



**- A REVIEW**

## **CONTINUUM FORMULATION FOR POLYMERS IN SOLUTION**

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### **ABSTRACT**

The Edwards equation for polymers in solution is rigorously derived (based on the work of Freed<sup>1</sup>) in this review. Then it is shown, how researchers have adapted this equation for describing polymers at surfaces. A brief comment on the validity of the random flight model, which forms the basis for the Edwards equation, is made.

**Key words:** Random flight model, Edwards equation, Polymer-polymer interactions, Continuum formulation.

### **Derivation of Edwards diffusion equation**

Consider a very dilute polymer solution. The system then consists of a polymer chain in an infinite medium and one can consider the configurational statistics of this single polymer chain. For this system, the following different interactions must be considered:

- (i) The polymer solvent interaction.
- (ii) Osmotic forces, which tend to make the polymer, have uniform concentration throughout the medium.
- (iii) Polymer-polymer interactions:
  - (a) Short-range interactions between neighboring or nearby monomers along a chain, also called “steric interactions”.

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- (b) Long-range interactions between monomers, which are far removed from each other along the chain. These are also referred to as “excluded volume” interactions.

There are numerous models of varying levels of complexity for polymers in infinitely dilute solutions. The simplest model, the random flight chain, considers the polymer to be composed of segments, which are joined by bonds of fixed length.

Consider a freely jointed chain composed of  $n + 1$  elements (the monomers), which are joined successively<sup>1</sup>. They are numbered  $0, 1, 2, \dots, n$ , from one end of the chain to another. The coordinates  $\{r_k\}$  represent the positions of the elements, with respect to the origin denoted by  $r_0 = 0$ .

The potential energy of a freely jointed chain in general is written as –

$$U(\{r_k\}) = \sum_{j=1}^n u_j(r_{j-1}, r_j) + W(\{r_k\}) \quad \dots(1)$$

where the first term accounts for the chain connectivity and the second term encompasses all other interactions.

This can be further written as:

$$U(\{r_k\}) = \sum_{j=1}^n u_j(r_{j-1} - r_j) + W(\{r_k\}) \quad \dots(2)$$

$$= \sum_{j=1}^n u_j(R_j) + W(\{r_k\}) \quad \dots(3)$$

where  $R_j = r_j - r_{j-1}$ .

All the statistical properties of the chain are contained in the distribution:

$$G(\{r_k\}) = \exp[-\beta U(\{r_k\})] \quad \dots(4)$$

$$= \exp\left[-\beta \sum_{j=1}^n u_j(R_j)\right] \cdot \exp[-\beta W(\{R_k\})] \quad \dots(5)$$

$$= \prod_{j=1}^n \tau_j(R_j) \cdot \exp[-\beta W(\{R_k\})] \quad \dots(6)$$

where  $\tau_j(\mathbf{R}_j) = \exp[-\beta u_j(\mathbf{R}_j)]$  are the bond probabilities.

Considering the case, where all bonds are the same:

$$\tau_j(\mathbf{R}_j) = \tau(\mathbf{R}_j) \quad \dots(7)$$

$$\therefore G(\{\mathbf{r}_k\}) = \left[ \prod_{j=1}^n \tau(\mathbf{R}_j) \right] \cdot \exp[-\beta W(\{\mathbf{R}_k\})] \quad \dots(8)$$

For a chain with  $n$  Gaussian links with average segment length  $\Delta s$  and contour length  $L$ , the bond probabilities are:

$$\tau(\mathbf{R}_j) = \tau(\mathbf{r}_j - \mathbf{r}_{j-1}) = \left( \frac{3}{2\pi\ell\Delta s} \right)^{3/2} \exp\left( -\frac{3\mathbf{R}_j^2}{2\ell\Delta s} \right) \quad \dots(9)$$

where  $n\Delta s = L$  and  $\ell = \langle \mathbf{R}^2 \rangle / L$ .

$$\therefore G(\{\mathbf{r}_k\}) = \left[ \prod_{j=1}^n \left( \frac{3}{2\pi\ell\Delta s} \right)^{3/2} \exp\left( -\frac{3\mathbf{R}_j^2}{2\ell\Delta s} \right) \right] \exp[-\beta W(\{\mathbf{R}_k\})] \quad \dots(10)$$

