1 Introduction

Polymers are large complex *chain* molecules made up of 'small', 'simple' subunits (*monomers*) [1, 2, 3, 4]. They come in a variety of shapes and sizes. ***Linear polymers*** which are the most commonly studied and produced are essentially a single open strand of monomers, but there has also been a lot of research on the properties of polymers with different back-bone structures such as branched polymers, ring polymers. We shall be interested here only in linear polymers. Polymers for which all the monomers are the same we refer to as *homopolymers* and those with chemically different monomers as *hetero-polymers*. In our discussion of polymers they will always be in solution, i.e. dissolved in a liquid (solvent). When in solution, the polymers can also be charged and are called *polyelectrolytes* (PEs). Applications of polymers in solution are widespread - they are essential in the chemical industry and *biopolymers* are crucial for numerous biological processes at the cellular scale [5]. Examples of polymers are polymethylmethacrylate $[CH_2 - C(CH_3)COOCH_3]_N$ which is used to make plexiglass or polyethylene $[CH_2 - CH_2]_N$ which is what the plastic bags that one gets at the supermarket are made of. Polyelectrolyte gels have an important application as super-absorbers. DNA, RNA are *charged* polymers of nucleotides present in the cells of all living organisms as well as numerous polymeric cytoskeletal proteins such as actin or microtubules.

Naturally, to understand the properties of polymeric materials or the functioning of a complex intercellular process we must understand how many polymers interacting with each other behave. Nonetheless we must begin first to understand how one single polymer behaves before we can start studying more complex scenarios.

There has been a lot of work on the properties of neutral (uncharged) polymers on which there is a general consensus in the scientific community and some rather good agreement between experiment and theory [2, 1]. Scaling theories in polymer physics have been particularly successful [2]. A very useful concept for the understanding of the behaviour of polymer solutions is *universality*: one finds that polymers with very different microscopic (chemical) structure all have the same quantitative *macroscopic* behaviour, the only difference between chemically different polymers being different pre-factors in front of scaling functions. This is due to a separation of length-scales (the microscopic or chemical length-scale and the size of the random coil).

For neutral polymers scaling theories and renormalization group calculations have worked hand in hand to produce some beautiful results.

Recently there has been renewed interest in the so-called *non-universal* aspects of polymer behaviour in particular with respect to biological applications and the effect of structure on physical properties and hence function [5]. The effect of rigidity i.e. resistance to bending and twisting of polymers has been particularly well studied.

Another important aspect of polymer theory is the effect of electrostatics on the behaviour of polymers in solutions as many useful industrial and biological polymers are charged. Charged polymers though long under study have not been able to produce the agreement between experiment and theory found for neutral polymers. There are a number of different but comparable lengths in the polyelectrolyte system in typical aqueous solutions. As a result it is difficult to find universal behaviour and construct unambiguous scaling theories. Nonetheless prompted by experiment and the expanding capacity of modern computers, the study of polyelectrolytes has become fashionable again. Charge affects both the microscopic and macroscopic structure of polymers so that electrostatics can lead to *new* universality classes of behaviour and *new* scaling theories.

Our plan is as follows: in the next section we review the properties of neutral polymers in solution focusing on universal properties and scaling theories. Several very good introductory texts [1, 2, 3, 4] have been used as the basis for this introduction. In Sec 3 we describe the statistical physics of semi-flexible polymers. We discuss some aspects of polyelectrolyte behaviour in Sec **??** and to round up we make our conclusions in Sec. **??**

2 Neutral Flexible Polymers

A linear polymer in solution on a large enough coarse-grained scale can be pictured as essentially a random coil. All linear polymers, no matter what their microscopic structure if they are long enough, can be considered to be *flexible* polymers. At very low temperatures, $T \to 0$ the polymer would be a rigid rod but of course would not dissolve in the solvent. The coarse-gaining procedure required to consider the polymer as a flexible coil is shown in Fig 1.

2.1 Random Walk Models - Ideal Chains

2.1.1 Freely Jointed chain

As a start, we consider a polymer essentially as a random walk (RW) of bonds between monomers [1]. Each bond's orientation is totally uncorrelated with all the other bonds. The RW consists of N bonds of length b_0 joining 'monomers', positions $\{\mathbf{R}_n\}$ with the bond vectors $\{\mathbf{r}_n \equiv \mathbf{R}_n - \mathbf{R}_{n-1}\}$. There are no interactions other than those between nearest neighbour bonds. In Sec.3 we will associate b_0 with the *persistence length* of the polymer. We ignore interactions between the polymer segments for now. We generalise to d dimensions not forgetting that we live in $d = 3$.

We can define a normalized bond distribution function

$$\psi(\mathbf{r}) = \frac{1}{\Omega_d b_0^{d-1}} \delta^d(|\mathbf{r}| - b_0) \tag{1}$$

where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the surface area of a unit radius d-dimensional hyper-sphere and from that the polymer distribution function

$$\Psi[\{\mathbf{r}_n\}] = \prod_{n=1}^{N} \psi(\mathbf{r}_n)\,, \tag{2}$$

from which we can calculate averages $\langle F[\{\mathbf{r}_n\}]\rangle = \int \prod_{n=1}^{N} d^d r_n F[\{\mathbf{r}_n\}]\;\Psi[\{\mathbf{r}_n\}]$ such as that of the the end-to-end distance $R = R_N - R_0$,

$$\langle R^2 \rangle = N b_0^2 \tag{3}$$

Similarly, the end-to-end distribution function, $P^{(2)}(\mathbf{R}, N)$ which is defined as $P^{(2)}(\mathbf{R}, N) = \langle \delta^d(\mathbf{R}_N - \mathbf{R}_0 - \mathbf{R})\rangle$ is

$$P^{(2)}(\mathbf{R}, N) = \int \frac{d^d k}{(2\pi)^d} e^{i\mathbf{k}\cdot\mathbf{R}} \left(\frac{\Omega_{d-1}}{\Omega_d} \int_{-1}^{1} \mathrm{d}x (1 - x^2)^{(d-3)/2} \exp\{ikb_0x\} \right)^N \tag{4}$$

2.2 The Gaussian model

If we consider the limit of a long chain $N \to \infty$ the integral in eqn. (4) will be dominated by the regime $k \to 0$ and after performing an expansion in k

and rexponentiating we obtain

$$\lim_{N\to\infty} P^{(2)}(\mathbf{R},N) \simeq \left(\frac{d}{2\pi N b_0^2}\right)^{d/2} \exp\left[\frac{-dR^2}{2Nb_0^2}\right] \tag{5}$$

This is an example of the *Central Limit Theorem* (CLT) which states that all distributions tend to become more and more Gaussian if samples are taken over larger and larger sets. As a result of the CLT, other random chain models with *only* short range interactions along the backbone all give the same distribution but with a different effective bond length [1]. We refer to all such chains as ***ideal***.

