamiltonian corresponding to any particular microscopic model. It has the pleasant property of self-similarity on scales larger than b, as revealed by the invariance of the Hamiltonian under a decimation followed by a scale transformation (see the following exercise). Upon taking the continuum limit (DGC → CGC), the large-scale universality and self-similarity are artificially extrapolated to arbitrarily short scales. Thereby, one obtains a so-called phenomenological model, a model of ultimate simplicity consistent with the mesoscopic properties of all flexible polymers without any reference to the (often elusive) microscopic scale.

Exercise: Establish the self-similarity of the DGC via decimation

Trace out every second monomer position in the distribution function for the DGC, i.e. compute

$$\int \prod_{n=1}^{\frac{N+1}{2}} \mathrm{d}\boldsymbol{r}_{2n} e^{-\beta \mathcal{H}} \propto e^{-\beta \tilde{\mathcal{H}}} \,. \tag{35}$$

Show that the effective free energy $\tilde{\mathcal{H}}$ of the coarse-grained chain thus obtained takes the form of the original Hamiltonian $\mathcal{H}$ after the scale transformation $N + 1 \to 2(\tilde{N} + 1)$, $b \to \tilde{b}/\sqrt{2}$.

Weakly bending rod (WBR)

In contrast, the *self-affine scaling limit* of a stiff polymer corresponds to the *stiff* limit or *weakly-bending rod* (WBR) limit of an infinitely stiff infinite polymer (by the infinite length one avoids ending up with a rigid rod),

$$\epsilon \equiv L/\ell_p \to 0 \qquad \text{with } \mathcal{R}_\perp^2 \equiv \epsilon \, L^2 \text{ finite.} \tag{36}$$

Taking advantage of the parametrization Eq. (4) in terms of small quantities, a consistent asymptotic theory can be formulated in the transverse fluctuations alone. The WBR Hamiltonian (in $d = 3$ space dimensions),

$$\beta \mathcal{H} = \frac{\ell_p}{2} \int_0^L \mathrm{d}\eta \, \left(\boldsymbol{r}''_{\perp s}\right)^2 = \frac{1}{2\mathcal{R}_\perp^2} \int_0^1 \mathrm{d}\eta \, \left(\boldsymbol{r}''_{\perp \eta}\right)^2 , \tag{37}$$

which follows from Eq. (28) by dropping terms of $\mathcal{O}(\epsilon^2)$ and keeping only the leading order terms, is a close relative of Eq. (31). Again, the second expression

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[7] Note that it need not even be a phantom chain by itself.

reveals that the WBR is a one-parameter model: since the small quantity $t_\parallel$ does not appear in the Hamiltonian, there is no external constraint to be imposed onto the Hamiltonian, which is moreover Gaussian. Make sure you understand that this represents a dramatic simplification with respect to the wormlike chain Hamiltonian Eq. (28). The single parameter $\mathcal{R}_\perp^2 = L^3/\ell_p$ plays in Eqs. (36), (37) exactly the same role as the parameter $\mathcal{R}^2 = bL$ in Eqs. (30), (31) for the CGC. As a side remark, we should add for later reference that the WBR limit may be realized in different ways that not necessarily require Eq. (36); e.g. one may apply a strong external force of magnitude $f \gg f_c \simeq \kappa/L^2$ that pulls the ends of a semiflexible polymer with $L \gg \ell_p$ apart to guarantee the condition $\boldsymbol{r}_\perp'^2 \ll 1$ and thus $r_\parallel \sim \boldsymbol{r}_\perp'^2/2$. Such a force is represented in the Hamiltonian, Eq. (37), by adding the work

$$fL - \boldsymbol{f} \cdot \boldsymbol{R} = f \int_0^L \mathrm{d}s \; t_{\parallel s} \sim \frac{f}{2} \int_0^L \mathrm{d}s \; \boldsymbol{t}_{\perp s}^2 \tag{38}$$

performed by the polymer against the force (z-coordinate chosen along the force). Finally, it may be noted in passing that the opposite limit $\epsilon \to \infty$ of the WLC leads back to the CGC, so that the two complementary single-parameter polymer caricatures, CGC and WBR are (in principle) both contained as extreme cases in the WLC model.

In summary, compared to the two- and three-parameter models, the one-parameter models CGC and WBR bring about a major technical simplification. The rigid constraints related to the fixed bond or tangent length are in some sense “automatically” obeyed by the equilibrium fluctuations, as suggested by the absence (divergence) of the length parameter L. Moreover, the approximations already inherent in the more complicated “microscopic” parametrizations (FJC, WLC) are often only justified in the limits of the reduced models; for example, the dynamics of a semiflexible polymer gets sensitive to its torsional stiffness and to corresponding dynamical modes not accounted for by the WLC model beyond the WBR limit. In this sense, the simple one-parameter models are the Platonic idols against which we may judge the usually more riddled reality.

3.1.3 Excluded volume effects (SAW)

To introduce excluded-volume effects, which seriously affect the physics of very flexible polymers, it seems desirable to start from the most simple flexible polymer model, the CGC, and add an interaction term. This is not entirely straightforward, though. It turns out that the interaction potential complicates the continuum limit ($b \to 0$), which can no longer be taken in a simple explicit manner. The problem arises from the diverging number of self-intersections of an ideal polymer in the continuum limit. It implies that self-intersections have to be largely avoided by a profound structural change once a finite penalty is assigned to them. As apparent in the corresponding interacting CGC model

