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1973 J. Phys. A: Math. Nucl. Gen. 6 L109

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LETTER TO THE EDITOR

**The mean square radius of a polyelectrolyte immersed in a 1 : 1 electrolyte**

P Richmond†

Unilever Research, Port Sunlight, Wirral, Cheshire L62 4XN, UK

Received 30 May 1973

**Abstract.** Methods introduced by Edwards and de Gennes for the study of polymer configurations with excluded volume are applied to the case of a uniformly charged polyelectrolyte immersed in a 1:1 strong electrolyte of density  $n_0$ . The electrolyte is treated using the Debye-Hückel approximation and the following expression is obtained for the asymptotic mean square radius:

$$R^2 = \left\{ \frac{5}{3} \frac{a}{\kappa^{2/3}} \left( \frac{2\beta q^2}{3a} \right) \right\}^{6/5} N^{6/5}$$

where  $N$  is the number of links in the polyelectrolyte.

It is eight years since Edwards (1965) first showed, using a mean field theory, that the mean square end-to-end distance  $R^2$  of a polymer was proportional to  $N^{6/5}$  where  $N$  is the number of links. The derivation has since been criticized on a number of grounds (see the review by de Gennes 1969) but represents a significant step forward and it does appear from numerical work to be essentially correct (Fisher and Hiley 1961). In 1969 de Gennes showed how the leading term of Edwards result could be derived in a very simple manner. In this note we shall apply the simple procedure of de Gennes to obtain an asymptotic expression for the mean square radius of a polyelectrolyte immersed in a 1:1 strong electrolyte.

Following de Gennes we picture the chain as an ideal collection of beads located at points  $r_1 \dots r_N$ . The length  $a = |r_i - r_{i+1}|$  is fixed. Now it is assumed that by applying an external force field the mean polarization of the  $(n, n+1)$  link is nonzero, that is,  $r_{n+1} - r_n = u_n$ . For small values of  $|u|$  ( $\ll a$ ) the associated decrease in entropy of the link is  $\Delta S_n = -3k u_n^2 / 2a^2$ . Summing over all links, the associated free energy is  $G = (3/2a^2\beta) \sum_n u_n^2$ . Differentiating this expression we can write 'Newton's law' for a bead. Thus the force  $F$  acting on a bead is

$$F(r_n) = -\frac{\partial G}{\partial r_n} = \frac{3}{2a^2\beta} \frac{\partial^2 r}{\partial n^2} \tag{1}$$

where the right-hand side is obtained by taking the continuum limit for the beads. When  $F$  can be derived from a scalar potential  $\psi$ , equation (1) can be integrated to obtain the 'energy integral':

$$\psi(r) - \frac{3}{2a^2\beta} \left( \frac{\partial r}{\partial n} \right)^2 = \text{constant.} \tag{2}$$

† On leave from Department of Applied Mathematics, Institute of Advanced Studies, Australian National University, Canberra, ACT, Australia.

The excluded volume result derived by Edwards can now be obtained by assuming that  $\psi(\mathbf{r}) \propto p(\mathbf{r})$  where  $p(\mathbf{r})$  is the density of monomers at  $\mathbf{r}$ . We shall neglect this excluded volume effect. Instead we suppose that each bead carries a positive charge  $q$ . Thus where  $\phi(\mathbf{r})$  is the electrostatic potential

$$\psi(\mathbf{r}) = q\phi(\mathbf{r}). \quad (3)$$

As we shall see, this potential can act at least as well as the hard core interaction in stretching the polymer. The electrostatic potential we now assume to be determined by Poisson's equation:

$$\nabla^2\phi(\mathbf{r}) = -4\pi\rho(\mathbf{r}) - 4\pi qp(\mathbf{r}), \quad (4)$$

where  $\rho(\mathbf{r})$  is the charge density at  $\mathbf{r}$  of electrolyte in which the polyelectrolyte is immersed. We relate this latter quantity to  $\phi$  using the Boltzmann factor and ignore any specific binding effects of ions with the polymer. Thus

$$\rho(\mathbf{r}) = n_0q(e^{-\beta q\phi} - e^{\beta q\phi}) \simeq -2n_0\beta q\phi(\mathbf{r}), \quad (5)$$

where  $n_0$  is the mean density of positive (or negative) ions in the absence of the polyelectrolyte. Combining equations (4) and (5) we obtain

$$\nabla^2\phi(\mathbf{r}) - \kappa^2\phi(\mathbf{r}) + 4\pi qp(\mathbf{r}) = 0; \quad \kappa^2 = 8\pi n_0\beta q^2. \quad (6)$$