This allows us to make a technical simplification: rather than use the freely jointed chain we work with a monomer distribution function which is already Gaussian (and technically easy to handle) which gives the same distribution as the freely jointed chain (and all other random chain models) in the long chain limit. We can consider a monomer distribution function $\psi_g(\mathbf{r}) = \left(\frac{d}{2\pi b_0^2}\right)^{d/2} \exp\left(-\frac{d\mathbf{r}^2}{2b_0^2}\right)$ and as a result a polymer distribution function $\Psi_g[\{\mathbf{R}_n\}] = \left(\frac{d}{2\pi b_0^2}\right)^{dN/2} \exp\left[-\frac{d}{2b_0^2}\sum_{n=1}^{N}(\mathbf{R}_n - \mathbf{R}_{n-1})^2\right]$. We can take the limit of continuous n $\sum_n \to \int dn \Rightarrow \Psi_g[\{\mathbf{R}(n)\}] \propto \exp\left[-\frac{3}{2b^2}\int_0^N \mathrm{d}n \left(\frac{\partial \mathbf{R}(n)}{\partial n}\right)^2\right]$

The statistical mechanics of a Gaussian polymer is described by a partition function Z and Free Energy F

$$\exp\{-\beta F\} = Z = \int \mathcal{D}[\mathbf{R}(s)] \exp\{-\beta H_p[\mathbf{R}]\} \tag{6}$$

where

$$\beta H_p = \frac{d}{2b_0^2}\int_0^N \mathrm{d}s |\partial_s \mathbf{R}(s)|^2 \tag{7}$$

and where $\partial_s A = \partial A/\partial s$ and $\beta = 1/k_B T$

Another useful quantity is the average radius of gyration, R_g defined by

$$R_g^2 \equiv \frac{1}{2N^2}\sum_{i,j=1}^{N} \langle(\mathbf{R}_i - \mathbf{R}_j)^2\rangle\,. \tag{8}$$

For the Gaussian chain

$$R_g \sim \frac{1}{\sqrt{6}} b N^{1/2}\,. \tag{9}$$

2.3 Experiments

Scattering experiments (see Fig. 2) are a good way to measure the structure of the polymer chain. Using X-rays, neutrons, or visible light one can obtain information about the structure on different length scales [2, 6].

The scattering function is calculated,

$$g(\mathbf{k}) \equiv \frac{1}{N} \sum_{i,j=1}^{N} \langle \exp[i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \rangle \tag{10}$$

One of most measured quantities in dilute solution is the radius of gyration of single polymers. R_g is obtained from the small k region of $g(k)$; $g(\mathbf{k}) \simeq g(0)(1 - \frac{k^2}{3} R_g^2 + \ldots)$

Using measurements of the viscosity of dilute solutions one can determine a 'hydrodynamic radius', R_η,

$$\eta = \eta_s \left[1 + 2.5 \frac{4\pi c}{3n} R_\eta^3 + \ldots \right] \qquad (c \rightarrow 0) \tag{11}$$

The diffusion constant, D of the polymers in solution is obtained from dynamic light scattering experiments and defines another estimate of the coil size R_D,

$$D = \frac{T}{6\pi \eta_s R_D} \tag{12}$$

All these experiments measure typically $R \sim N^{0.57} \rightarrow N^{0.60}$ so we can conclude after comparison with eqns. (3,9) that most polymers are not ideal chains. A possible reason is discussed in Sec. 2.4 below : repulsion of the monomers on the chain.

The osmotic pressure Π of polymer solutions is another often measured quantity. Naively one expects $\Pi \sim c$ where c is the concentration of polymers for low concentrations of polymer [4, 7]. This is known as Van't Hoff's law (VH). Big deviations from VH are obtained for very low concentrations of long polymers.

2.4 Excluded Volume Interaction

If a chain is in solution, because the monomers have a finite volume we expect that chain will be self-repelling. Therefore monomers far from each other along the chain will repel each other. Whilst short range interactions (along the chain backbone) do not change the scaling behaviour of R_g, long range ones do! The random coil will become *swollen*. As a result, $R_g^{(0)} \sim b\sqrt{N}$ will be changed to $R_g(N)$

A simple argument due to Flory gives a very good estimate of this effect [3]. To model this one must include the interaction energy of each monomer with all the other monomers. If each monomer has a volume v_0, the free energy, F can be written

$$F = E_I - T\Delta S = v_0\, N \left(\frac{N}{R_g^d}\right) + \frac{3k_B T}{2b^2 N}(R_g^2) \tag{13}$$

The free energy is minimised w.r.t. R_g to obtain

$$R_g = \left(\frac{v_0 d b^2}{3k_B T}\right)^{1/(d+2)} N^{3/(d+2)} \tag{14}$$

with the Flory exponent $\nu_F(d) = 3/(d+2)$ which is exact in $d = 1, 2, 4$ and very good in $d = 3$. Experiments obtain $\nu \simeq 0.57 - 0.60$ very close to the $\nu_F = 0.6$ for $d = 3$.

2.5 Simulations

Many problems in polymer physics are analytically intractable. Numerical simulations are very often a very good way to check if one has understood the underlying physics of the problem. There are essentially two types of simulation techniques widely used for studying the properties of flexible polymers.