Now the partition function is:

$$Z = \int d\{\mathbf{r}_k\} \exp[-\beta U(\{\mathbf{r}_k\})] \quad \dots(11)$$

$$= \int d\{\mathbf{r}_k\} G(\{\mathbf{r}_k\}) \quad \dots(12)$$

and the distribution for the entire chain configuration is –

$$P(\{\mathbf{r}_k\}) = Z^{-1} G(\{\mathbf{r}_k\}) \quad \dots(13)$$

Using the following normalization for  $\tau(\mathbf{R}_j)$ :

$$\int d(\mathbf{R}_j) \tau(\mathbf{R}_j) = 1 \quad \dots(14)$$

and setting  $W = 0$  in Equation (10), leads to the probability distribution function  $P(\{r_k\})$  for the entire chain configuration:

$$\therefore P(\{r_k\}) = \prod_{j=1}^n \left\{ \left( \frac{3}{2\pi\ell\Delta s} \right)^{3/2} \exp \left( -\frac{3(r_j - r_{j-1})^2}{2\ell\Delta s} \right) \right\} \quad \dots(15)$$

$$= \aleph \exp \left[ -\sum_{j=1}^n \frac{3(r_j - r_{j-1})^2}{2\ell\Delta s} \right] \quad \dots(16)$$

where  $\aleph = \left( \frac{3}{2\pi\ell\Delta s} \right)^{3n/2}$  is the normalization factor and is fixed by the condition that  $P(\{r_k\})$  satisfy:

$$\int d\{r_k\} P(\{r_k\}) = 1 \quad \dots(17)$$

Now comes a crucial part. Since Equation (16) gives the “probability” of a particular chain configuration  $r_0 = 0, r_1, \dots, r_n$ , it is clear that this chain configuration  $\{r_k\}$  can be taken to be the discrete representation of the continuous curve  $r(s)$ .

Let  $r_j = r(j\Delta s) = r(s_j)$  denote the position of the ‘j’th segment with respect to the origin ( $s_0 = 0$ ) which, without loss of generality, is taken as  $r_0 = 0$ . One can now take the limit  $\Delta s \rightarrow 0, n \rightarrow \infty, n\Delta s = L$  to obtain a representation of a continuous equivalent random flight chain.

$$\begin{aligned} \therefore \lim_{\substack{\Delta s \rightarrow 0 \\ n \rightarrow \infty \\ n\Delta s = L}} \sum_{j=1}^n \left[ \frac{r(s_j) - r(s_j - \Delta s)}{\Delta s} \right]^2 \Delta s \\ = \lim_{\substack{\Delta s \rightarrow 0 \\ n \rightarrow \infty \\ n\Delta s = L}} \sum_{j=1}^n \left[ \frac{\partial r(s)}{\partial s} \Big|_{s=s_j} \right]^2 \Delta s \\ = \int_0^L ds \left[ \frac{\partial r(s)}{\partial s} \right]^2 = \int_0^L ds [\dot{r}(s)]^2 \end{aligned}$$

Thus, in this limit, the probability  $P(\{r_k\})$  becomes:

$$P(\{r_k\}) \prod_{j=1}^n dr_j \rightarrow P[r(s)] \delta r(s) \quad \dots(18)$$

and  $P[r(s)] \delta r(s)$  is the probability that the chain configuration lies between the continuous space curves  $r(s)$  and  $r(s) + \delta r(s)$ .

One need not worry about the fact that

$$\lim_{\substack{\Delta s \rightarrow 0 \\ n \rightarrow \infty}} \mathfrak{N} \rightarrow (\infty)^\infty$$

because the normalization can be subsumed into a single differential for curve  $r(s)$ ,

$$\mathfrak{N} \delta r(s) = D[r(s)]$$

Thus, finally

$$P[r(s)] \delta r(s) = D[r(s)] \exp \left[ -\frac{3}{2\ell} \int_0^L [r'(s)]^2 ds \right] \quad \dots(19)$$

gives the probability of the chain configuration  $r(s)$  and is the well-known Wiener measure.

