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1988 J. Phys. A: Math. Gen. 21 4173

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A polymer in a fractal pore space

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Received 7 March 1988, in final form 13 May 1988

Abstract. The structure of a polymer chain, with excluded-volume interaction and residing in a fractal space, is determined using the Edwards path integral formulation of the calculation of the configuration Green function. To implement this calculation the position-dependent diffusion constant of O'Shaughnessy and Procaccia, appropriate to diffusion on a fractal, is employed in place of the usual ∇^2 . The scaling of R with N and the monomer density at large $r \ll R$ are determined. The results, $R \sim N^\nu$, $\nu = 3/(d_t + d_w)$ are in agreement with a simple Flory argument and confirm the essential correctness of the O'Shaughnessy-Procaccia continuum description of diffusion on a fractal for $r \ll R$.

1. Introduction

In recent years there have been numerous studies of fractal objects and the influence of fractal geometry on dynamics, e.g. the diffusion of a tracer particle in a fractal pore space obeys $\langle x^2 \rangle \sim t^{2/d_w}$. Let us ask the question: what is the structure of a polymer that is required to reside in a fractal space? The various possible monomer arrangements of an N -unit (monomer) polymer in a fractal space are equivalent to the possible random walks that can occur in this space on a timescale $t \propto N$ [1]. The excluded-volume interaction between the monomers of which the polymer is built limits the possible monomer arrangements to those that are self-avoiding. Thus the question we have posed translates into the question of determining the structure of self-avoiding random walks on a fractal. To answer this question we start with the traditional path integral description of polymer configurations due to Edwards [1]. Essential to our application of this description is modification of the behaviour of the entropy springs appropriate to random walking on a fractal. Calculation using this modification, involving the O'Shaughnessy-Procaccia [2] position-dependent diffusion constant and a variant of the usual computational procedure, leads to results that are in accord with a simple Flory argument. Herein we describe these calculations.

This paper is organised as follows. In § 2 we outline the connection between the path integral formulation of the problem and the equations that we manipulate to learn about polymer structure. We use the steepest descent method of Kholodenko [3] to derive self-consistent equations for $G(r, r'; N)$, the Green function that describes polymer configurations. These equations are cast in the form of a single equation for the self-consistent field, $\phi(r)$, from which features of the polymer structure can be

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learned. The equation for $\phi(r)$ is treated using a factorisation approximation due to Wigner and Kirkwood [4]. In § 3 we employ the formal apparatus displayed in § 2 to solve two problems. First we look at a polymer with excluded-volume interaction in a uniform $d = 3$ space, finding well known results. Thus we confirm, for a known case, the computational apparatus we have introduced. Then we look at a polymer with excluded-volume interaction in a fractal space. We work out the scaling of polymer size with monomer number, $R \sim N^\nu$, $\nu = 3/(d_f + d_w)$, and we determine the monomer density in the polymer at $l \ll r \leq R$, where l is the monomer length scale. Our conclusions are in § 4.

2. Method of calculation: general

In this section we sketch the formulation of the description of a single polymer chain that we employ in § 3. To find the end-to-end distance of a polymer chain of length N we study $G(\mathbf{r}, \mathbf{r}'; N)$, a measure of the number of configurations available to a chain of this length that has one end fixed at \mathbf{r}' and the other end fixed at \mathbf{r} . $G(\mathbf{r}, \mathbf{r}'; N)$ is given by

$$G(\mathbf{r}, \mathbf{r}'; N) = \int_{\mathbf{x}(0)=\mathbf{r}'}^{\mathbf{x}(N)=\mathbf{r}} D[\mathbf{x}(s)] \exp\{-H[\mathbf{x}(s)]\} \quad (1)$$

where $D[\mathbf{x}(s)]$ denotes a functional integral over all configurations $\mathbf{x}(s)$ of the chain $\mathbf{x}(0) = \mathbf{r}'$, $\mathbf{x}(N) = \mathbf{r}$ and $H[\mathbf{x}(s)]$ is an appropriate weight function. For $H[\mathbf{x}(s)]$ we consider

$$H[\mathbf{x}(s)] = \int_0^N ds \left(\frac{d\mathbf{x}}{ds} \right)^2 + W \int_0^N ds \int_0^N ds' \delta(\mathbf{x}(s) - \mathbf{x}(s')) \quad (2)$$

where the first term is an 'energy' associated with the random walk (rw) of the chain in a uniform space and the second term is the excluded-volume interaction with strength parameter W [1]. The 'energy' in (2) is that for a self-avoiding walk (saw) in a uniform space.