2.5.1 Monte-Carlo

The technique of Monte Carlo simulation [8] is a very useful way of determining the equilibrium properties of the system. One can consider the ubiquitous Metropolis algorithm as an illustration [9]. The energy, E_i of the system is calculated using the effective Hamiltonian. Using the accepted library of dynamical moves, an attempt is made to put the system in a new state and the new energy, E_f of the system is calculated. If $\Delta E = E_f - E_i \leq 0$, then the system stays in the new state. If on the other hand, $\Delta E > 0$, a random number between 0 and 1 is generated; if the random number is greater than the Boltzmann factor, $p = \exp(-\Delta E / k_B T)$, where T is the temperature and k_B Boltzmann's constant, then the system stays in the new state. If the random number is less than the Boltzmann factor then the system goes back to the original state. We always respect the principle of detailed balance. By exploring the phase space this way, one eventually arrives at the equilibrium condition. This can be a very efficient way to find the equilibrium configurations of complex systems. There is usually no way to relate the parameters of the model directly to real parameters and so it is useful only in describing the qualitative behaviour of the system. The advantage is that generally, one *can* find the equilibrium [10].

2.5.2 Molecular dynamics

In Molecular Dynamics simulation, one implements the interaction between monomers using potentials [11]. The forces are given by the gradient of the potentials and by numerically integrating Newton's second Law - the system *slowly* evolves in a *physical* way towards its equilibrium state. In this picture, the simulation results can be related to 'real' measured parameters. The simulations can also be performed using *explict* solvent molecules. The disadvantage of this approach is that it is computationally very expensive, requiring long execution times. With present day computers, one can normally only simulate nanoseconds making equilibrium configurations extremely difficult to calculate. For studying dynamical problems it is the best way to proceed. One numerically solves the classical solutions of Newton's equations for the 'monomers' positions and velocities $\{\mathbf{R}_i, \mathbf{v}_i\}$ with a force on the monomers due to their potentials $U[\mathbf{R}_j]$ given by $\mathbf{f}_{ij} = \nabla_j U(|\mathbf{R}_i - \mathbf{R}_j|) = -\mathbf{f}_{ji}$. To model the chain connectivity a commonly used potential is a bead-spring model such as the Finitely Extensible Non-linear Elastic (FENE) model

$$U_{bs}(|\mathbf{r}_i|) = \frac{a}{2}\left(\frac{R}{\sigma}\right)^2 \ln\left[1 - \left(\frac{r_i}{R}\right)^2\right] \quad ; \qquad \sigma \equiv \text{monomer size} \tag{15}$$

Between all the monomers the excluded volume interaction is modeled by a Lennard-Jones potential ($r_c = 2^{1/6}\sigma$).

$$U_{ex}(|\mathbf{R}_i - \mathbf{R}_j|) = 4\epsilon\left[\left(\frac{\sigma}{|\mathbf{R}_i - \mathbf{R}_j|}\right)^{12} - \left(\frac{\sigma}{|\mathbf{R}_i - \mathbf{R}_j|}\right)^{6}\right] \tag{16}$$

To model a finite temperature, the system is coupled to a heat bath

$$m_i \frac{d^2\mathbf{R}_i}{dt^2} = \mathbf{f}_{ji} - \Gamma \mathbf{v}_i + \mathbf{W}_i(t) \tag{17}$$

where $\langle \mathbf{W}_i \rangle = 0$ and $\langle \mathbf{W}_i(t)\mathbf{W}_j(t') \rangle = 6\Gamma k_B T \delta(t - t')\delta_{ij}$

2.6 Solvent Quality

The size of a polymer in solution depends strongly on the solvent quality. In a *good* solvent the polymer tends be expand (due to the excluded volume interaction) whilst in a *bad* solvent the polymer shrinks into a compact structure. The effect of solvent quality may be easily described by the simple model below [4].

We consider a lattice of coordination number z whose sites are occupied either with monomers or with solvent molecules of volume v_0. A schematic is drawn in Fig. 3. The interaction energy between monomers is given by $-\epsilon_{pp}$, monomer and solvent $-\epsilon_{ps}$, and solvent molecules $-\epsilon_{ss}$ where since they are due to Van der Waals type interactions $\epsilon_{ij} \propto \alpha_i \alpha_j > 0$ where α_i is the electrical polarizability of species j.

The number of neighbouring monomer pairs $N_{pp}^{(i)}$, solvent pairs $N_{ss}^{(i)}$, monomer-solvent pairs $N_{ps}^{(i)}$ respectively. From this we calculate the total interaction energy $E_i = -N_{pp}^{(i)}\epsilon_{pp} - N_{ss}^{(i)}\epsilon_{ss} - N_{ps}^{(i)}\epsilon_{ps}$. We can define the volume fraction $\phi = N v_0 / R_g^d$ which is the probability lattice site is occupied.

The average number of pairs is given by $\langle N_{pp}^{(i)} \rangle \simeq zN\phi/2$, $\langle N_{ps}^{(i)} \rangle \simeq zN(1-\phi)$ $\langle N_{ss}^{(i)} \rangle \simeq N_{ss}^{(0)} - zN\phi/2 - zN(1-\phi)$ and (*at a mean field level* where we have *ignored* the interconnectivity of the chain) hence the average interaction energy

$$\langle E_i \rangle \simeq -\frac{z v_0 N^2}{R_g^d} \Delta\epsilon \, ; \qquad \Delta\epsilon = \frac{1}{2}(\epsilon_{pp} + \epsilon_{ss}) - \epsilon_{ps} \, . \tag{18}$$

The free energy is given by

$$F = v_0(1 - 2\chi)\ N \left(\frac{N}{R_g^d} \right) + \frac{3k_B T}{2b^2 N}(R_g^2) \tag{19}$$

with the χ parameter defined by

$$\chi = \frac{z\Delta\epsilon}{k_B T} \tag{20}$$

By comparison to the free energy in eqn. (13) we can then identify a temperature, Θ for which the chains are ideal, i.e. behave like Gaussian chains given by $\Theta = \frac{2z\Delta\epsilon}{k_B}$. For $T > \Theta$ the chain is swollen or extended (coil) and is referred to as being in a ***good solvent*** whilst for $T < \Theta$ the chain is compact (globule) and is said to be in a ***bad solvent***. At $T = \Theta$ it is evidently in an ***ideal solvent***.