Equations (2), (3) and (6) are now made self-consistent by assuming that the various functions are radially symmetric. Thus in the interval  $r, r + dr$  the average number of monomer units is

$$p(r)4\pi r^2 dr = dn. \quad (7)$$

Assuming that  $p, \phi$  and  $dr/dn$  vanish as  $r \rightarrow \infty$  we obtain from equations (2), (3) and (7)

$$q\phi(r) - \frac{3}{2a^2\beta} \left( \frac{1}{4\pi r^2 p(r)} \right)^2 = 0. \quad (8)$$

We can now eliminate  $p$  from equations (6) and (8) to obtain

$$\nabla^2\phi - \kappa^2\phi + \left( \frac{3}{2a^2q\beta\phi} \right)^{1/2} \frac{q}{r^2} = 0. \quad (9)$$

Making the substitutions  $\phi = y/r$  and  $x = \kappa r$  we obtain the equation

$$\frac{d^2y}{dx^2} - y + \frac{\lambda}{(xy)^{1/2}} = 0$$

where

$$\lambda = \frac{q^{3/2}}{(\kappa a)^{3/2}} \left( \frac{3a}{2\beta q^2} \right)^{1/2}. \quad (10)$$

Despite the obvious nonlinearity of this equation it is possible to obtain asymptotic solutions in the regions  $x \rightarrow 0$  and  $x \rightarrow \infty$ . We consider each region separately.

In the limit  $x \rightarrow 0$  we apply the boundary condition  $\phi \rightarrow q/r$  since a link of the chain is situated at the origin. Thus  $y(0) = q$ . Clearly then in the limit  $x \rightarrow 0$  we can drop the second term on the left-hand side of equation (10) to obtain

$$\frac{d^2y}{dx^2} = \frac{-\lambda}{q^{1/2}\sqrt{x}}. \quad (11)$$

Integrating this equation yields

$$\phi(r) = -\frac{\lambda\kappa^{3/2}}{3q^{1/2}}r^{1/2} + A\kappa + \frac{q_0}{r} \quad (12)$$

where  $A$  is a constant. Obviously this expression is dominated by the unscreened Coulomb potential  $q/r$  due to the link at the origin.

It is amusing to substitute this form for  $\phi(r)$  into equations (8) and (7). We obtain from (8)

$$p(r) = \left(\frac{3}{2a^2q^2\beta}\right)^{1/2} \frac{1}{4\pi r^{3/2}} \quad (13)$$

Substituting equation (13) into equation (7) and integrating we then obtain

$$R^2 = \left\{ \frac{3q}{2} \left( \frac{2\beta a^2}{3} \right)^{1/2} \right\}^{4/3} N^{4/3}. \quad (14)$$

Of course it is not consistent to use a potential valid for small  $r$  to deduce the large  $r$  behaviour of the polymer chain but one might interpret the result as being valid for the inner region of the polymer.

Of more interest is the behaviour of the polymer for large  $r$ . If  $\lambda = 0$  the solution to equation (10) is  $y = e^{-x}$ . Clearly for large  $x$ , this is not a solution when  $\lambda \neq 0$  since the third term, proportional to  $y^{-1/2}$ , then diverges. In any case a solution of this kind leads to a monomer density  $p(r)$  which also diverges as  $r \rightarrow \infty$  (see equation (8)). This essentially rules out any perturbation expansion in  $\lambda$  and indicates the polyelectrolyte has a singular effect on the electrolyte. Now by inspection it can be seen that for  $x^2 \gg 1$ , an asymptotic solution to equation (10) is  $y = (\lambda^2/x)^{1/3}$ . Thus

$$\phi(r) = \frac{\lambda^{2/3}}{\kappa^{1/3}r^{4/3}} = \frac{q}{(\kappa r)^{4/3}a} \left( \frac{3a}{2\beta q^2} \right)^{1/3}. \quad (15)$$

Hence from equation (8) we obtain

$$p(r) = \left( \frac{3a}{2\beta q^2} \right)^{1/3} \frac{\kappa^{2/3}}{4\pi ar^{4/3}}. \quad (16)$$

Finally from equations (2), (3) and (15) we find, after integrating, that

$$R^2 = \left\{ \frac{5}{3} \frac{a}{\kappa^{2/3}} \left( \frac{2\beta q^2}{3a} \right) \right\}^{6/5} N^{6/5}.$$

At first sight it is surprising that the exponent of  $N$  is the same as that obtained for the excluded volume case. However, we recall that the electrolytic solution acts to screen the long range Coulomb force between polymer links so the net effect will be that individual polymer links interact via a short range repulsive potential.

The author is grateful to Professor S F Edwards and V Urumov for checking the analysis.

## References

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