The quantity we wish to study, the average end-to-end distance, is related to $G(\mathbf{r}, \mathbf{r}'; N)$ by

$$R^2(N) := \frac{\int d^d \mathbf{r}(\mathbf{r})^2 G(\mathbf{r}, \mathbf{0}; N)}{\int d^d \mathbf{r} G(\mathbf{r}, \mathbf{0}; N)}. \quad (3)$$

Of particular interest is the scaling of R^2 with N , i.e. the determination of the Flory exponent, ν , defined by

$$R^2(N) \sim N^\nu. \quad (4)$$

Thus the programme of calculation is in principle: solve (1) with (2), for use in (3) to examine (4).

The first step in carrying out this programme is to find an equation of motion for $G(\mathbf{r}, \mathbf{r}'; N)$. To this end we use the steepest descent approximation of Kholodenko [3]. The outline is as follows.

(a) Introduce a random field, $\psi(x)$, so that the excluded-volume interaction appears as a single-particle term. That is, use the Hubbard-Stratonovich identity to write

$$G(\mathbf{r}, \mathbf{r}'; N) = A \int D[\psi] P(\psi) G(\mathbf{r}, \mathbf{r}'; N | \psi) \quad (5)$$

where

$$G(\mathbf{r}, \mathbf{r}'; N | \psi) = \int_{\mathbf{x}(0)=\mathbf{r}'}^{\mathbf{x}(N)=\mathbf{r}} D[\mathbf{x}(t)] \exp\{-H[\mathbf{x}(t), \psi]\} \tag{6}$$

$$H[\mathbf{x}(t), \psi] = \int_0^N dt \left(\frac{d\mathbf{x}}{dt} \right)^2 + \int_0^N dt i\psi(\mathbf{x}(t)) \tag{7}$$

$$P(\psi) = \exp\left(- \int d\mathbf{z} \int d\mathbf{z}' \psi(\mathbf{z}) w^{-1}(\mathbf{z} - \mathbf{z}') \psi(\mathbf{z}') \right) \tag{8}$$

$$\int d\mathbf{z}'' w^{-1}(\mathbf{z} - \mathbf{z}'') w(\mathbf{z}'' - \mathbf{z}') = \delta(\mathbf{z} - \mathbf{z}')$$

and

$$A^{-1} = \int D[\psi(z)] P(\psi). \tag{9}$$

(b) Find an equation of motion for $G(\mathbf{r}, \mathbf{r}'; N | \psi)$. As illustrated in Freed [5]:

$$\left(\frac{\partial}{\partial N} - \frac{\partial^2}{\partial \mathbf{r}^2} + i\psi(\mathbf{r}) \right) G(\mathbf{r}, \mathbf{r}'; N | \psi) = \delta(N) \delta(\mathbf{r} - \mathbf{r}'). \tag{10}$$

(c) Develop a self-consistent equation for $G(\mathbf{r}, \mathbf{r}'; N | \psi)$. This is accomplished most conveniently in terms of the Laplace transform of $G(\mathbf{r}, \mathbf{r}'; N | \psi)$. The Laplace transforms of (5) and (10) are

$$G(\mathbf{r}, \mathbf{r}'; s) = A \int D[\psi] P(\psi) G(\mathbf{r}, \mathbf{r}'; s | \psi) \tag{11}$$

and

$$\left(s - \frac{\partial^2}{\partial \mathbf{r}^2} + i\psi(\mathbf{r}) \right) G(\mathbf{r}, \mathbf{r}'; s | \psi) = \delta(\mathbf{r} - \mathbf{r}') \tag{12}$$

where the Laplace transform is

$$f(s) := \int_0^\infty dN e^{-Ns} f(N).$$

Approximating the integrand in (11) by $\bar{\psi}(\mathbf{x})$, the mean-field function found by a steepest descent analysis of $P(\psi) G(\mathbf{r}, \mathbf{r}'; s | \psi)$, leads to the self-consistent equations

$$\left(s - \frac{\partial^2}{\partial \mathbf{r}^2} + iW\bar{\psi}(\mathbf{r}) \right) G(\mathbf{r}, \mathbf{r}'; s | \psi) = \delta(\mathbf{r} - \mathbf{r}') \tag{13}$$

and

$$i\bar{\psi}(\mathbf{r}, s) = G(\mathbf{r}, \mathbf{r}; s | \bar{\psi}) \equiv \phi(\mathbf{r}; s). \tag{14}$$

It is this pair of self-consistent equations that we shall employ in finding $G(\mathbf{r}, \mathbf{r}'; N)$, etc.