2.7 Renormalization group calculations

In the scaling theories above we used the ν exponent of the excluded volume chain to calculate the scaling behaviour of a host of physical quantities. Whilst the Flory exponent is a good approximation to the behaviour it is incorrect. A much better approximation to the exponent can be calculated using renormalization group techniques at the expense of *slightly* more involved calculations.

2.7.1 The Edwards model

The continuum model of neutral polymers in a good solvent was introduced by Edwards [14] and is the starting point of modern polymer theory with a partition function

$$Z = \mathrm{Tr}_{\mathbf{R}} e^{-\beta H_E[\mathbf{R}]} = \int [\mathcal{D}\mathbf{R}] \exp[-\beta H_E[\mathbf{R}(s)]] \tag{21}$$

where

$$\beta H_E[\mathbf{R}(s)] = \frac{3}{2b^2}\int_0^N \mathrm{d}s\, |\partial_s \mathbf{R}|^2 + v_0 \int_0^N \mathrm{d}s' \int_0^N \mathrm{d}s\, \delta^d[\mathbf{R}(s) - \mathbf{R}(s')] \tag{22}$$

The short range repulsion between all the monomers is described by a δ-function potential. We can rescale the size all the monomers by a factor $1/\lambda$ so that $s \to \lambda s$; $\mathbf{R}(s) \to \lambda^\nu \mathbf{R}(s)$; $\delta^d[\mathbf{R}(s) - \mathbf{R}(s')] \to \lambda^{-\nu d}\delta^d[\mathbf{R}(s) - \mathbf{R}(s')]$. If the chain is Gaussian($\nu = 1/2$) then we find that the short range interaction becomes 'relevant' (i.e. scales with at least the same power of λ as the Gaussian part) for dimensions $d \leq 4$. We can also recover the Flory theory by demanding that both terms grow under rescaling in the same way.

2.7.2 Mapping to spin model

De Gennes pointed out that the critical properties of a spin model described also the scaling behaviour of long chains [15]. The Laplace transform $G^{(2)}(\mathbf{R},t) = \int_0^\infty \mathrm{d}N \exp[-tN] P^{(2)}(\mathbf{R},N)$ of the two point distribution function $P^{(2)}(\mathbf{R},N) \equiv \langle \delta^d[\mathbf{R} - (\mathbf{R}(N) - \mathbf{R}(0))] \rangle$ is equal to the correlation function of a $n = 0$ component spin model

$$\tilde{G}^{(2)}(\mathbf{R},\tau) = \langle S_1(\mathbf{R}) S_1(\mathbf{0}) \rangle = \int [\mathcal{D}\mathbf{S}] e^{-h[\mathbf{S}]} S_1(\mathbf{R}) S_1(\mathbf{0}) \tag{23}$$

where

$$h[\mathbf{S}] = \frac{1}{2} \int d^d r \left[|\nabla \mathbf{S}|^2 + \tau \mathbf{S}^2 + u \left| \mathbf{S}^2 \right|^2 \right] , \tag{24}$$

where $\mathbf{S}$ is a $n = 0$ component field. The scaling properties of the correlation function can be calculated (near $\tau = \tau_c$ the correlation length of the spin model diverges like $\xi \sim |\tau - \tau_c|^\nu$) and

$$\langle R^2 \rangle = \left. \frac{dP^{(2)}(\mathbf{k},N)}{dk^2} \right|_{k=0} \sim b^2 N^{2\nu} , \tag{25}$$

where $P^{(2)}(\mathbf{k},N) = \int \mathrm{d}^d r e^{i\mathbf{k}\cdot\mathbf{R}} P^{(2)}(\mathbf{R},N)$. The exponents are calculated using standard RG techniques [16] and in $d = 3$, $\nu = 0.588$. Using this value of ν we can calculate better estimates of all the scaling quantities above. The most accurate values of the exponents have been calculated using this method.

2.7.3 Direct RG

This method was pioneered by des Cloizeaux [17] and here one performs directly a perturbation expansion of Eqn. (21) in v_0 which is then reorganised using the RG to obtain the same exponent and scaling behaviour [6, 16].

3 Semiflexible Polymers

If we look at a polymer on intermediate length-scales, the chain structure becomes important. One of the most simple structural properties that affects the macroscopic behaviour of polymer solutions is the rigidity or stiffness of a polymer.

3.1 Worm-like Chain

The simplest model is the worm-like chain (WLC) model of Kratky and Porod [18]. The polymer can be considered locally to behave like a rigid rod [19]. We have a potential energy which places a penalty on any local bending of the polymer. A continuum model can be written for a chain of length L.

$$Z_{wlc} = \sum_{conf} \exp[-\beta H_{wlc}] = \int \mathcal{D}[\mathbf{R}] \exp\{-\beta H_{wlc}[\mathbf{t}(s)]\} \qquad (26)$$

where

$$H_{wlc}[\mathbf{t}(s)] = \frac{\kappa}{2}\int_0^L \mathrm{d}s \left(\frac{\partial \mathbf{t}}{\partial s}\right)^2 ; \qquad \ell_p = \frac{\kappa}{k_B T}, \qquad (27)$$

with $\mathbf{t}(s)$ the unit tangent vector to the chain at point s (see Fig 7).

$$\mathbf{t}(s) = \left(\frac{\partial \mathbf{R}}{\partial s}\right) ; \qquad |\mathbf{t}(s)|^2 = 1 . \qquad (28)$$

Note that from the Frenet-Seret formulae [20], $|\partial_s \mathbf{t}|^2 = \mathcal{K}^2$ where $\mathcal{K}(s)$ is the 'curvature' of the chain at point s. The potential uses the simplest quadratic form (by symmetry it must be at least quadratic) that places a penalty on bending.

