Mechanical simulation of the diffusion of long macromolecules

Mechanical simulation of the diffusion of long macromolecules

N H HANCOCK, G J HARDISTY and F H READ

Physics Department, Schuster Laboratory, Manchester University, Manchester, M13 9PL, UK

Abstract. A method is described of mechanically simulating the random motion of long macromolecules. The method has been used to study the time dependence of the diffusion of a single point in a molecular chain.

In this letter we wish to report some preliminary results on a mechanical simulation of the diffusion of a long molecular chain. Although other methods of simulation have been used previously for demonstration purposes (eg Busse 1966), we feel that the present method may be more than a demonstration and hope that it may be useful for studying some features of the motion of large molecules which are difficult to study by more conventional means. For example, the initial motivation for the present work was to try to simulate the knotting of long chain molecules and to study such features as the equilibrium number of knots, since it is difficult to do this by known theoretical or computational techniques (eg Edwards 1970). The experimental work of the present investigation was carried out by two of the authors (N H Hancock and G J Hardisty) as part of their third year undergraduate project experiment.

In the present method the macromolecule was simulated by a light aluminium chain of length 15 cm and diameter 1·5 mm, consisting of approximately 100 links. The molecular environment in which the macromolecule moves was simulated by bombarding the chain with steel spheres (of diameter 2·4 mm) moving with random directions and velocities. These spheres, of which there were about 2000, were contained in a cubic air filled box (with sides of length 30 cm) and they were maintained in motion by an oscillatory movement of a disc which formed part of the bottom surface of the containing box. The frequency (20 Hz) and amplitude (2 cm) of this motion were such that the mean height of the moving spheres was approximately 6 cm above the bottom of the box. The aluminium chain was maintained in random motion by collisions with the moving spheres, and the chain touched the bottom of the box only occasionally. Collisions between the spheres, and the presence of sloping surfaces inside the box, served to randomize the motion of the spheres and chain in both the horizontal and vertical directions.

The motion of the moving chain was recorded by a Bolex cine camera mounted vertically above the container (which was constructed of transparent perspex.) The high speed of the chain necessitated the use of short exposure times (1/500 s, at f 8), high illumination (4 theatre spotlights of 500 W each) and a fast film (Kodak 4X film, with Kodak D19 x ray developer). Crossed polarizers (4 in square sheets of polaroid) were used to reduce the unwanted light scattered from the shiny surfaces of the spheres. The amount of unpolarized light scattered from the ends of the chain was increased by coating these ends with white zinc sulphide mixed with a glue.

With this system of illumination and photography, the ends of the chain could be easily identified on typical exposures, and the position of the rest of the chain could also usually be seen.

As a first simple experiment we have studied the time dependence of the diffusion of a single point in the chain. Figure 1 shows the results of an analysis of 90 consecutive
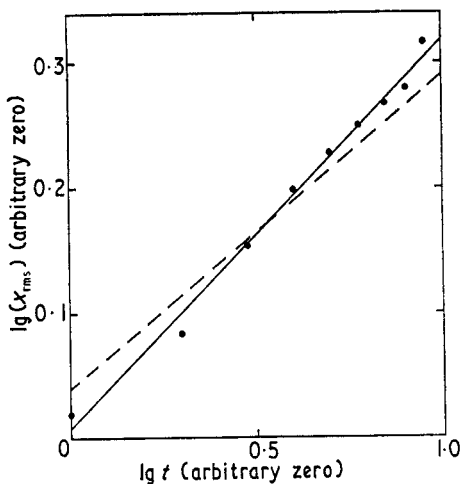

Figure 1. The time dependence of the diffusion of a single point in a molecular chain. The full line is the least squares fit to the data points, and has a slope of 0·31. The broken line has a slope of 0·25, as required by the theory of De Gennes (1967). For normal Brownian diffusion the slope would be 0·5.

exposures, covering a total time of 1·4 s, during which the chain did not touch the bottom or sides of the container: it shows the root mean square displacement x_{rms} (in the horizontal plane) of one end of the chain, as a function of the time interval t.

The diffusion of macromolecules in the high viscosity limit is a classic problem which was first studied by Rouse (1953), Zimm (1956) and Beuche (1954). The problem was further investigated more recently by De Gennes (1967) who showed that in the absence of perturbations due to end effects the points in the figure should lie on a line of slope 0·25. The broken line in the figure has been drawn with this slope. With normal Brownian diffusion one would expect a slope of 0·5 (ie the root mean square displacement of any one point of the chain would be proportional to the square root of the time). In fact the full line in the figure, which is the linear least squares fit to the points, has a slope of $0·31 \pm 0·01$, which is more in accordance with De Genne's result than with simple Brownian motion.

It cannot be said yet that this method of simulating the diffusion of polymer chains is useful in providing answers to questions which are difficult to obtain by more conventional means. Much remains to be done in the evaluation of the method, particularly with regard to the choice of size and mass of the chain and sphere, and with the difficult problems of scaling the viscosity, temperature, density, pressure, time, and so on. Further experiments are planned, and it is also proposed to investigate the use of a fluid in an ultrasonic tank as the bombarding medium.

References

Beuche F 1954 *J. chem. Phys.* **22** 603–9
Busse W F 1966 *J. Polymer Sci.* (*part* C) no 14 15–9
Edwards S F 1970 *Disc. Faraday Soc.* **49** 43–50
De Gennes P-G 1967 *Physics* **3** 37–45
Rouse P E 1953 *J. chem. Phys.* **21** 1272–80
Zimm B H 1956 *J. chem. Phys.* **24** 269–78

Neutrino processes in the lepton era of the universe and hot big bang cosmology

D RAY

Department of Physics, Presidency College, Calcutta-12, India

Abstract. The neutrino interactions in the lepton era of the universe have been studied here according to the photon–neutrino coupling theory. It is found that neutrinos were decoupled from electrons from the beginning of the universe and remained so throughout the lepton era of the universe in hot big bang cosmology.

Zeldovich (1965) and Graaf (1970) have investigated the interactions $\nu_e + \bar{\nu}_e \rightleftharpoons e^- + e^+$ and $\nu_e + e^- \rightarrow \nu_e + e^-$ in the early stage of cosmic evolution in hot big bang cosmology. Both have studied the interactions according to the current–current coupling theory. Graaf (1970) also considered the problem assuming the existence of a neutral lepton current as well.

In a recent paper Bandyopadhyay (1968) has suggested an alternative theory to the current–current coupling theory which has been called the photon–neutrino weak coupling theory, in which photons are considered to interact weakly with neutrinos. It is of some interest to see how the results of Zeldovich and Graaf change in the new theory.

According to the photon–neutrino coupling theory we have for the process $\nu_e + \bar{\nu}_e \rightleftharpoons e^- + e^+$, a rate of neutrino energy loss $d\epsilon_{\nu\bar{\nu}}/dt$ given by the relation (Bandyopadhyay 1968)

$$\frac{d\epsilon_{\nu\bar{\nu}}}{dt} = 1 \cdot 75 \times 10^{15} T_9^5 \qquad (T_9 = T/10^9). \tag{1}$$

The neutrino energy density $\epsilon_{\nu\bar{\nu}}$ is given by (Zeldovich 1965)

$$\epsilon_{\nu\nu} = 7 \cdot 8 \times 10^{21} T_9^4. \tag{2}$$