Self-consistent equations, identical to those we have displayed, can be found in a perturbation theory treatment of (11) (see figure 1) in which the perturbation series is summed in a Hartree-like manner, figure 1(b). As observed by Moore and Bray [6] it is the loop contribution in figure 1(b) that is the source of the effective potential, $\bar{\psi}$, in (13).

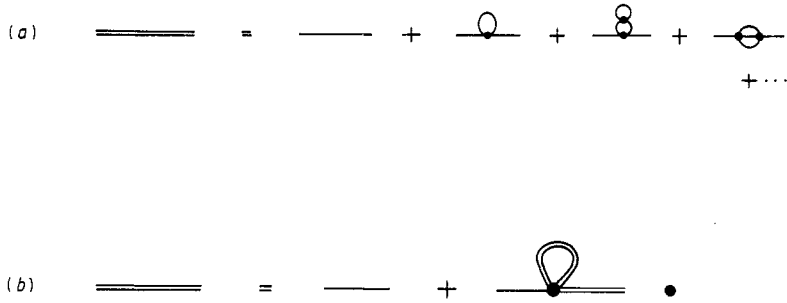


Figure 1. (a) Perturbation series for $G(r, r'; N)$, double line, in terms of G_0 and W . G_0 is a single line; W acts at the vertices. (b) Resummations of the series in (a) in the Hartree approximation.

In dealing with (13), following an argument by Moore and Bray, we use the isotropic form of $\partial^2/\partial r^2$ and write:

$$\left(s - \frac{\partial^2}{\partial r^2} - \frac{2}{r} \frac{\partial}{\partial r} + W\phi(r; s) \right) G(r, r'; s | \phi) = \frac{\delta(r - r')}{rr'} \tag{15}$$

and

$$\phi(r; s) = G(r, r; s | \bar{\psi}). \tag{16}$$

Physically this is equivalent to approximating the polymer as a diffused sphere, whose radius is to be determined self-consistently. This corresponds to taking only the $l = 0$ mode (S wave) into consideration and was shown by Moore and Bray to be valid in the strong-coupling region, for it is here that the centrifugal barrier can be set equal to zero.

We may solve (15) formally for $G(r, r'; s | \phi)$ in the form

$$G(r, r'; s | \phi) = \int_0^\infty d\lambda \langle r | \exp[-\lambda(s - D_r^2 + W\phi)] | r' \rangle \tag{17}$$

where

$$D_r^2 = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \quad \langle r | r' \rangle = \frac{\delta(r - r')}{rr'}. \tag{18}$$

Upon putting $r = r'$ in this equation we have a self-consistent equation for $\phi(r; s)$, equation (16):

$$\phi(r; s) = \int_0^\infty d\lambda \langle r | \exp[-\lambda(s + W\phi - D_r^2)] | r \rangle. \tag{19}$$

To make progress in handling the rhs of (19) we employ the Wigner-Kirkwood [4] factorisation of e^{A+B} and write

$$\phi(r, s) \sim \int_0^\infty d\lambda \exp[-\lambda(s + W\phi)] K(r, r; \lambda) \tag{20}$$

where

$$K(r, r'; \lambda) = \langle r | \exp(\lambda D_r^2) | r' \rangle. \tag{21}$$

The strategy at the start was to solve an equation for $G(r, r'; N)$ to obtain $R^2(N)$ as in (3). The equation for $G(r, r'; N)$ was reduced, upon approximation, to a self-consistent equation, the self-consistency involving the diagonal part of $G(r, r'; s)$, $\phi(r; s)$. Equations (20) and (21) are a statement of this self-consistency. From them we obtain first $\phi(r; s)$ and then $G(r, r'; s | \phi)$, equation (15) and then $R^2(N)$ from (3). Instead of proceeding in this way we may use $\phi(r; s)$ directly to obtain $R^2(N)$ upon recalling that $\phi(r)$ is the monomer density and using [7]:

$$\int_0^R r^{d-1} dr \phi(r) = N. \tag{22}$$

Thus the original computational programme, outlined below (4), has been transformed into the self-consistent solution to (20) and (21) for $\phi(r)$ to be used in (22). Below we will show how this scheme works by using it to describe a polymer with excluded volume (SAW) in a uniform $d=3$ space. We will then use it to describe a polymer with excluded volume (SAW) in a fractal space. This latter application, involving a modification of the structure of the space in which the polymer resides, is implemented directly in (20)—(22).

3. Method of calculation: specific

In this section we describe the use of (20)–(22) to study R^2 for a polymer in a uniform $d=3$ space (§ 3.1) and a fractal space (§ 3.2).

