A Review of Elasticity Models for Extension of Single Polymer Chains

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I. The *Freely-Jointed Chain (FJC) Model*

I.A. Microscopic Model and General Statistical Mechanical Formulas

A polymer chain wants to be in its equilibrium state of maximum entropy, the random coil. At room temperature, the chain is continually moving due to thermal agitation and can take on a huge number of configurations over a period of time. Since all configurations can not be defined explicitly, a statistical mechanical approach is necessary to specify the average properties of the system. The ***freely jointed chain (FJC) model*** (also called the *randomly jointed chain model*) considers a single isolated, flexible, polymer chain consisting of n rigid bonds joined in linear succession and connected by revolving pivots. Each bond is represented by a vector of fixed length, $\mathbf{l}$. Hence, the fully extended chain length or *contour length*, $L_{contour}$, is $n\mathbf{l}$. The vector $\mathbf{r}$ represents the instantaneous chain end-to-end separation. The FJC model assumes that in the absence of external constraints (e.g. forces) there is (1) no bond angle (directional) preference; i.e. all bond angle values equally probable and uncorrelated to the directions of all other bonds in the chain (i.e. the chain follows a *random walk* in space), (2) free rotation at the bond junctions, and (3) no self-interactions (e.g. excluded volume effects).

All of the relevant statistical mechanical properties can be calculated from the *radial probability density function* of **r**, P(**r**), which is defined as follows, assuming that chain end A is fixed at the origin, P(**r**) is the probability per unit volume that chain end B is situated within a spherical shell of radius **r** and thickness d**r** (i.e. a volume element of $4\pi r^2 d\mathbf{r}$) located a distance **r** from chain end A. P(**r**) is directly proportional to the number of chain configurations, Ω. The average chain configuration can be characterized by the root-mean-square end-to-end distance, $<\mathbf{r}^2>^{1/2}$, where <> denotes a statistical mechanical (time) average over all chain configurations. $<\mathbf{r}^2>^{1/2}$ can be calculated from P(**r**):

$$< \mathbf{r}^2 >^{1/2} = \sqrt{\int_0^\infty \mathbf{r}^2 P(\mathbf{r}) dr} \qquad (1)$$

The configurational entropy, S, is

$$S(\mathbf{r}) = k_B \ln P(\mathbf{r}) \qquad (2)$$

Assuming that the internal energy of the molecule stays the same for all chain configurations (i.e. each link is rigid and does not deform), then entropy is the sole contribution to the Helmholtz free energy, A:

$$A(\mathbf{r}) = -TS(\mathbf{r}) = k_B T \ln P(\mathbf{r}) \qquad (3)$$

where k_B is Boltzmann's constant, and T is the absolute temperature.

If an external tensile force, **F**, is applied to the ends of the freely jointed chain in the direction of **r**, the chain will extend or "uncoil" by free rotation of backbone bonds and each segment will begin to align along the direction of **F**. The deformation is concentrated solely at the segment junction sites. Increasing **F** leads to a reduction in the number of possible chain configurations and hence, also a reduction in the configurational entropy. As a result, an elastic restoring force, $\mathbf{F}_{\mathbf{elastic}}$, is induced which tends to disorder the segment. $\mathbf{F}_{\mathbf{elastic}}$ is directly related to the Helmholtz free energy:

$$\mathbf{F}_{\mathbf{elastic}} = \frac{\partial \mathrm{A}(\mathbf{r})}{\partial \mathbf{r}} \quad (4)$$

The stiffness of the chain, k_{chain}, can be defined as follows:

$$\mathrm{k}_{\mathrm{chain}} = \frac{\partial \mathbf{F}_{\mathbf{elastic}}}{\partial \mathbf{r}} \quad (5)$$

A hypothetical statistical representation of the "real" FJC may be devised, the ***equivalent random chain (ERC)***, in which *n* statistically independent segments are joined in linear succession and randomly oriented with respect to all other segments. If each segment is taken as a monomer unit, *n* is approximately equal to the degree of polymerization, *N*. The *statistical segment length* or *Kuhn segment length*, **a**, is related to local chain stiffness or resistance to bending (i.e. the stiffer the molecule, the longer **a**). The freely jointed chain model is usually defined in terms of *n* and **a** where $L_{contour} = n\mathbf{a}$. This notation will be employed in the following sections.