Hamiltonian (in d spatial dimensions),

$$\mathcal{H}_E = \frac{d}{2\mathcal{R}_0^2}\int_0^1 \mathrm{d}\eta \left(\partial_\eta \boldsymbol{r}_\eta\right)^2 + g\frac{\mathcal{R}_0^4}{2b^{4-d}}\int_0^1 \mathrm{d}\eta \int_0^1 \mathrm{d}\mu \;\; \delta(\boldsymbol{r}_\eta - \boldsymbol{r}_\mu) \; . \tag{39}$$

known as the regularized Edwards Hamiltonian, the problem is to scale this penalty in an appropriate way in the continuum limit of diverging backbone length $L = bL$. In Eq. (39) the (hard-core) excluded volume interaction is already written in the form appropriate in the continuum limit $N \to \infty$, where the monomer size b vanishes, and the corresponding divergence in space dimensions $d \leq 4$ is fully isolated in the prefactor. Though writing the Hamiltonian in this form may not seem very intuitive at first sight, it has the advantage that it contains no spurious parameters and that the coupling constant g is a number on the order of 1. It also makes the identification of $d_c = 4$ as the upper critical dimension for the self-avoiding walk (SAW) problem straightforward. In higher dimensions $d > d_c$ self-avoidance is not a problem, simply because self-intersections of a random walk become so improbable that their effect is negligible. In lower dimensions, however, the excluded volume causes the coil to expand substantially such that $\mathcal{R}/\mathcal{R}_0 \to \infty$ in the continuum limit $N \to \infty$ and ν is no longer equal to 1/2. A very plausible strategy for calculating the fractal exponent ν for the SAW is therefore to extrapolate down from the upper critical dimension, where $\nu = 1/2$. The basic idea is as follows. In departing from $d = d_c$ to $d < d_c$ for small but finite b, the interaction term blows up. The excluded volume obliges the polymer to swell so that its typical end-to-end distance R increases beyond the value $\mathcal{R}_0$ without self-interactions. This helps to calm down the divergence of the second term in the Hamiltonian, but, in return, it causes the first term to blow up. For the optimum conformation that minimizes the overall free energy, one thus expects both terms to be of similar magnitude. Anticipating no more than a single characteristic length scale, one estimates their contributions by dimensional analysis, i.e.

$$\beta H_E \simeq \frac{R^2}{\mathcal{R}_0^2} + \frac{g\mathcal{R}_0^4}{R^d b^\epsilon} \qquad (\varepsilon \equiv 4 - d) \; , \tag{40}$$

and hence

$$\frac{R^2}{\mathcal{R}_0^2} \simeq \frac{\mathcal{R}_0^4}{R^d b^\varepsilon} \quad \Rightarrow \quad R \simeq \mathcal{R}_0^{6/(2+d)} b^{-\varepsilon/(2+d)} \; . \tag{41}$$

The jargon is that R, which has physical units of length and hence must be proportional to the elementary physical length scale b on dimensional grounds, has thereupon acquired an *anomalous dimension* $-\varepsilon/(2+d)$. The apparent contradiction is of course immediately resolved by inserting Eq. (9) for $\mathcal{R}_0$, which yields[8].

$$R \simeq bN^{\nu_F} \; , \qquad \nu_F \equiv \frac{3}{2+d} \; . \tag{42}$$

In the proper continuum limit, the phenomenological (observed) size of the polymer should of course remain constant. Assuming the latter to be given by

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[8] For a more satisfactory derivation of the Flory exponent see Ref. [**?**].

Eq. (42), the prefactors R_0^{-2} and $R_0^4 b^{-\varepsilon}$ in the Hamiltonian, and therefore the whole "bare" Hamiltonian $H_E \propto b^{-\varepsilon/(2+d)}$, must be divergent—albeit somewhat less than naively expected from Eq. (39). Within the dimensional estimate in Eq. (40), the Hamiltonian may be identified with the free energy $F(\boldsymbol{R})$ of the chain as a function of its the end-to-end vector $\boldsymbol{R}$, and $e^{-\beta F(R)}$ is up to normalization and measure factors the radial distribution function. The moment $\langle R^2 \rangle$ is expected to be dominated by the minimum of $F(\boldsymbol{R})$ obtained in Eq. (42), hence

$$\langle R^2 \rangle \simeq \mathcal{R}^2 \equiv b^2 N^{2\nu_F} \ . \tag{43}$$

After the Flory approximation to the exponent ν has once been obtained in this crude way, a much better approximation to $F(R)$ and to the radial distribution function is easily derived by simple arguments, as demonstrated in Sec. 3.3.2.

A more sophisticated (and in principle controlled) version of the foregoing argument is the so-called $\varepsilon-$expansion in the "small" parameter $\varepsilon = 4 - d$. On a qualitative level, it is easy to see that the double perturbation expansion in ε and in the interaction term helps to calm down the divergencies that would occur in a naive perturbation expansion of $e^{-\beta \mathcal{H}_E}$, so that they no longer spoil the calculation of exponents. To this end, one rewrites the singular factor $b^{-\varepsilon}$ in $\mathcal{H}_E$ in the form

$$b^{-\varepsilon} = e^{-\varepsilon \ln b} = \sum_{l=0}^{\infty} \frac{(-\ln b)^l}{l!} \varepsilon^l \tag{44}$$

so that to each order in ε only logarithmic divergencies remain, which do not affect power-law exponents. In practice, since one is interested in $\varepsilon = 1$ (at least), one has to push the expansion to high powers in ε and afterwards apply resummation techniques to get useful quantitative results via this otherwise very appealing strategy. The same techniques may also be applied directly to the strongly divergent naive perturbation expansion of $\mathcal{H}_E$ in the (bare) interaction term. In any case, one has to work hard to beat the Flory approximation ν_F for the exponent ν. To arrive at a detailed quantitative understanding and characterization beyond the level of mere exponents requires even more sophisticated tricks [?].

This ends the introduction of the models required for the remainder of the lecture. It is thus the right point to clearly state that there exist other useful coarse-grained models not discussed in this lecture, such as the *finitely extensible, nonlinear elastic* (FENE) dumbbell model or the *bead-rod* model [**?**] commonly used in molecular dynamics simulations of flexible and semiflexible polymers, respectively.