We can write a restricted 2-point probability distribution function of the polymer having a tangent $\mathbf{T}$ at $s = L$ given a tangent vector $\mathbf{T}_0$ at $s = 0$,

$$P[\mathbf{T}, L; \mathbf{T}_0, 0] = \int [\mathcal{D}\mathbf{t}]_{\mathbf{t}^2=1} \delta(\mathbf{T} - \mathbf{t}(L)) \delta(\mathbf{T}_0 - \mathbf{t}(0)) \exp[-\beta H_{wlc}] , \qquad (29)$$

and w.l.g. we can set $\mathbf{T_0} = (0, 0, 1)$. This corresponds to diffusion on a sphere (or Quantum Mechanics of a spinning sphere) $\mathbf{t}(s) = (\sin\theta(s)\cos\phi(s), \sin\theta(s)\sin\phi(s), \cos\phi(s))$

$$\frac{\partial P}{\partial s} = \frac{1}{2\ell_p} \nabla^2_{\hat{\mathbf{t}}} P , \qquad (30)$$

where $\nabla_{\hat{\mathbf{t}}}$ is the gradient operator on a sphere. We can write the solution in terms of Spherical harmonics

$$P(\theta, \phi, s) = \sum_{n,m} Y_{nm}(\theta, \phi) Y_{nm}(0, 0) \exp\left[-\frac{n(n+1)s}{2\ell_p}\right] . \qquad (31)$$

This gives a tangent correlation function

$$\langle \mathbf{t}(s).\mathbf{t}(s')\rangle = \exp\{-s/\ell_p\} \tag{32}$$

and consequently the mean square end-to-end distance $\mathbf{R} = \mathbf{R}(L) - \mathbf{R}(0)$

$$\langle R^2\rangle = \int_0^L ds \int_0^L ds' \langle \mathbf{t}(s).\mathbf{t}(s')\rangle = \frac{\ell_p^2}{2} \left(\exp[-2L/\ell_p] - 1 + 2L/\ell_p\right) \tag{33}$$

interpolates (illustrated in Fig 8) between a rod $\langle R^2\rangle \sim L^2$ and a 'flexible coil' (RW) $\langle R^2\rangle \sim \ell_p L$ with ℓ_p taking the role of 'monomer size' in Sec 2. We can identify ℓ_p as the persistence length, which is the length-scale over which the WLC is rod-like (i.e. retains memory of it's orientation).

3.2 Semi-dilute/Concentrated solutions

We are often interested in systems with many interacting polymers rather than a single isolated chain. A useful concept is that of the *overlap concentration* c_* (see Fig. 4) which is the concentration at which the chains begin to interact with one another. It can be defined

$$\frac{c^* R_g^d}{N} \sim 1 \Rightarrow c^* \sim b^{-d} N^{1-d\nu} \tag{34}$$

Using the Flory exponent we obtain $c^* \sim N^{-4/5}$ so we find that long chain polymers $N \to \infty$ are almost always interacting and can hardly ever be considered isolated. One of the quantities most calculated is the osmotic pressure of a polymer solution.

To study the behaviour of concentrated solutions of polymers the mean-field model of Flory and Huggins is used [3, 2, 4]. The derivation of the Flory-Huggins free energy is only sketched below but may be found in detail several standard texts [2, 4].

3.2.1 Lattice Model: Flory-Huggins

We have n_p polymers with N 'monomers' on a lattice of coordination number z (see Fig 3). $\Omega \equiv$ total number of lattice sites, and hence the number of solvent sites $n_s = \Omega - n_p N$. We define a volume fraction $\phi = n_p N/\Omega$.

The partition function is given by $Z = \sum_{conf} \exp\left[-\beta E_{conf}\right]$ Assuming small density fluctuations, we can replace E_{conf} by its average $\langle E_{conf}\rangle/(\Omega z) \simeq -\frac{1}{2}\phi^2\epsilon_{pp} + \phi(1-\phi)\epsilon_{ps} + \frac{1}{2}(1-\phi)^2\epsilon_{ss}$

The mean field approximation *ignores* the connectivity of the chain and considers a smeared out uniform chain density. The partition function is then approximated by $Z \simeq W \exp[-\beta\langle E_{conf}\rangle]$ where W is the number of ways of arranging n_p chains. $W = \frac{1}{n_p!}\prod_{j=1}^{n_p} w_j$, and w_i is the number of ways of arranging the ith chain, The first chain can be placed $w_1 = \Omega z(z-1)^{N-2}$ ways and subsequently the $j+1$-th chain $w_{j+1} \simeq (\Omega - Nj)\left[(z-1)\left(1 - Nj/\Omega\right)\right]^{N-1} \simeq \Omega(z-1)^{N-1}\left(1 - \frac{Nj}{\Omega}\right)^N$ ways. The free energy is given by $F(\Omega,\phi) = -k_B T \ln W + \langle E_{conf}\rangle$ and we use the fact that $\ln W = \sum_{j=1}^{n_p} \ln(w_j/j) \simeq \int_0^{n_p} dj\,(\ln w_j - \ln j)$

The free energy of mixing F_m is calculated from the free energy F by subtracting the part that is due to just polymer or just solvent i.e., $F_m(\Omega,\phi) = F(\Omega,\phi) - F(\Omega\phi, 1) - F(\Omega(1-\phi), 0)$ giving the ***Flory-Huggins*** free energy [3, 2, 4] of mixing per site $f_m = \beta F_m/\Omega$

$$f_m(\phi) \simeq \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \tag{35}$$

3.2.2 Osmotic pressure

The Gibbs free energy is given by $G(n_p, n_s, p, T) = F + pV = F + pv_0(n_p N + n_s)$ from which we can calculate the solvent chemical potential which is the change in the Gibbs free energy upon adding one solvent molecule to the system $\mu_s(\phi, p.T) \equiv G(n_p, n_s+1, p, T) - G(n_p, n_s, p, T)$ Using the expressions for F, n_p, n_s we find $\mu_s(\phi,p,T) = \left(\frac{\partial F}{\partial \Omega}\right)_{\phi,T}\left(\frac{\partial \Omega}{\partial n_s}\right)_{n_p} + \left(\frac{\partial F}{\partial \phi}\right)_{\Omega,T}\left(\frac{\partial \phi}{\partial n_s}\right)_{n_p} + pv_0$ and hence the osmotic pressure Π which is defined as the pressure required to keep the chemical potential constant (i.e. equilibrium) across a semipermeable membrane, $\mu_s(\phi, p+\Pi, T) = \mu_s(0, p, T)$ giving

$$\Pi = \frac{k_B T}{v_0}\left(\phi\frac{\partial f_m}{\partial \phi} - f_m\right) \tag{36}$$

Using eqns. (35,36) and making an expansion for ϕ small we obtain

$$\Pi = \frac{k_B T}{v_0}\left[\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \frac{\phi^3}{3} + \ldots\right] \tag{37}$$

showing big deviations from 'ideal gas' (Van't-Hoff's law) behaviour even for low concentrations. VH is only true for very small volume fractions $\phi << \frac{1}{(1/2-\chi)N}$. This deviation had long puzzled polymer scientists but it is now accepted that the mean-field model above captures the essential physics. We see that at the Θ-temperature the second virial coefficient of the osmotic pressure vanishes. This is often used in experiments to determine the Θ-temperature.