I.B. Gaussian Chain Statistics

P($\mathbf{r}$) for the FJC model does not lend itself to simple mathematical expression, but has been proven to be Gaussian for sufficiently long chains at low extensions ($\mathbf{r}<\tfrac{1}{3}n\mathbf{a}$):

$$
\begin{aligned}
&\mathrm{P(r)} = 4\pi\left(\frac{\beta}{\pi^{1/2}}\right)^{3}\mathbf{r}^{2}\exp\left(-\beta^{2}\mathbf{r}^{2}\right)\\
&\text{where}: \beta = \sqrt{\frac{3}{2\mathrm{na}^{2}}}\\
&<\mathbf{r}^{2}> = 3/2\beta^{2}\\
&\mathrm{P}(\mathbf{r}) = \left(\frac{3}{2}\pi<\mathbf{r}^{2}>\right)^{3/2}\exp\left(-\left(\frac{3}{2}<\mathbf{r}^{2}>\right)\mathbf{r}^{2}\right)
\end{aligned}
\qquad \textit{(6)}
$$

Substituting eqs. (6) into eq. (2), a simple expression for $<\mathbf{r}^{2}>^{1/2}$ can be derived:

$$<\mathbf{r}^{2}>^{\frac{1}{2}} = n^{1/2}\mathrm{a} \quad (7)$$

The Helmholtz free energy is then :

$$A = \left[\frac{3k_{B}T}{2L_{contour}a}\right]\mathbf{r}^{2} \quad (8)$$

and the elastic restoring force is :

$$\mathbf{F}_{\mathbf{elastic}} = \left[\frac{3k_{B}T}{L_{contour}a}\right]\mathbf{r} \quad (9)$$

It is observed that $\mathbf{F}_{\mathbf{elastic}}$ is proportional to $\mathbf{r}$ and opposite to $\mathbf{F}$ and thus, possesses a linear elasticity governed by Hooke's law (i.e. can be modeled by a classical spring of zero unstrained length). Equation (9) forms the basis for the classical theory of rubber elasticity. k_{chain} is found to be a constant and equal to the prefactor in eq. (9):

$$k_{chain} = \frac{3k_BT}{L_{contour}a} \quad (10)$$

It is noted that k_{chain} is directly proportional to the thermal energy, $\sim k_BT$, and inversely proportional to the square of the statistical segment length, $\sim 1/\mathbf{a}^2$.

I.C. Non-Gaussian Chain Statistics

Since the Gaussian distribution implies nonvanishing probabilities for $\mathbf{r} > n\mathbf{a}$, a more accurate distribution function was developed.

$\mathscr{L}(\beta)$ = Langevin Function = fractional chain extension or extension ratio

$$\mathscr{L}(\beta) = \frac{r}{na} = \mathrm{COTH}(\beta) - (1/\beta)$$

$$\beta = \mathscr{L}^{-1}\left(\frac{\mathbf{r}}{na}\right) = \text{Inverse Langevin Function}$$

$$= 3\left(\frac{\mathbf{r}}{na}\right) + \left(\frac{9}{5}\left(\frac{\mathbf{r}}{na}\right)^3\right) + \left(\frac{297}{175}\left(\frac{\mathbf{r}}{na}\right)^5\right) + \left(\frac{1539}{875}\left(\frac{\mathbf{r}}{na}\right)^7 + \dots\right)$$

$$P(\mathbf{r}) = \frac{A\beta}{\mathbf{r}a^2}\left(\frac{\sinh\beta}{\beta}\right)^n \exp\left(-\frac{\beta\mathbf{r}}{a}\right) \qquad (11)$$

If eq. (11) is substituted for eq. (3) the following result is obtained for the Helmholtz free energy:

$$A(\mathbf{r}) = -T(c - k_Bn)\left(\beta\frac{\mathbf{r}}{na} + \frac{\beta}{\sinh\beta}\right) \qquad (12)$$

where : c is an arbitrary constant. Leading to the exact inverse formula :

$$\mathbf{r}(\mathbf{F}_{\mathbf{elastic}}) = na\left(\coth(x) - \frac{1}{x}\right) \text{where } x = \left(\frac{fa}{k_BT}\right) \quad \mathbf{(13a)}$$

Similarly, the elastic contractive force is calculated using the inverse Langevin function:

$$\mathbf{F}_{\mathbf{elastic}} = \left(\frac{k_B T}{a}\right)\beta \quad (13b)$$

$\mathbf{F}_{\mathbf{elastic}}$ versus **r** for Gaussian and non-Gaussian elasticity are compared in Figure 2. For small displacements ($\mathbf{F}_{\mathbf{elastic}}\mathbf{a} << k_BT$) eq. (13b) reduces to the Gaussian curve. Non-Gaussian effects start to become significant at moderate displacements ($\mathbf{r} > \frac{1}{3}n\mathbf{a}$) and lead to a dramatic nonlinear upturn in the force at high displacements; i.e. the chain becomes harder and harder to stretch as it straightens out. A limiting finite extensibility is imposed and the force converges as the contour length is approached. For large displacements ($\mathbf{F}_{\mathbf{elastic}}\,\mathbf{a} >> k_BT$) eq. (13b) takes the following form:

$$\mathbf{F}_{\mathbf{elastic}} = \frac{k_B T}{a}\left(1 - \frac{\mathbf{r}}{L_{\text{contour}}}\right) \quad (14)$$