3.2 Response: nonlinear deformations

Equipped with the complete Hamiltonian characterizations of our toy models introduced in the preceding section, the problems encountered in the course of our preliminary calculations of the longitudinal response of a stiff polymer at the end of Sec. 2.3 can now be overcome.

3.2.1 Force-extension relation of a WBR

Consider again a stiff polymer as introduced in Secs 2.1, 2.2.4, and 3.1.2 subject to a stationary pulling force $\boldsymbol{f}$ applied between the ends. The appropriate Hamiltonian is the sum of the energies in Eqs. (37) and (38)

$$\begin{aligned}\beta\mathcal{H}_f &= \frac{\ell_p}{2}\int_0^L \mathrm{d}s\, \left(\boldsymbol{r}''_{\perp s}\right)^2 + \frac{\beta f}{2}\int_0^L \mathrm{d}s\, \left(\boldsymbol{r}'_{\perp s}\right)^2 \\ &= \frac{1}{2\mathcal{R}_\perp^2}\int_0^1 \mathrm{d}\eta\, \left(\boldsymbol{r}''_{\perp\eta}\right)^2 + \frac{1}{2\mathcal{R}_{\perp f}^2}\int_0^1 \mathrm{d}\eta\, \left(\boldsymbol{r}'_{\perp\eta}\right)^2 \\ &= \frac{1}{2\mathcal{R}_\perp^2}\int_0^1 \mathrm{d}\eta\, \left[\left(\boldsymbol{r}''_{\perp\eta}\right)^2 + N_b^2\left(\boldsymbol{r}'_{\perp\eta}\right)^2\right]\end{aligned} \tag{45}$$

with $\mathcal{R}_\perp^2 = L^3/\ell_p$ as defined in Eq. (2) and

$$\mathcal{R}_{\perp f}^2 \equiv k_BTL/f \qquad N_b \equiv \mathcal{R}_\perp/\mathcal{R}_{\perp f} = L/\ell_f = \pi\sqrt{f/f_c} \qquad \ell_f \equiv \sqrt{\kappa/f}\ . \tag{46}$$

The second line in Eq. (45) makes explicit, what was already announced above, namely that the WBR limit can be realized even for quite flexible polymers (i.e., $\epsilon = L/\ell_p$ can be any finite number) if the chain is stretched by a sufficiently strong force so that

$$f,\, L,\, \mathcal{R}_\perp,\, N_b \to \infty \qquad \text{with } \mathcal{R}_{\perp f}^2 = k_BTL/f \text{ finite.} \tag{47}$$

It also immediately suggests a *crossover phenomenon* on the characteristic scale ℓ_f, called the *"blob"* scale, a notion originally introduced by Pincus and de Gennes for flexible polymers. On shorter lengths, the bending energy dominates and one expects an (essentially) undisturbed WBR conformation of the wormlike chain characterized by the usual self-affine correlations as discussed above. As already noted above, $\ell_f \ll \ell_p$ is required to guarantee weak bending; which determines the minimum stretching force $f = k_BT/\ell_p$ to maintain the WBR geometry. Consequently, one can say that the WBR correlations extend along the whole contour for $N_b \ll 1$. For large $N_b \gg 1$, on the other hand, the tension term dominates on scales larger than the blob scale ℓ_f, where the Hamiltonian effectively reduces to a diffusion Hamiltonian with transverse diffusion coefficient $D_\perp = \mathcal{R}_{\perp f}^2/2L = k_BT/2f$. It encodes a random walk of "duration" L and mean square transverse excursions

$$\langle \boldsymbol{R}_\perp^2\rangle_f = 4D_\perp L = 2\mathcal{R}_{\perp f}^2 \tag{48}$$

(with the force f playing the role of the friction coefficient in Brownian motion). Physically speaking, the limiting Hamiltonian describes a "taut string" with weak excursions from the ground state or, equivalently, a transverse random walk of N_b blobs, each contributing a random transverse step of length $\ell_f^{3/2}\ell_p^{-1/2}$ summing up to a transverse mean-square displacement $\ell_f^3/\ell_p N_b$, which is, of course, again k_BTL/f.

The smart way: blobs

The intuitive notion of blobs is often a very useful practical tool to estimate the conformational change in presence of strong disturbances without actually calculating. As an example, we estimate the nonlinear force-extension relation of the WLC via the blob picture. The main idea is to exploit the analysis of the Hamiltonian in the preceding paragraph, and to regard a chain of length $L \gg \ell_f$ as an effective FJC consisting of N_b blobs, which are simply segments of virtually undisturbed stiff WLCs of length ℓ_f, as illustrated in Fig. **??**. The contraction of the end-to-end distance with respect to full stretching is simply N_b times the length contraction caused by a single segment of length ℓ_f. The latter involves two equivalent contributions—as commonly the case for that sort of crossover arguments. Coming from the large scale description of the chain as a transverse random walk of blobs, we obtain from the orientation fluctuation of the segment a length reduction of about k_BT/f per blob. Exploiting the analogy with a taut FJC of blobs this can directly be taken over from Eq. (59) below, or from the equivalent textbook result for the magnetization of a classical paramagnet in a strong field[9]. From the complementary perspective of regarding a segment of length ℓ_f as an unperturbed weakly bending WLC, a second contribution is equal to the equilibrium contraction of a WLC segment itself, which, according to Eqs. (13), (14) is given by $\langle \delta R_{\|\ell_f} \rangle \simeq \ell_f^2/\ell_p \simeq k_BT/f$. Either way (or altogether) one thus estimates the total equilibrium contraction of the chain against the force f as

$$\langle \delta R_{\|} \rangle_f \simeq N_b k_B T/f \simeq L\ell_f/\ell_p \simeq k_B T L/\sqrt{\kappa f}\ . \tag{49}$$

Note that via the second route, the blob picture miraculously yields the nonlinear response of a WLC to strong tension (up to a numerical prefactor, which turns out to be 1/2) from nothing more than the knowledge of low equilibrium moments of the end-to-end distance of a WLC-segment of a certain length ℓ_f. This is generally the case for problems that exhibit crossover scaling: knowing from the Hamiltonian or from some physical intuition one (often trivial) limiting case of the law and the crossover scale, one gets the non-trivial limit for free via a scaling argument. A further variant of the same argument is given in Sec. 3.2.3, below.