3.3 Scaling Theories

3.3.1 Osmotic pressure

The mean-field approach above explains qualitatively the big deviations from Van't Hoff's law at even very low monomer concentrations but experiments show deviation from the mean field behaviour in semi-dilute solutions, $\Pi(c) \sim c^{\alpha}$; $\alpha > 2$ showing that fluctuations and the chain connectivity which were ignored in the mean field approach are important. A dimensional argument due to des Cloizeaux [12] gives $\Pi(c, N) = ck_B T f(cb^3, N)$. Using c^* as a scaling variable we find $\Pi(c, N) = ck_B T f(\frac{c}{c^*})$ where $\lim_{x\to 0} f(x) = 1+x+\dots$ Now Π is independent of N for $c >> c^*$ as many short chains entangled will have the same behaviour as one long chain as long as the monomer density is the same.

$$\lim_{c\to\infty} f \sim \left(\frac{c}{c^*}\right)^{1/(d\nu-1)} \tag{38}$$

with the Flory exponent $\nu_F(d = 3) = 3/5$ one obtains $\Pi \sim c^{9/4}$

3.3.2 Screening length (Mesh Size)

In concentrated solutions excluded volume does not swell the chain because there is no free energy gain in being swollen because of all the other chains around. In short the other chains ***screen*** or reduce the self-repulsion of the chain. We can define a *screening length* above which the excluded volume interaction does not have an effect. The screening length of the concentrated solution (or mesh size) will be of the order of the mean separation of the chains (see Fig 5) and can be estimated using a scaling argument [2].

The correlation length ξ is given by $\xi = R_g g\left(\frac{c}{c^*}\right)$ where $R_g \sim N^\nu b$. As above it must be independent of chain length for $c > c^*$

$$\xi \sim R_g \left(\frac{c}{c^*}\right)^{-\nu/(d\nu-1)} \tag{39}$$

Using the flory exponent $\xi_F \sim c^{-3/4}$. It is interesting to see that the osmotic pressure is then given by

$$\Pi \simeq \frac{k_B T}{\xi^3} \tag{40}$$

3.3.3 Blobs

The idea of the ***blob*** introduced by Pincus [13] is a very useful concept for understanding the physics of polymer solutions (see Fig. 6). The polymer chain is in an expanded coil (excluded volume or good solvent statistics) until it interacts with other chains after which the excluded volume interaction becomes screened. The blob is the unit of chain which is swollen. We define $g \equiv$ number of monomers per blob and $\xi \equiv$ blob size. The blob size is given by

$$\xi \simeq b g^\nu \Rightarrow g \simeq (\xi/b)^{1/\nu} \tag{41}$$

The polymer makes a random walk of N/g blobs of size ξ

$$R_g^2 \simeq \frac{N}{g}\xi^2 \sim N b^2 c^{(1-2\nu)/(d\nu-1)} \tag{42}$$

Using the Flory value for ν in $d = 3$ we obtain $R_g \sim b^{5/4} N^{1/2} c^{-1/8}$.

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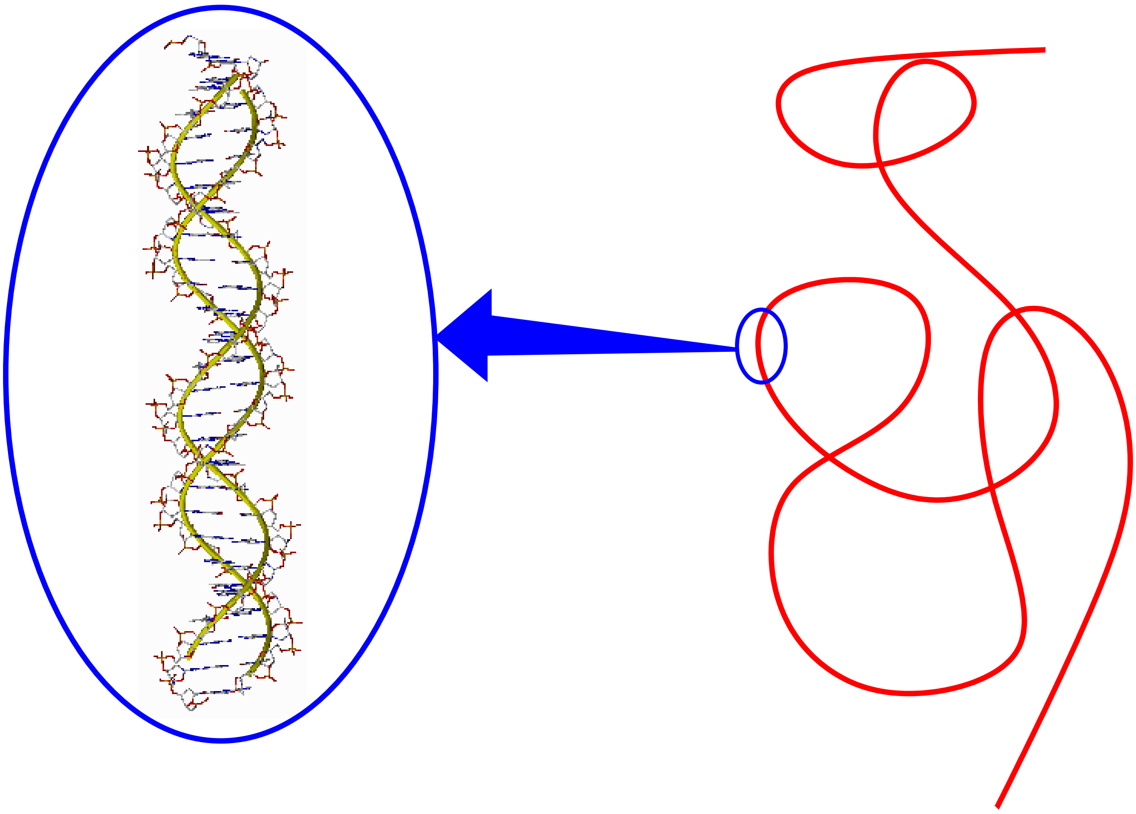