Equation (10) suggests that the distribution function for the discrete chain is:

$$G(\{r_k\}) d\{r_k\} = \mathfrak{N} d\{r_k\} \exp \left[ -\frac{3}{2\ell\Delta s} \sum_{j=1}^n (r_j - r_{j-1})^2 - \beta\Delta s \sum_{j=1}^n W\left(\frac{r_j + r_{j-1}}{2}\right) \right] \quad \dots(20)$$

Letting  $\tilde{u} = \beta W$ , in the limit of a continuous chain, one obtains

$$\beta \sum_{j=1}^n W\left(\frac{r_j + r_{j+1}}{2}\right) \Delta s \rightarrow \int_0^L ds \tilde{u}[r(s)]$$

so that

$$G[r(s)] \delta r(s) = D[r(s)] \exp \left( - \int_0^L ds \left\{ \frac{3}{2\ell} \dot{r}^2(s) + \tilde{u}[r(s)] \right\} \right) \quad \dots(21)$$

Denote  $G(R, R'; L)$  as the distribution of those chains that have  $r_0 = R'$  and  $r_n = R$ .

Then:

$$\begin{aligned} G(R, R'; L) &= \int \delta r(s) \int dr_0 \delta[r(0) - R'] \delta[r(L) - R] G[r(s)] \\ &= \int_{r(0)=R'}^{r(L)=R} D[r(s)] \exp \left\{ - \int_0^L ds \left( \frac{3}{2L} \dot{r}^2(s) + \tilde{u}[r(s)] \right) \right\} \quad \dots(22) \end{aligned}$$

It can be shown<sup>2</sup> that  $G(R, R'; L)$  satisfies the following diffusion equation for a particle in the external potential  $\tilde{u}(R)$ :

$$\left[ \frac{\partial}{\partial L} - \frac{\ell}{6} \nabla_R^2 + \tilde{u}(R) \right] G(R, R'; L) = 0 \text{ for } L \neq 0 \quad \dots(23)$$

subject to the boundary condition that

$$\lim_{L \rightarrow 0} G(R, R'; L) = \delta(R - R') \quad \dots(24)$$

It is worth noting that the analogy of the random flight model to the trajectory of a quantum mechanical particle starts here. Equation (23) is strongly reminiscent of the Schrodinger equation. The proof that Equation (22) is equivalent to Equation (23) involves the path integral formulation used by Feynman to show that the Hamiltonian version of non-relativistic quantum mechanics is equivalent to the Lagrangian version. More on this analogy is given by Feynman and Hibbs<sup>2</sup>.

### Formulation of W

As seen previously, W takes into account all the interactions other than chain connectivity. As mentioned earlier, for a single chain in solution, the following different interactions (or forces) must be considered: polymer-solvent interactions, osmotic interaction and polymer-polymer (short-range and long-range) interactions.

Only the long-range polymer-polymer interactions (excluded volume) was considered in Edwards' work<sup>3</sup>. Consider a polymer chain with 'n' equivalent links, with some short-range repulsive interaction:

$$W_{ij} = W(r_i - r_j) \quad \dots(25)$$

$$W(\{r_k\}) = \frac{1}{2} \sum_{i \neq j} W(r_i - r_j) \quad \dots(26)$$

This leads to:

$$G(\{r_k\}) = \left[ \prod_{j=1}^n \left( \frac{3}{2\pi\ell\Delta s} \right)^{3/2} \exp\left(-\frac{3(r_j - r_{j-1})^2}{2\ell\Delta s_j}\right) \right] \exp\left[-\frac{\beta}{2} \sum_{i \neq j} W(r_i - r_j)\right] \quad \dots(27)$$

Putting  $\tilde{u}_{ij} = (1 - \delta_{ij}) \left( \frac{\beta}{\ell^2} \right) W_{ij}$ , it can be shown that<sup>1</sup>, upon passage to the continuum

limit, one obtains:

$$G(R0; L0) = \int_{r(0)=0}^{r(L)=R} D[r(s)] \exp\left\{-\frac{3}{2L} \int_0^L ds r^2(s) - \frac{1}{2} \int_0^L ds \int_0^L ds' \tilde{u}[r(s) - r(s')]\right\} \quad \dots(28)$$

In an appendix, Freed<sup>1</sup> showed that this can be equivalently represented as a hierarchy of equations. The hierarchy begins with:

$$\left[ \frac{\partial}{\partial L} - \frac{\ell}{6} \nabla_R^2 \right] G(R0; L0) + \int dR' \tilde{u}(R - R') \int_0^L ds G_3 = \delta(R) \delta(L) \quad \dots(29)$$

where  $G_3$  is a "three-point Green's function" and has an analogous equation for  $G_3$  in terms of a four-point  $G_4$  etc. Note that for a continuous chain, the hierarchy never terminates.