3.1. Polymer in a uniform $d=3$ space

To solve (20) and (21) self-consistently for $\phi(r)$ we begin with (21) for $K(r, r'; \lambda)$. From (21) we have

$$\left(\frac{\partial}{\partial \lambda} - D_r^2 \right) K(r, r'; \lambda) = \delta(\lambda) \frac{\delta(r-r')}{rr'} \tag{23}$$

i.e. $K(r, r'; \lambda)$ solves the diffusion equation. Thus using D_r^2 from (18) we have

$$K(r, r'; \lambda) = \frac{1}{2\lambda} \frac{1}{(r_<r_>)^{1/2}} \exp[(-r_<^2 + r_>^2)/4\lambda] I_{1/2} \left(\frac{r_<r_>}{2\lambda} \right) \tag{24}$$

where $r_> := \max(r, r')$, $r_< := \min(r, r')$ and I is the modified Bessel function. For $r = r'$ at large r we have

$$K(r, r; \lambda) \sim \sqrt{\lambda}/r^2. \tag{25}$$

Upon using this asymptotic form for $K(r, r, \lambda)$ in the RHS of (20) we obtain

$$\phi(r, s) \sim \frac{1}{r^2(s + W\phi(r, s))^{1/2}}. \tag{26}$$

In the limit $W\phi \gg s$ this equation is solved for $\phi(r)$:

$$\phi(r) \sim r^{-4/3}. \tag{27}$$

Using this asymptotic form of ϕ in (22) we find

$$N \sim R^{5/3} \tag{28}$$

or $\nu = \frac{3}{5}$, i.e. the well known Flory result. The procedure illustrated here may be generalised to integer dimension with the result $\nu = 3/(d + 2)$.

Before we go on, several remarks are in order.

(a) To find $N \sim R^{5/3}$ we have used (22), i.e.

$$N \sim \int_0^R r^{d-1} \frac{1}{r^\mu} dr \sim R^{d-\mu}. \tag{29}$$

Because of the excluded-volume interaction the polymer generates an effective potential that reduces its density below uniformity, $r^{-\mu}$, and as a consequence the number of monomers in the interior of the polymer, at $r \leq R$, goes as $R^{d-\mu}$. In using $\phi(r)$ as we have in (29) we require a form $\phi(r)$ valid at $r \leq R$. Making the association of s with N^{-1} we see that the inequality below (26) becomes $r^{4/3} \ll N \sim R^{5/3}$ or $r \leq R$. Thus the limit $W\phi \gg s$ which we have used in (26) is the correct limit in which to glean information about $\phi(r)$ in the interior of the polymer.

(b) In dealing with the self-consistent equations, (15) and (16), we seem to have made things harder by using the inverse formula in (17). Then, by using the Wigner-Kirkwood factorisation to achieve (20) we seem to have taken a compensating step. Equations (20) and (21) permit us to achieve the same results as those achieved by Moore and Bray [6] in examination of (15) and (16). Whereas Moore and Bray have to work out the joint consequence of $-D_r^2 + W\phi(r)$, i.e. they solve the differential equation involving this operator, we need only work out the consequence of D_r^2 . However, in contrast to Moore and Bray who set $s = 0$ at the outset, we must obtain D_r^2 for all λ , i.e. solve an equation involving $\exp(\lambda D_r^2)$ for all λ . As λ acts like N (23) we can say that the method of solving the equation for $G(r, r'; s | \phi)$ introduced, substitutes knowledge of the motion of a free chain for all N for knowledge of an interacting chain at a particular N .

3.2. Polymer in a fractal space

Consider a polymer in the pore space of a porous material. The polymer is so large that it achieves an equilibrium configuration by wending its way among a great number of pores. Let us take the pore space to be fractal with dimension d_f . As a consequence of its fractal structure the diffusion of a test particle in the pore space will be anomalous and characterised by the dimension of the walk, d_w :

$$\langle x^2 \rangle \sim t^{2/d_w}. \tag{30}$$

Since the random walk of the monomers through the pore space is analogous to the random walk of the test particle, we may expect the equilibrium configuration of the polymer to show evidence of d_w as well as d_f .

There are two modifications of (20)-(22) that are necessary to deal with this case.

(a) To describe the random walk of the monomers in the fractal pore space we use the position-dependent diffusion constant of O'Shaughnessy and Procaccia [2] for D_r^2 (21):

$$D_{r,f}^2 = \frac{1}{r^{d_f-1}} \frac{\partial}{\partial r} \left(r^{d_f-1-\theta} \frac{\partial}{\partial r} \right) \tag{31}$$

where $\theta = d_w - 2$. The underlying fractal space, of course, cannot be viewed as an isotropic medium on a microscopic scale. However, on a 'coarse-grained' scale, we may take the position-dependent diffusion constant as a working hypothesis, a practice

commonly adopted in problems concerning porous media. It will be shown in the conclusion that the hypothesis is essentially an accurate one.