The precise way: calculate

The problem of an almost completely strechted polymer is simple enough to be accessible to direct quantitative calculations [**?**, **?**, **?**]. The present paragraph may please readers who either dislike the foregoing discussion for its lack of explicit calculations or browse these notes for prefactors. Otherwise it may be skipped.

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[9] Alternatively, consider that the contour length required for making transverse excursions is “stolen” from the longitudinal extension. For a chain consisting of one virtually straight segment of length $L \simeq \ell_f$, $(L - \delta R_{\|})^2 + \boldsymbol{R}_{\perp}^2 = L^2$, hence $\langle \delta R_{\|\ell_f} \rangle \simeq k_BT/f$ from Eq. (48).

For computational convenience, we require a force of magnitude f that pulls exactly along the end-to-end distance $\boldsymbol{R}$ such that the average deviations from the straight conformation are small[10]. Decomposing the undulations $\boldsymbol{r}_{\perp s}$ into the appropriate eigenmodes for hinged ends ($\boldsymbol{R}_\perp = 0$),

$$\boldsymbol{r}_{\perp s} = \sqrt{2/L} \sum_n \boldsymbol{a}_n \sin p_n s \; , \qquad p_n \equiv n\pi/L \; , \tag{50}$$

the Hamiltonian in Eq. (45) is diagonalized into a sum of terms that are quadratic in the statistically independent mode amplitudes $\boldsymbol{a}_n$,

$$\beta \mathcal{H}_f = \frac{\ell_p}{2} \sum_n (p_n^4 + p_n^2 \ell_f^{-2}) \boldsymbol{a}_n^2 \; . \tag{51}$$

Noting that $\boldsymbol{a}_n$ is a two-component vector, equipartition implies

$$\langle \boldsymbol{a}_n^2 \rangle_f = \frac{2 k_B T}{\kappa \, p_n^2 (p_n^2 + \ell_f^{-2})} \; . \tag{52}$$

The average contraction $\langle \delta R_\parallel \rangle$ of the chain with respect to the fully stretched state follows by integrating over $\langle t_{\parallel s} \rangle_f \sim \langle (\boldsymbol{r}'_{\perp s})^2 \rangle_f / 2$:

$$\langle \delta R_\parallel \rangle_f = \frac{1}{2} \sum_n p_n^2 \langle \boldsymbol{a}_n^2 \rangle_f = \frac{k_B T}{f} \sum_n \frac{1}{1 + (p_n \ell_f)^2} \; . \tag{53}$$

To evaluate this result one may proceed perturbatively. The occurence of $(p_n \ell_f)^2 = n^2 f_c / f$ with the Euler force $f_c = \kappa \pi^2 / L^2$ of the lowest hinged bending mode in the denominator suggests to consider forces f that are either weak or strong with respect to f_c. Alternatively, one may apply methods from complex analysis to show that the infinite sum in Eq. (53) has an exact representation in terms of the Langevin function $\mathcal{L}(x) \equiv \coth(x) - 1/x$, namely

$$\langle \delta R_\parallel \rangle_f = \frac{\ell_f}{2\ell_p} \mathcal{L}(N_b) \sim \begin{cases} \sqrt{k_B T / 4 \ell_p f} & (f \gg f_c) \\ L^2 / 6\ell_p - f L^4 / 90 \kappa \ell_p & (f \ll f_c) \; . \end{cases} \tag{54}$$

The upper asymptotics, which (in contrast to the lower) does not require $L/\ell_p \ll 1$ but only $\ell_f / \ell_p \ll 1$, has been quite successful in applications involving the nonlinear mechanical response of DNA molecules [?]. The negative inverse of the coefficient multiplying the force f in the last expression is—for the particular boundary condition of hinged ends—the effective longitudinal spring constant of a weakly undulating polymer[11], which was elusive within the backdoor entrance approach of Section 2.3; see Eq. (22). Also note that the asymptotic approximation for strong forces only holds for *pulling* forces $f > 0$. For a *pushing* force, $\ell_f^2 \propto f^{-1} < 0$, so that ℓ_f becomes imaginary. As a consequence, the

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[10] Such a force is difficult (if not impossible) to realize experimentally. Results for more relevant cases are summarized further below.

[11] The leading terms given in Eq. (54) are insensitive to the difference between the WLC- and WBR-Hamiltonian.

lowest mode amplitude in Eq. (52) and the coth in the Langevin function (which becomes a cot) diverge as f approaches $-f_c$. Physically it is quite obvious that the weakly bending rod assumption must break down when the pushing force approaches the critical force. In summary, the range of validity of Eq. (54) extends to $f \to \infty$ if the chain is stretched, while it is limited by $|f| \ll f_c$ under compression.

Exercise

Repeat the above derivation for a WBR confined to a plane (e.g. for an amphiphilic biopolymer trapped at a liquid-gas or liquid-liquid interface or on fluid membrane), considering the reduced degrees of freedom and Eq. (29).

3.2.2 Force-extension relation of the FJC

Exercise

Show that

$$\langle \Delta R \rangle_f = L\mathcal{L}(f\, b/k_B T) \tag{55}$$

for the FJC consisting of $N = L/b$ segments of length b and discuss its asymptotic behavior for large and small forces f. (Hinged ends are not advisable, here.) What about a FJC confined to a plane?