The self-consistent field (SCF) approximation of Edwards, deals away with this hierarchy. Instead of dealing with a  $G$ , which depends on  $G_3$ , which in turn depends on  $G_4$  and so forth, the SCF approximation states that we deal with a  $G_{SCF}$  that obeys the diffusion equation:

$$\left[ \frac{\partial}{\partial s} - \frac{\ell}{6} \nabla_R^2 + \tilde{u}_{SCF}(R' [RL]) \right] G_{SCF}(R'R''; ss' [RL]) = \delta(R' - R'') \delta(s - s') \quad \dots(30)$$

where  $\tilde{u}_{SCF}$  is some functional of  $G_{SCF}$  and is called a self-consistent field. The notion of self-consistency was also introduced by Edwards. Since  $\tilde{u}_{SCF} = \tilde{u}_{SCF}(G_{SCF})$ , one can follow the Hartree procedure, where the form of  $G_{SCF}$  is assumed, the pde solved to get a more accurate form of  $G_{SCF}$  and the procedure repeated.

### The Hong and Noolandi<sup>4</sup> approach

As mentioned before, Edwards<sup>3</sup> considered only intramolecular potentials so that:

$$W(\{r_k\}) = \frac{1}{2} \sum_{i \neq j} W(r_i - r_j)$$

Hong and Noolandi<sup>4</sup> consider a general *intermolecular potential* so that:

$$\begin{aligned} \hat{W}(\{r_{si}\} \{r_{pj}\}) = & \underbrace{\frac{1}{2} \sum_{ss'} W_{ss'}(r_{si} - r_{s'i'})}_{\text{interaction between solvent molecules}} + \underbrace{\sum_{sp} \int_0^L ds W_{sp}[r_{si} - r_{pj}(s)]}_{\text{interaction between solvent and polymer}} \\ & + \underbrace{\frac{1}{2} \sum_{pp'} \int_0^L ds \int_0^{L'} ds' W_{pp'}[r_{pj}(s) - r_{p'j'}(s)]}_{\text{polymer-polymer interactions}} \end{aligned} \quad \dots(31)$$

Using a method similar to that used in Edwards' formal derivation<sup>1</sup>, Hong and Noolandi<sup>4</sup> carefully show that the final SCF equations are of the form:

$$\left[ \frac{\partial}{\partial s} - \frac{\ell}{6} \nabla_r^2 + w_{SCF} \right] G_p(r, s | r_0, 0) = \delta(r - r_0) \delta(s) \quad \dots(32)$$

or in terms of  $t \ell = s$ ,

$$\left[ \frac{\partial}{\partial t} - \frac{\ell}{6} \nabla^2 + w_p \right] G_p(r, t | r_0, 0) = \delta(r - r_0) \delta(t) \quad \dots(33)$$



where  $w_p$  is worked out to be:

$$w_p = \Delta\mu_p - \frac{1}{Z_p} \ln\left(\frac{\rho_p}{\rho_{0p}}\right) - \frac{\rho_{0s}}{\rho_{0p}} \left( \Delta\mu_s + \frac{1}{6} \sum_{k'} V_{sk'} \nabla^2 \rho_{k'} \right) + \frac{1}{6} \sum_{k'} V_{pk'} \nabla^2 \rho_{k'} \quad \dots(34)$$

where the  $\rho_k$  are the microscopic particle densities,  $Z_p = \frac{L}{\ell}$  and  $\Delta\mu_k$  is the deviation of the chemical potential of the component 'k' in an inhomogeneous system.

### The freely jointed chain and adsorption at the interface

The logical next step would be to explore the behaviour of the random flight chain at interfaces or between two confining surfaces. de Gennes<sup>5</sup> was the first to propose a boundary condition for adsorption of a random flight chain at a solid surface. Drawing upon the analogy of the case of a single, flexible chain, weakly bound to the adsorbing surface to the quantum mechanical case of the bound state of the deuteron, he suggested the following boundary condition:

$$\frac{1}{G} \frac{\partial G}{\partial x} \Big|_{x=0} = -k(T)$$

where  $k(T)$  is a phenomenological constant that depends on temperature.