I.D. Modified Non-Gaussian Elasticity : The Extensible FJC

Smith, et al. [26b] extended the FJC model to take into account the enthalpic deformability of the chain segments by modeling them as elastic springs and replacing $L_{contour}$ with L_{total}:

$$L_{\text{total}} = L_{\text{contour}} + n\frac{\mathbf{F}_{\mathbf{elastic}}}{k_{\text{segment}}} \quad \mathbf{(15)}$$

where $k_{segment}$ is the spring constant of a single chain segment. $k_{segment}$ represents the segmental resistance to longitudinal strain and is of enthalpic origin. The "softening" of the segments leads to a reduction in the force at high displacements. The finite extensibility of the chain is eliminated and instead the curve approaches a constant slope value.

II. The *Worm-Like Chain (WLC) Model*

II.A. Microscopic Model

The ***worm-like chain (WLC) model*** (also called the *Kratky-Porod model*) describes a polymer chain which is intermediate between a rigid-rod and a flexible coil, and takes into account both local stiffness as well as long-range flexibility. The WLC model considers a single isolated, polymer chain consisting of n bonds each of length, $\mathbf{l_w}$, joined in linear succession. Each bond is oriented at an angle, γ, with respect to its neighbor. The distinguishing property of the WLC is that the chain is treated as an isotropic, homogeneous elastic rod whose trajectory varies continuously and smoothly through space, as opposed to the jagged contours of the more flexible FJC. The direction of curvature is assumed to be random at any point along the chain and the bonds are considered to be freely rotating.

When considering the WLC, it is convenient to define the *persistance length*, **p**, as the average projection of **r** on the first bond of the chain $\mathbf{l}_1$ in the limit of infinite chain length:

$$p = < (\frac{\hat{l}_1}{l_1}) \cdot \sum_{i=l}^{n} \hat{l}_i > \quad \textbf{(16)}$$

p is a measure of the length over which the chain "persists" in the same direction as the first bond or in other words, the distance over which two segments remain directionally correlated. As n approaches ∞, **p**= $\mathbf{l}_w$ (1-cos γ). **p** is directly related to the local chain stiffness and similar to the statistical segment length, expresses the local ability of the chain to bend back upon itself. In the absence of external forces **p** is equivalent to 0.5**a**.

II.B. Parameter Calculations

The root mean square end-to-end separation for an ensemble of wormlike chains, as a function of the persistence length is

$$< \mathbf{r}^2 >^{1/2} = \sqrt{2p^2\left[\frac{L_{contour}}{p} - 1 + \exp\left(-\frac{L_{contour}}{p}\right)\right]} \quad (17)$$

Although the complete force law for the WLC can be calculated numerically, both the large and small force limits have analytically asymptotic solutions that are described by the following interpolation formula:

$$\mathbf{F}_{\mathbf{elastic}} = \left(\frac{k_B T}{p}\right)\left[\frac{1}{4}\left(1 - \frac{\mathbf{r}}{L_{contour}}\right)^{-2} - \frac{1}{4} + \frac{\mathbf{r}}{L_{contour}}\right] \quad (18)$$

Eq. (18) differs from the exact solution up to ~10% for F ≈ 0.1 nN [31b]. For small displacements ($\mathbf{F}_{\mathbf{elastic}}\mathbf{p} << k_B T$) the polymer conformation becomes a "directed" random walk and takes the form

$$\mathbf{F}_{\mathbf{elastic}} = \frac{3k_B T}{2p}\left(\frac{\mathbf{r}}{L_{contour}}\right) \quad (19)$$

For large displacements ($\mathbf{F}_{\mathbf{\textit{elastic}}}\mathbf{p} << k_BT$), the accessible conformations reduce to quadratic fluctuations around a straight line and take the form

$$\mathbf{F}_{\mathbf{elastic}} = \frac{k_BT}{4p}\left(1 - \frac{\mathbf{r}}{L_{contour}}\right)^2 \quad (20)$$

The $\mathbf{F}_{\mathbf{elastic}}$ for the stiffer WLC begins to rise sooner than that for the FJC and also diverges less strongly since the polymer is able to bend continuously rather than at a limited number of isolated points. Equation (20) can be arranged as follows:

$$\mathbf{r} = L_{contour} - [(k_BT)^{\frac{1}{2}} \frac{L_{contour}}{2\sqrt{p}}][\mathbf{F}_{\mathbf{elastic}}]^{-\frac{1}{2}} \quad (21)$$

Hence, $\mathbf{p}$ and $L_{contour}$ can be obtained from a plot of $[\mathbf{F}_{\mathbf{elastic}}]^{-1/2}$ versus $\mathbf{r}$ from the y- and x- intercepts respectively.

