Polymers in solution-an instantonic conformation?

1984 J. Phys. A: Math. Gen. 17 L591

(http://iopscience.iop.org/0305-4470/17/11/006)

J. Phys. A: Math. Gen. 17 (1984) L591–L592. Printed in Great Britain

LETTER TO THE EDITOR

Polymers in solution—an instantonic conformation?

Thomas Vilgis

Abteilung Experimentelle Physik, Universität Ulm, D-7900 Ulm, FRG

Received 18 April 1984

Abstract. The well known power law for the mean square distance of a polymer chain in a good solvent is considered by using the typical behaviour of instantons. It is shown that the mean field and self consistent field exponent coincide with the instanton treatment.

Excluded volume effects of polymers in solution have been well studied by different methods. Mostly they are treated by the renormalisation group method (de Gennes 1972, des Cloizeaux 1975) using a zero component Lagrangian for very long chains. The critical exponent of the correlation length is given by the ε-expansion (Wilson and Kogut 1974). The resulting power law for the mean square distance, which is identical to the correlation length in phase transitions in the long chain limit is given by

$$R^2 \sim L^{2\nu} \tag{1}$$

where $\nu = \frac{1}{2}(1 + \frac{1}{8}\varepsilon)$ considering the two-body interaction only. ε has the usual meaning $4 - d$, where d denotes the space dimensionality. L is the total contour length of the polymer chain.

On the other hand, the excluded volume problem can also be treated by elementary scaling methods. Following Isaacson and Lubensky (1983), one writes for the free energy

$$F = R^2/L + gL^2R^{-d} + wL^3R^{-2d} \tag{2}$$

omitting numerical constants. The last term, connected with three body collisions, will be neglected for good solvents. The first term is related to the entropy elastic situation and the second to the two body interaction. g is the usual coupling constant. Minimising the free energy, $\mathrm{d}F/\mathrm{d}R = 0$, the power law for the mean square distance is given by

$$R^2 \sim L^{2\nu}, \qquad \nu = 3/(2+d), \tag{3}$$

which is the classical Flory result (1949). For $d = 3$, the famous $\nu = \frac{3}{5}$ law appears.

The similar behaviour of the exponent ν is given by the more accurate self consistent field approximation (Edwards 1965). In this approach the problem is treated by the diffusion equation with an external potential

$$\{\partial_L - \tfrac{1}{6}l\nabla^2 + gr^{-4/3}\}G(r, L) = \delta(r)\delta(L). \tag{4}$$

The asymptotic long chain power law is given by

$$R \sim L^{3/5}. \tag{5}$$

(see also Edwards 1975, Edwards and Singh 1979). This result can be recovered very

easily by an instanton configuration. The instanton method is described by Coleman (1979) and Vainshtein *et al* (1982). Considering a quantum particle in an external potential, the Lagrangian is given by

$$\mathscr{L}(\dot{r}, r, t) = \tfrac{1}{2}m\dot{r}^2 - V(r). \tag{6}$$

Performing a Wick rotation, by the analytic continuation of the time, introducing

$$t = -\mathrm{i}L \tag{7}$$

where L is a 'complex time' and here the contour length of the polymer, the Lagrangian becomes

$$\mathscr{L} = -\tfrac{1}{2}m(\mathrm{d}r/\mathrm{d}L)^2 - V(r) \tag{8}$$

leading to the diffusion equation (4). Finite action solutions are obtained by 'steepest descent' for the path integral, and the instanton is characterised by 'equations of motion' under zero energy (Vainshtein *et al* 1982).

$$\tfrac{1}{2}m(\mathrm{d}r/\mathrm{d}L)^2 = V(r). \tag{9}$$

From this equation of motion we are led to

$$L = \left(\frac{2}{m}\right)^{1/2} \int_0^L \mathrm{d}r \frac{1}{[V(r)]^{1/2}} \tag{10}$$

according to classical mechanics, if we perform a coordinate transformation as done by Freed (1972), so that the radial component obeys a quasi one-dimensional problem. The particle mass can be chosen as

$$m = d/l \tag{11}$$

(we call such a particle 'conformon' (Vilgis 1984)). The integration in equation (10) can be done with the self consistent field $v \sim r^{-4/3}$. Thus we obtain the well known power law

$$R \sim L^{3/5}. \tag{12}$$

By the aid of equation (7) the result for the mean diffusion length in the electron localisation problem, as given by Abram and Edwards (1972) remains.

This very easy example shows that the treatment of considering the instanton method in any polymer problem can be fruitful and further application will follow.

References

Abram R and Edwards S F 1972 *J. Phys. C: Solid State Phys.* **5** 1183, 1196
Coleman S 1979 in *The Whys of Subnuclear Physics* ed A Zichichi (New York: Plenum)
de Gennes P G 1972 *Phys. Lett.* **36A** 339
des Cloizeaux J 1975 *J. Physique* **36** 281
Edwards S F 1965 *Proc. Phys. Soc.* **85** 613
—— 1975 *J. Phys. A: Math. Gen.* **8** 1670
Edwards S F and Singh P 1979 *J. Chem. Soc. Faraday Trans.* II **75** 1001
Flory P J 1949 *J. Chem. Phys.* **17** 303
Freed K F 1972 *Adv. Chem. Phys.* **22** 1
Isaacson J and Lubensky T C 1983 *Preprint*
Vainshtein A I, Zakharov V I, Novikov V A and Shifman M A 1982 *Sov. Phys.–Usp.* **25** 195
Vilgis T 1984 *PhD Thesis* Universität Ulm
Wilson K G and Kogut J 1974 *Phys. Rep.* **12C** 77