3.2.3 Force-extension relation of the SAW

For flexible polymers there is an intermediate scaling regime between the ultimate model-specific response near complete stretching—which may obey Eq. (54), Eq. (55) or yet some other relation depending on the microscopic structure of the polymer—and the universal linear response of Eq. (19). This intermediate regime is a nonlinear regime, yet completely universal and model independent. It is dominated by the non-trivial fractal correlations resulting from the comptetition of conformational entropy and self-avoidance. Since only elaborate perturbation techniques but no exact analytical solution is available, the blob picture really pays in this case. For pedagogic reasons it shall be rephrased in a slightly different way, in the form of a standard crossover scaling argument. To this end, one first estimates the crossover scale from the linear response relation, Eq. (19), as the force for which Eq. (19) predicts a deformation of the same order of magnitude as the equilibrium fluctuations[12], i.e. $f_c \simeq dk_BT/\mathcal{R}$. Accordingly, one may rewrite Eq. (19) in the scaling form

$$\langle \boldsymbol{R} \rangle_f = \mathcal{R}\Phi\big(f/f_c\big) \qquad \Phi(x \ll 1) = x\,. \tag{56}$$

For intermediate forces, the polymer will again have the large-scale conformation of a string of blobs. The deformation will thus be proportional to the total length L of the chain. In case of unease, imagine how a chain twice as long can be

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[12] This natural phenomenological rule for defining the crossover scale is supported by the above results for the WBR.

realized by linking two identical blob chains together. (The crucial property underlying this intuition is of course the absence of non-trivial conformational correlations beyond the blob scale.) Since $\mathcal{R} \propto L^{\nu}$ from Eq. (1),

$$\begin{aligned} f \gg f_c \;\Rightarrow\; \langle \boldsymbol{R} \rangle_f \propto L \;\Rightarrow\; \Phi(x \gg 1) \propto x^{1/\nu - 1} \\ \Rightarrow\; \langle \boldsymbol{R} \rangle_f \simeq \mathcal{R}(f/f_c)^{1/\nu-1}\ . \end{aligned} \tag{57}$$

The miraculous thing about this derivation of a non-linear force-extension relation does not even require the knowledge of a Hamiltonian (let alone any calculations) but only phenomenological information about the equilibrium coil size and its scaling with polymer mass. Accordingly, one should not be surprised by the following

Exercise

Reassure yourself that by a force-extension experiment information about the microstructure (e.g. FJC or WLC, or anything beyond) of a long flexible polymer can only be gained with forces on the order of $(k_BT/\mathcal{R})N^{\nu}$. (A polymer 10^5 Kuhn lengths long will reveal details upon a hundred-fold stretching of the coil.) In particular, there is nothing to be learned about the specific polymer at hand from a force-extension experiment in the above SAW-regime.

3.2.4 Force-extension summary

Summarizing, the force-extension relations for the weakly bending WLC (with hinged ends) and the FJC (with free ends) can be cast into a simple scaling form with the scaling function given by the Langevin function $\mathcal{L}(x) = \coth x - 1/x$,

$$\langle \Delta R \rangle_f \simeq \begin{cases} L\mathcal{L}(f/f_c)\ , & f_c \equiv k_BT/b \quad \text{(FJC)} \\ (L^2/6\ell_p)\big[1-(3/\pi)\sqrt{f_c/f}\,\mathcal{L}\big(\pi\sqrt{f/f_c}\big)\big]\ , & f_c \equiv \pi^2\kappa/L^2 \quad \text{(WBR)} \\ \mathcal{R}(f/f_c)^{1/\nu-1}\ , & f_c \equiv dk_BT/\mathcal{R} \quad \text{(SAW)} \end{cases} \tag{58}$$

The SAW result is restricted to $\mathcal{R} \ll \langle \boldsymbol{R} \rangle_f \ll L$, i.e. to forces that considerably deform the coil but leave at least part of the SAW correlations undisturbed. The characteristic difference between the force-extension relations of a *flexible* WLC with persistence length $\ell_p \ll L$ and a FJC is best appreciated if both have the contour length L and the FJC has the bond length $b = 2\ell_p$ (so that they have the same equilibrium coil size and linear response). In the strong force limit

$$\langle \delta R_{\|} \rangle_f \sim \begin{cases} \mathfrak{f}^{-1} & \text{(FJC)} \\ (2\mathfrak{f})^{-1/2} & \text{(WBR)} \end{cases} \qquad \mathfrak{f} \equiv \frac{2\ell_p f}{k_BT} \gg 1\ . \tag{59}$$

Mind the different definitions of the quantities $\langle \Delta R \rangle_f$ and $\langle \delta R_{\|} \rangle_f$ given in Eqs. (12) and Eq. (18), respectively.

In deriving the above force-extension relations, we have always assumed the most convenient boundary conditions, which should not matter for those results that pertain to infinite chains (SAW, leading order results for the WBR). However, as already emphasized in Sec. (2.2), absolute values and prefactors are generally sensitive to the boundary conditions for *finite* chains (FJC, SFC), and so are higher order corrections to the asymptotic results for the WBR. Moreover, also the "ensembles" matter. The force-extension relations measured with devices that fix the extension or the force, respectively, will generally not be the same. A more quantitative disussion of this issue is provided in the following subsection.

3.3 Fluctuations: radial distribution functions and propagators

Can one somehow reverse the line of arguments that gave the linear response from the free fluctuations, to make use of the nonlinear response results from the preceding subsection for gaining a deeper understanding of fluctuations? This is indeed a fruitful direction to pursue, as it gives a quick and dirty access to some functions containing a more comprehensive characterizations of fluctuations as the low moments obtained so far. The most important ones are the radial distribution functions $P(r)$ that provide the probability that a certain polymer will be found with end-to-end distance $R = r$. For a better understanding of the idea behind this "upgrade" of the nonlinear response laws it is useful, to first recall the relationships between distribution functions, generating functions and their respective generalized free energies.