II.C. The Extensible WLC

The WLC can be extended to take into account the enthalpic deformability of the chain segments in a similar fashion to the treatment described for the FJC. The high force regime ($|\mathbf{r} - L_{contour}| / L_{contour} <<1$) can be approximated by :

$$\mathbf{r} = L_{\text{contour}}\left[1 - 0.5\left(\frac{k_B T}{\mathbf{F}_{\mathbf{elastic}}p}\right)^{\frac{1}{2}} + \frac{F_{\text{elastic}}}{k_{\text{segment}}}\right] \quad (22)$$

Appendix

I. Force Sensitivity in Single Molecule Force Spectroscopy Experiments

While the precision of the tip deflection measurements can be of the order < 0.1 nm, the accuracy is typically 1 nm - 2 nm due to piezo nonlinearities, uncertainties in the optical lever detection system, thermal fluctuations, acoustic vibrations, and lateral motion of the probe tip. The sensitivity of the force measurements in a single molecule force spectroscopy experiment can be understood by modeling the system as a series of springs each of which represents the cantilever, the probe tip, the polymer chain entropic elasticity, and the substrate, as shown schematically in Figure 15a. [78]. The force is each of elements in the system is equal:

$$F_{cantilever} = F_{tip} = F_{chain} = F_{substrate} \qquad (5)$$

and the displacements are additive:

$$\delta_{total} = \delta_{cantilever} + \delta_{tip} + \delta_{chain} + \delta_{substrate} \qquad (6)$$

where δ_{total} is the displacement of the piezo. Since the probe tip and substrate are much stiffer than the cantilever and the entropic elasticity of the polymer chain, it is reasonable to neglect their contributions to the system. The cantilever is modeled by a linear, elastic Hookean spring:

$$\sigma_{cantilever} = \frac{F}{k_{cantilever}}$$

$$\delta_{cantilever} = F/k_{cantilever} \qquad (7)$$

where $k_{cantilever}$ is a constant and equal to 0.032 N/m in our case. The polymer chain is modeled by a nonlinear elastic spring (independent of time in the regime of our experiments):

$$\sigma_{chain} = \frac{F}{k_{chain}}(F)$$

$$\delta_{chain} = F/k_{chain}\,(F) \qquad (8)$$

where k_{chain} is a nonlinear function of the force, F, and calculated from the slope of the force versus distance curve. Substituting eqs. (7) and (8) in (6) and rearranging the terms, we can derive an expression for $\delta_{cantilever}$ as a function of ($k_{cantilever}/k_{chain}$) :

$$\delta_{cantilever} = \delta_{total}[(\frac{k_{cantilever}}{k_{chain}}) + 1]^{-1} \qquad (9)$$

A plot of eq. (9) for δ_{total} = 200 nm is given in Figure 15b. At large ($k_{cantilever}/k_{chain}$), such as in the initial Gaussian regime, the total displacement is dominated by the polymer chain and the sensitivity of the measurement is low. At small ($k_{cantilever}/k_{chain}$), such as in the initial Gaussian regime, the total displacement is dominated by the cantilever and the sensitivity of the measurement is high. This is the reason why optical tweezers have a much higher sensitivity (< 1 pN) than the atomic force microscope; the optical tweezer force transducer is 1000 times softer than the AFM cantilever [31b].

II. Accuracy of Distance Measurements in Single Molecule Force Spectroscopy Experiments

The error in the distance measurements of single molecule force spectroscopy experiments (Figure 16.) is the difference in vertical height (z) between grafted chain end and probe tip apex, z_{error}, can be defined as follows :

$$z_{error} = z_{(\mathrm{rtip})} + z_{anisotropy} + L_{O} \qquad (10)$$

where : $z_{(\mathrm{rtip})}$ is the error due to tip flattening or the contact area, $z_{anisotropy}$ = error due to molecular anisotropy (= zero for our measurements), and L_{O} = error due to initial, unperturbed molecular height.

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[76] Following the terminology set forth in [1], the chain *configuration* is defined as the spatial arrangement of atoms, regardless of shape or symmetry, as opposed to the term *conformation* which denotes a more specific subset of configurations which are defined depending on their form and symmetrical arrangement.

[77] Another type of probability density function, P(**x,y,z**) can be defined as follows : if chain end A is fixed at the origin, P(**x,y,z**) is the probability per unit volume that chain end B is situated within a volume element of d**x** d**y** d**z** located a distance **r** from chain end A.

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