Figure 1: DNA on microscopic and on a macroscopic scale. An example of a coarse-grained polymer as a random coil

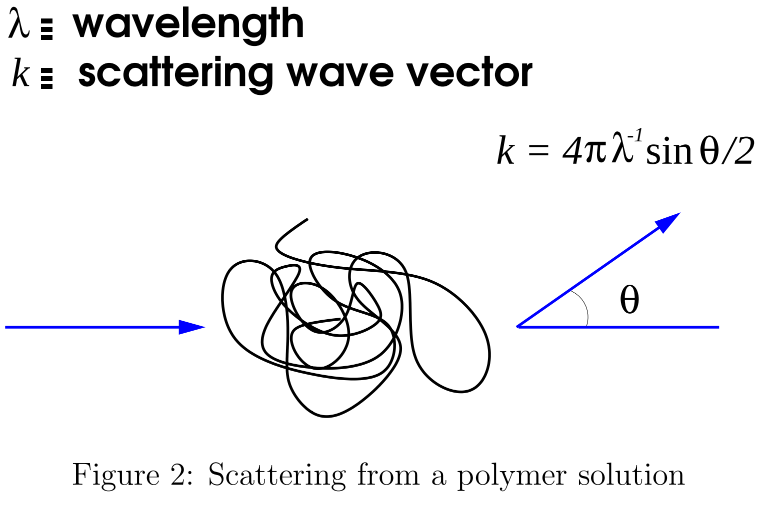

Figure 2: Scattering from a polymer solution

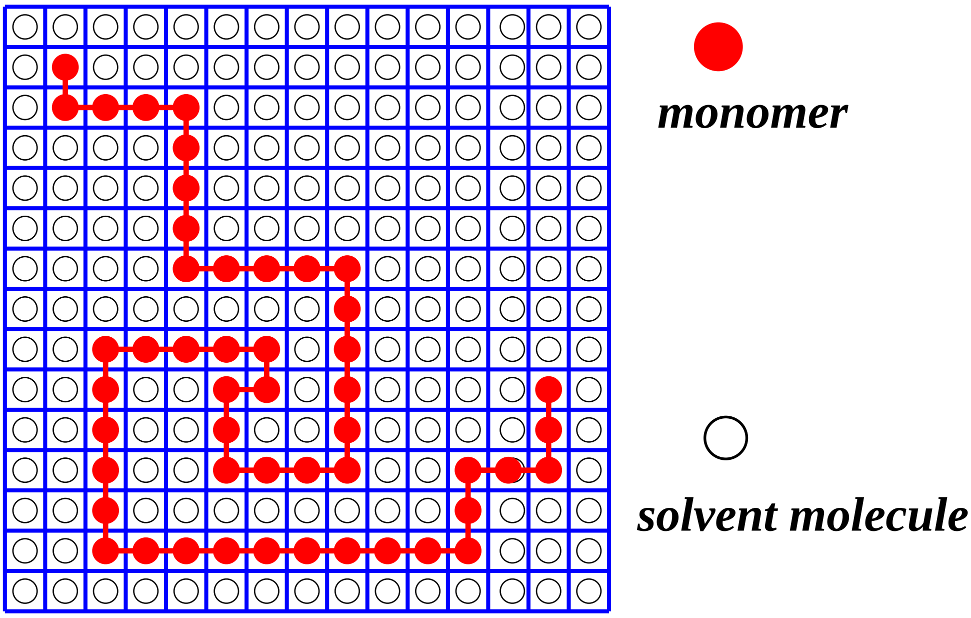

Figure 3: The solvent-monomer lattice model.