3.3.1 Ensembles, free energies and reduced distribution functions

The usual partition sum Z and free energy F are related to the Hamiltonian via

$$Z = \sum_{\{\boldsymbol{r}_n\}} e^{-\beta\mathcal{H}(\{\boldsymbol{r}_n\})} = e^{-\beta F} \; , \tag{60}$$

so that Z and βF can both be interpreted as functions of the model parameters ℓ_p and L. It is useful to also consider incomplete or constrained partition sums and corresponding free energy functions, for example if instead of the full microscopic information characterizing a polymer conformation only a reduced parametrization is of interest. In particular, the distribution function $Z(\boldsymbol{r})$ of the end-to-end vector $\boldsymbol{R}$ and its corresponding free energy $F(\boldsymbol{r})$ are defined by

$$Z(\boldsymbol{r}) \equiv \langle \delta(\boldsymbol{r}_N - \boldsymbol{r}_0 - \boldsymbol{r}) \rangle \equiv \frac{1}{Z} \sum_{\{\boldsymbol{r}_n\}} \delta(\boldsymbol{r}_N - \boldsymbol{r}_0 - \boldsymbol{r}) e^{-\beta\mathcal{H}(\{\boldsymbol{r}_n\})} \equiv \frac{e^{-\beta F(\boldsymbol{r})}}{Z} \; . \tag{61}$$

The reduced free energy $F(\boldsymbol{R})$ represents an effective thermodynamic potential which gives you the average force

$$\langle \boldsymbol{f} \rangle_{\boldsymbol{R}} = -\partial_{\boldsymbol{R}} F(\boldsymbol{R}) \tag{62}$$

excerted by a polymer on a device that fixes its end-to-end vector to $\boldsymbol{R}$. The functions $Z(\boldsymbol{r})$ and $F(\boldsymbol{R})$ are for a free polymer independent of the direction of the end-to-end vector $\boldsymbol{R}$ and only dependent on the end-to-end distance R. To emphasize that they are only depend on a single additional scalar parameter (or variable) R, it is useful to define the *radial distribution function*,

$$P(r) \equiv 4\pi r^2 Z(\boldsymbol{r}) \ , \qquad \int_0^\infty \mathrm{d}r\ P(r) = 1 \ , \tag{63}$$

which explicitly refers to the isotropy. Another useful definition is the *characteristic function* or force distribution function

$$\begin{aligned} Z(\boldsymbol{f}) \equiv & \langle e^{\beta \boldsymbol{f}\cdot\boldsymbol{R}} \rangle \equiv e^{-\beta G(\boldsymbol{f})} \\ \equiv & \int \mathrm{d}\boldsymbol{r}\ Z(\boldsymbol{r}) e^{\beta \boldsymbol{f}\cdot\boldsymbol{r}} \equiv \frac{1}{Z}\int \mathrm{d}\boldsymbol{r}\ e^{-\beta F(\boldsymbol{r}) + \beta \boldsymbol{f}\cdot\boldsymbol{r}} \end{aligned} \tag{64}$$

as the (multi-dimensional) Laplace transform of $Z(\boldsymbol{r})$. In thermodynamics, $G(\boldsymbol{f})$ is called the Gibbs free energy, which is the appropriate convex Lyapunov function for the prescribed-force ensemble, as opposed to the Helmholtz free energy $F(\boldsymbol{R})$, which is the corresponding quantity in case of prescribed spatial constraints. Since taking the n'th derivative of $Z(\boldsymbol{f})$ with respect to $\beta\boldsymbol{f}$ at $\boldsymbol{f} = 0$ produces the n'th moment of $\boldsymbol{R}$, it is also known as the moment generating function. Its knowledge is equivalent to the knowledge of infinitely many moments, which suggests that it is in general considerably more difficult to calculate than the low moments obtained so far. Similarly, upon taking the derivative of the logarithm of the generating function, one generates the so-called cumulants, e.g.

$$-\partial_{\boldsymbol{f}} G(\boldsymbol{f}) = \langle \boldsymbol{R}\, e^{\beta \boldsymbol{f}\cdot\boldsymbol{R}} \rangle / \langle e^{\beta \boldsymbol{f}\cdot\boldsymbol{R}} \rangle \equiv \langle \boldsymbol{R} \rangle_{\boldsymbol{f}} \tag{65}$$

$$-k_B T\ \partial_{\boldsymbol{f}}^2 G(\boldsymbol{f})\big|_{\boldsymbol{f}=0} = \langle \boldsymbol{R}^2 \rangle_{\boldsymbol{f}} - \langle \boldsymbol{R} \rangle_{\boldsymbol{f}}^2 \qquad \text{etc.} \tag{66}$$

Propagators …

3.3.2 "Inverse Langevin approximation"

There is a quick way of getting qualitatively useful simple results for the radial distribution function if the static force-extension is known. It is sometimes called the inverse Langevin approximation, since it was first proposed for the FJC, where it involves the inversion of Eq. (55). Starting point is Eq. (65) and Eq. (62). After integration, they read

$$G(\boldsymbol{f}) = -\int_0^{\boldsymbol{f}} \mathrm{d}\boldsymbol{f}' \ \cdot \langle \boldsymbol{R} \rangle_{\boldsymbol{f}'} \ , \qquad F(\boldsymbol{R}) = \int_0^{\boldsymbol{R}} \mathrm{d}\boldsymbol{R}' \ \cdot \langle \boldsymbol{f} \rangle_{\boldsymbol{R}'} \ . \tag{67}$$

Now, since we are looking for $F(\boldsymbol{R})$ while we know $\langle \boldsymbol{R} \rangle_{\boldsymbol{f}'}$, the idea is to invert $\langle \boldsymbol{R} \rangle_{\boldsymbol{f}'}$ and use it as an approximation for $\langle \boldsymbol{f} \rangle_{\boldsymbol{R}'}$ in the second Eq. (67). This approximation is expected to work well if the fluctuations are not too large, particularly if the distributions $Z(\boldsymbol{R})$ and $Z(\boldsymbol{f})$ are nicely peaked around their maxima. Technically, it amounts to replacing the Laplace transform Eq. (64) relating $Z(\boldsymbol{R})$ and $Z(\boldsymbol{f})$ by a Legendre transform between $F(\boldsymbol{R})$ and $G(\boldsymbol{f})$, which is up to a logarithmic correction a saddle point approximation (see appendix B). Inversion of the asymptotic WLC force-extension relation Eq. (59) yields

$$f(R \to L) \sim \frac{k_B T}{4\ell_p (1 - R/L)^2} \; . \tag{68}$$

Integration gives

$$F(R \to L) = -\int \mathrm{d}r \; f(R) = \frac{k_B T}{4\ell_p (1 - R/L)} \; . \tag{69}$$