Juvekar et al.<sup>6</sup>, have made three major contributions to the study of polymer adsorption:

- (i) They have introduced a 'surface phase' concept, which leads to the so-called "two-phase continuum model" explored in greater detail in Austine<sup>7</sup>,
- (ii) They have proposed a boundary condition for polymer adsorption; in this they have used the heuristic approach to the Edwards diffusion equation rather than the rigorous one outlined above, and
- (iii) They have proposed a finite-element-method based solution technique to solve the self-consistent random flight equations without invoking any further approximations such as the ground-state approximations<sup>8,9</sup>. Austine<sup>7</sup> has used the "two-phase continuum model" for describing polymer chains confined between two parallel plates, polymers at air-water interface and adsorption of polymer chains with complex architecture.

### Reason for success of the random flight model

It is true that the random flight model incorporates the connectivity that distinguishes a macromolecule from a small molecule. Nonetheless, it completely ignores the precise details such as fixed valency angles and hindered rotation about the bonds. Thus, some authors have asserted that the random flight model is incapable of providing quantitative predictions about the behaviour of real polymer molecules but qualitative features may be explained (as mentioned in Napper<sup>10</sup>). The reason, why the random flight model has proved so popular stems from its simplicity. Casting the problem in a Schrodinger-wave-equation-like formalism allows us to explore analogies with well-studied problems. This is an antidote to a prevailing tendency to apply extremely sophisticated mathematical procedures to really very primitive models for polymer chains<sup>10</sup>. Whether such sophisticated procedures merit any attention cannot yet be assessed objectively. An alternative approach suggested by Napper<sup>10</sup> is to aim for a simpler mathematical description of more complex models of polymer chains.

Evans<sup>11</sup> and Evans and Needham<sup>12</sup> have proposed a departure from the random flight model. As per this heuristic approach, one postulates that the total Helmholtz free energy of a system containing 'n' components ( $k = 1, \dots, n$ ) with volume (surface) fraction  $\phi_k$  ( $\varphi_k$ ) is:

$$\begin{aligned}
 A = V^b \sum_{k=1}^n \frac{\varphi_k^b}{V_k} \mu_k + V^b \zeta^b \left( \sum_k \varphi_k^b - 1 \right) + A_s \int_0^d \left\{ \sum_k \frac{\varphi_k}{V_k} (\mu_k^H - \varepsilon_k) + \zeta \left( \sum_k \varphi_k - 1 \right) \right\} dz \\
 + A_s \sum_k \frac{\varphi_k^*}{a_k} (\mu_k^{*H} - \varepsilon_k^*) + A_s \zeta^* \left( \sum_k \varphi_k^* - 1 \right) \quad \dots(35)
 \end{aligned}$$

The chemical potential of component  $k$  in the interphase,  $\mu_k^H - \varepsilon_k$ , is the sum of a local contribution,  $\mu_k^H$ , evaluated as though the mixture were homogeneous at the local composition, plus a nonlocal contribution,  $-\varepsilon_k$ , arising from the spatial inhomogeneity. It is helpful to view  $-\varepsilon_k$  as an "extra" potential energy field, which maintains the inhomogeneous density distribution of component  $k$ . Note that the equation also incorporates the constraints  $\sum_k \varphi_k^b = 1$ ;  $\sum_k \varphi_k = 1$  and with the assumption of a surface phase at  $z = *$  and the consequent constraint  $\sum_k \varphi_k^* = 1$ .  $\zeta^b$ ,  $\zeta$  and  $\zeta^*$  are Lagrange multipliers.

The equilibrium condition is determined by minimizing the system's free energy, i.e., by taking the variation:

$$\delta A = 0 \quad \dots(36)$$

This allows the evaluation of the nonhomogeneity parameter as –

$$\varepsilon_k = (\mu_k^H - \mu_k^b) - (\mu_s^H - \mu_s^b) \frac{V_k}{V_s} \quad \dots(37)$$

where 's' in the subscript refers to the solvent. Knowing  $\varepsilon_p$ , the SCF potential  $u_p$  can be evaluated as –

$$u_p = \varepsilon_p - \frac{1}{r} \ln \left( \frac{\phi_p}{\phi_p^b} \right) \quad \dots(38)$$

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