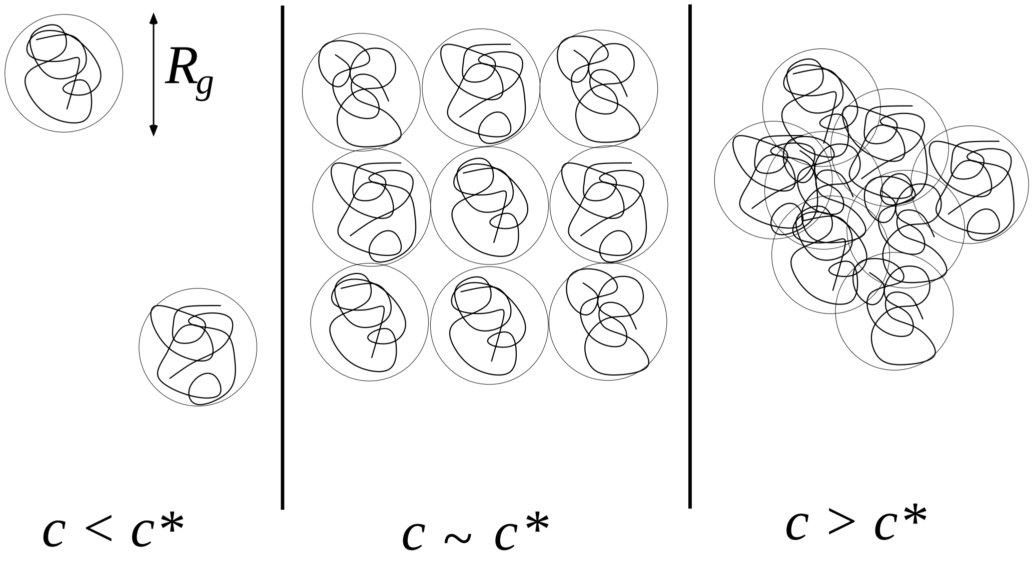

Figure 4: The overlap concentration c^*

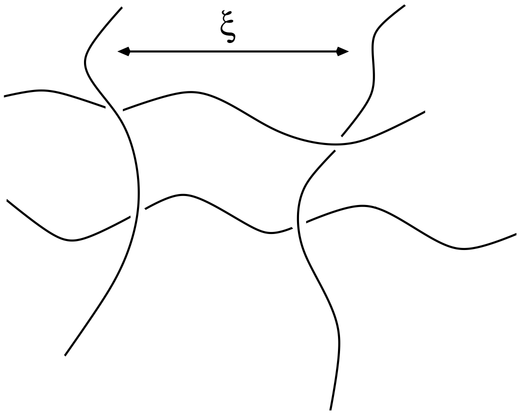

Figure 5: The mesh size or screening length of polymer solution. We show just the mean path of the polymers whose conformations will be much more convoluted paths around their mean.

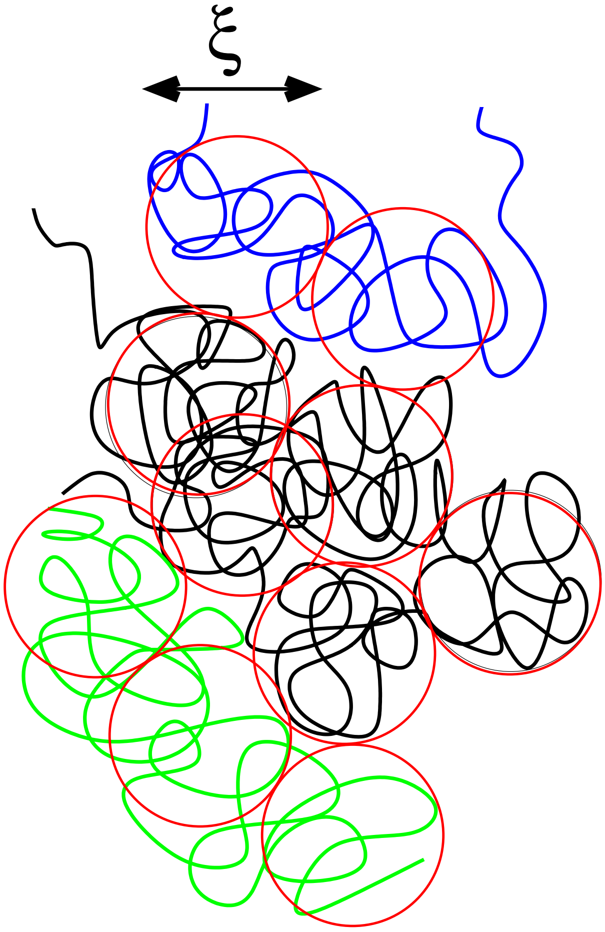

Figure 6: The blobs of a semi-dilute solution of polymers

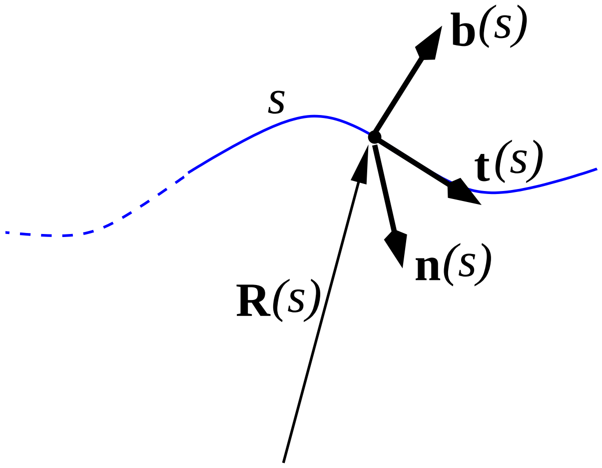

Figure 7: The orthonormal trihedron of vectors describing the rod-like chain. For the worm-like chain we keep track of only the tangent vector $\mathbf{t}(s)$

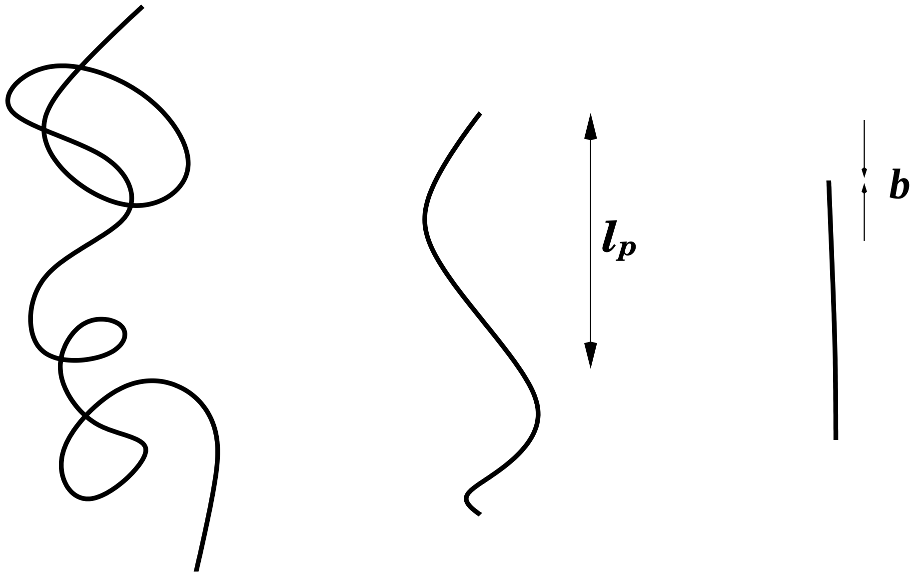

Figure 8: The ratio of L to ℓ_p.

flexible	semiflexible	Rigid
$L >> \ell_p >> b$	$L \sim \ell_p >> b$	$\ell_p >> L >> b$.