These results, just as the WBR calculation leading to Eq. (59), break down for small $R \ll L$. They accurately reflect the statistical mechanics of the thermal undulations that have to be straightened out when a stiff polymer is stretched, but they fail to capture the mechanics of elastic rod buckling governing conformations with small R. Now, while the contour roughness due to thermal fluctuations is essential when the polymer is stretched, it does not matter much under strong buckling, e.g. if the ends are brought into close contact to form a loop. This suggests to approximate the free energy for small R by the purely mechanical buckling energy,

$$F(R \ll L) \sim f_c (L - R) \tag{70}$$

with the critical Euler buckling force $f_c \equiv \pi^2 \kappa / L^2$ of the lowest bending mode. Altogether, one thus arrives at the free energy of a stiff polymer ($\ell_p / L \ll 1$)

$$\beta F(\xi) = \pi^2 \xi + \frac{1}{4\xi} + \frac{1}{2} \ln \xi^3 \; , \qquad \xi \equiv \frac{\ell_p}{L} (1 - R/L) \; , \tag{71}$$

where the logarithmic correction from Appendix B has been smuggled in. Except for this minor correction, the free energy, depicted in Fig. 1 has a very intuitive interpretation. It is a sum of the cost for buckling and the cost for straightening out the thermal undulations, the former increasing for small R, the latter diverging at full stretching $R \to L$. Exponentiation of F gives up to a measure factor $4\pi r^2$ (remember that for the calculation of the force-extension relation the end-to-end vector was constrained to be parallel to the force, which can of course point in any arbitrary direction) and normalization the radial distribution function,

$$Z(\xi) \propto \xi^{-3/2} e^{-\pi^2 \xi - 1/4\xi} \; , \qquad \xi \equiv \frac{\ell_p}{L} (1 - R/L) \; . \tag{72}$$

The results for $F(R)$ and $P(R)$ are depicted for various ℓ_p / L in Fig. 1, and match the exact WBR result (an infinite series with contributions from all Euler modes) [**?**] relatively well. The comparison with exact (Monte Carlo) data for the WLC show that the simple inverse Langevin trick fails for intermediate values of L/ℓ_p, where the minimum of $F(R)$ becomes flat and ceases to be strongly peaked. The failure is primarily due to the breakdown of the WBR/FJC approximations, though, as more elaborate approaches such as the exact FJC

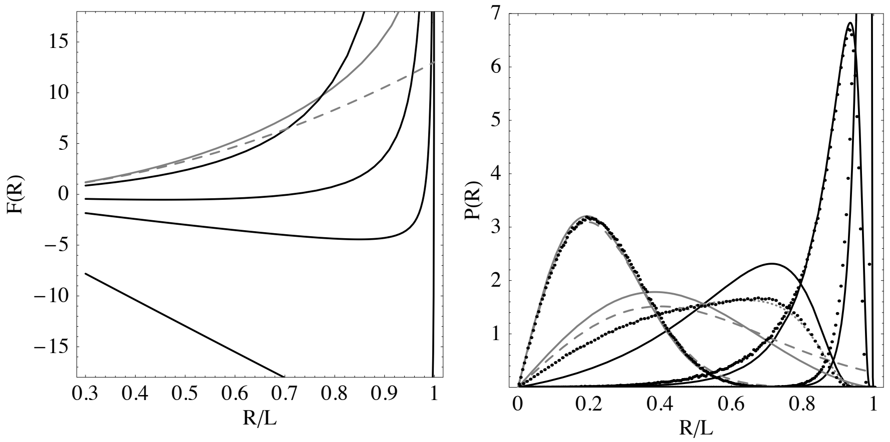

Figure 1: Approximate free energy $F_{2d}(R)$ and radial distribution function $P_{2d}(R) \propto R\ e^{-\beta F_{2d}(R)}$ of a WLC in two dimensions, the latter in comparison with exact (Monte Carlo) data for $\ell_p/L = 5^{-2}$, 5^{-1}, 1, 5. Black solid lines correspond to the saddle-point approximation of the WBR, Eq. (72); grey lines depict the FJC-inverse-Langevin (solid) and Gaussian (dashed) approximations adjusted for the exact $\langle R^2 \rangle$ from Eq. (10). For intermediate persistence lengths, such as $\ell_p = L/5$, where the inverse Langevin trick fails as $F(R)$ becomes flat near its minimum, and both FJC and WBR cease to be appropriate idealizations, the data happen to resemble their linear superposition (dotted-grey).

calculation Ref. [?], the exact WBR calculation [**?**], and even the leading order WLC correction to the CGC [**?**, ?], turn out to fail in this region. See [**?**] for further technicalities.

From Eq. (72) one can readily calculate the probability for the ends to collide accidentally, the so-called loop-closure probability, in the WBR approximation. It is found to vanish for both small and large L/ℓ_p, with an intermediate maximum that becomes quite pronounced, if the calculation is repeated numerically with the WLC model, and which is thought to be of relevance for DNA cyclization and protein folding [**?**, **?**].

Some of the charm of the inverse Langevin approximation derives from the fact that it is readily applicable also to the FJC (see Fig. 1) and SAW. In particular in the latter case the back-of-the-envelope calculation turns out to be qualitatively superior to quite laborious Hartree calculations reviewed in Ref. [?]. Starting from Eq. (57), inverting it and integrating over the extension, one obtains

$$F(R) \approx f_c \int \mathrm{d}R\, (R/\mathcal{R})^{\nu/(1-\nu)} = d(1-\nu) k_B T (R/\mathcal{R})^{1/(1-\nu)} \,. \tag{73}$$

Exponentiating and adding again the logarithmic correction from the saddle-point approximation (appendix B) then yields

$$Z(\boldsymbol{R}) \propto R^{\frac{\nu-1/2}{1-\nu}} e^{-d(1-\nu)(R/\mathcal{R})^{1/(1-\nu)}} \approx R^{\frac{4-d}{2(d-1)}} e^{-d\frac{d-1}{d+2}(R/\mathcal{R})^{(d+2)/(d-1)}} \,. \tag{74}$$

This result has essential qualitative features predicted by renormalization group calculations, in particular the proper exponent $1/(1-\nu)$ for the compressed exponential decay at large R, and it reduces to the appropriate Gaussian (δ-function) in $d=4$ ($d=1$) dimensional embedding space, respectively. It fails to capture the quantitative change of the exponent of the pre-exponential factor (as familiar e.g. from Ornstein-Zernicke theory) between the limits $R \ll \mathcal{R}$ (roughly $1/(3\nu)$, $1/(6\nu)$) and $R \gg \mathcal{R}$ (roughly 2/3, 2/6) for $d=2$, 3, which in fact involve another critical exponent besides ν [?, ?].

A Linear Response

A general linear response relation may be expressed either in integral form or with help of a functional derivative,

$$\langle \Delta x(t) \rangle_f \equiv \int_{-\infty}^{\infty} \mathrm{d}t'\, \chi(t,t') f(t') \,, \qquad \frac{\delta \langle \Delta x(t) \rangle_f}{\delta f(t')} = \chi(t,t') \,. \tag{75}$$

Under stationary conditions the susceptibility $\chi(t,t') \equiv \chi(t,t')$ is a function of the time difference $t-t'$ only; i.e. it does not matter, whether the experiment is performed today or tomorrow. What matters is the difference between the time t when the response is measured and the time t' when the force $f(t')$ was applied. Moreover, a macroscopic physical response is causal (or retarded) with respect to a macroscopic cause, there is no response to the future force history, so that the susceptibility vanishes for negative arguments. Using the step function $\theta(t)$ and introducing a function[13] $2i\,\chi''(t)$ that coincides with $\chi(t)$ for positive arguments, one can thus write

$$\chi(t-t') = 2i\,\chi''(t-t')\theta(t-t') \; . \tag{76}$$

In Einstein's historical discussion of Brownian motion presented in the main text, $2i\,\chi''(t) = \zeta^{-1}\mathrm{sgn}\, t$. It is not a coincidence of the simple example that the function χ'', which is directly related to the correlation function according to the FDT, plays the role of a friction responsible for energy dissipation (and therefore changes sign under time reversal). This is generally true and is the origin of the name "fluctuation-dissipation theorem". For the given example, the FDT is checked directly by noting that the equilibrium average $\langle x^2(t)\rangle$ is time independent, so that the time derivative of the mean-square fluctuations $\langle [x(t)-x]^2\rangle$ in Eq. (16) is (after expanding the square) found to be solely due to that of the (time inversion invariant) cross-term $2\langle x(t)x\rangle$ appearing on the left hand side of Eq. (17).

B Legendre transformation, saddle-point & inverse Langevin approximation

For simplicity consider again the (somewhat artificial) case of a WLC with a force acting strictly along to the end-to-end vector, $\boldsymbol{f}\|\boldsymbol{R}$. Or in other words, if $\boldsymbol{f}$ has to be regarded as a fixed quantity, as appropriate for the integration in Eq. (64), assume for the moment that the polymer ends are constrained to slide along the axis of the force. Then one only has to deal with scalar quantities R, f and integrals in Eqs. (64-67), and the orientational degrees of freedom may later be restored through the measure factor $4\pi r^2$. Expanding the exponent of the corresponding scalar version of last expression in Eq. (64) around its maximum at $R(f)$ (which gives the leading contribution) one has

$$e^{-\beta G(f)} \approx e^{-\beta F(R)+\beta f R}\frac{1}{Z}\int_{-\infty}^{\infty}\mathrm{d}r\; e^{-\beta F''(R)(r-R)^2/2} \; . \tag{77}$$

The Gaussian integration yields up to some uninteresting terms

$$F(R) \approx G(f) + fR - \frac{k_BT}{2}\ln F''(R) \; . \tag{78}$$

The explicit form of $G(f)$ is obtained from the integration Eq. (67) using the asymptotic WLC force-extension relation, Eq. (59),

$$G(f) \approx -L\int_0^f \mathrm{d}f' \left[1-(4\beta\ell_p f)^{-1/2}\right] = -Lf + L\sqrt{k_BTf/\ell_p} \; . \tag{79}$$

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[13] The factor of $2i$ is convention. Given the time inversion invariance of equilibrium correlation functions, the FDT suggests to continue the (real) function $2i\,\chi''(t)$ to negative times such that it changes sign under time reversal. Hence, its Fourier transform is imaginary and the Fourier transform χ''_ω of $\chi''(t)$ is real. The factor of 2 makes χ''_ω the imaginary part of the Fourier transform of $\chi(t)$.

One has still to get rid of the f's. Neglecting the logarithmic term in Eq. (78) for a moment, $F(r)$ is seen to be the Legendre transform of $G(f)$, which implies that $\langle f(R)\rangle = \partial_f G$ is the inverse function (not the reciprocal) of $\langle R(f)\rangle = \partial_R F(R)$, so that one recovers the approximation Eq. (69) for $F(R)$ obtained by integrating the inverted force-extension directly. As a check, one may easily verify the saddle point condition, namely that the maximum of $F(R) - fR$ is indeed at $R(f)$. With Eq. (78), the approximation in Eq. (69) can now be improved by adding the logarithmic correction, as in Eq. (71).