(b) To describe the density of the pore space in which the polymer resides we use

$$\rho(r) \sim r^{d_f-d}. \tag{32}$$

Thus (20) is unchanged; in place of (21) and (22) we have

$$K(r, r'; \lambda) = \langle r | \exp(\lambda D_{r,r'}^2) | r' \rangle \tag{33}$$

and

$$N = \int_0^R dr r^{d_f-1} \phi(r). \tag{34}$$

From (32) and (33) we find

$$\left[\frac{\partial}{\partial \lambda} - \frac{1}{r^{d_f-1}} \frac{\partial}{\partial r} \left(r^{d_f-1-\theta} \frac{\partial}{\partial r} \right) \right] K(r, r'; \lambda) = \delta(\lambda) \frac{\delta(r-r')}{(rr')^{(d_f-1)/2}}. \tag{35}$$

This equation has a solution

$$K(r, r'; \lambda) = \frac{((r > r')^\gamma)}{2\gamma\lambda} \exp[-(r_{<}^{2\gamma} + r_{>}^{2\gamma})/4\lambda\gamma^2] I_\mu \left(\frac{r_{<}^\gamma r_{>}^\gamma}{2\lambda\gamma^2} \right) \tag{36}$$

where

$$\begin{aligned} 2\alpha &= 2 - d_f + \theta \\ \gamma &= 1 + \frac{1}{2}\theta \\ \mu &= \alpha/\gamma. \end{aligned} \tag{37}$$

Proceeding as in § 3.1 we find the large- r behaviour of $K(r, r; \lambda)$:

$$K(r, r; \lambda) \sim \sqrt{\lambda}/r^{\gamma-2\alpha}. \tag{38}$$

Thus

$$\phi(r) \sim r^{-\mu} \tag{39}$$

and

$$R \sim N^\nu \tag{40}$$

with $\mu = (2d_f - d_w)/3$ and $\nu = 3/(d_f + d_w)$. Equations (39) and (40) are our principal results.

As expected for $d_f = d$ and $d_w = 2$, we recover the Flory result. Equation (40) can also be achieved using an analysis of $D_{r,r}^2 + W\phi(r)$ along the lines of that of Moore and Bray [6]. Further, (40) is in agreement with a simple Flory argument [7] using the energy

$$E(R, N) \sim \frac{R^{d_w}}{N} + \frac{N^2}{R^{d_f}}. \tag{41}$$

Minimisation with respect to R leads to $R^{d_w+d_f} \propto N^3$.

4. Conclusion

In this paper we have studied some features of the structure of a self-avoiding polymer chain that resides in a fractal space. This study has been carried out employing a variation on the usual computational procedure. Here we summarise our findings and call attention to a number of interesting results.

(i) The 'variation on the usual computational procedure' was tested on self-avoiding polymer chains in a uniform space of integer dimension with the results $R \sim N^\nu$, $\nu = 3/(d+2)$, i.e. the correct Flory exponent.

(ii) Application of this computational procedure to a self-avoiding polymer chain in a fractal space characterised by d_f and d_w led to

$$R \sim N^\nu \quad \nu = 3/(d_f + d_w) \quad (40)$$

and to monomer density

$$\phi(r) \approx r^{-\mu} \quad \mu = (2d_f - d_w)/3 \quad (39)$$

for large $r \ll R$.

These results, equations (39) and (40), are consistent with treatment of the problem by the computational procedure of Moore and Bray [6] and, in the case of (40), with a simple Flory argument [7]. They are also consistent with the earlier results of Rammal *et al* [8] and Ben-Avraham and Havlin [9]. In achieving these results we have used the O'Shaughnessy-Procaccia [2] position-dependent diffusion constant, i.e.

$$D(r) \sim r^{-\theta}$$

where $\theta = d_w - 2$, or equation (31). Thus the agreement between (40) and the simple Flory argument, achieved using (31), lends support to an assertion about the suitability of the O'Shaughnessy-Procaccia continuum description of particle motion on a fractal [10]†.

How general are the results in (39) and (40)? The calculation called for upon using (31) and (32), the determination of $K(r, r'; \lambda)$ using (35), fails at $d_s = 2$ $d_f/d_w < 1$ where $\mu < 0$ and $\phi(r) \sim r^{|\mu|}$. On physical grounds we expect a more severe limit. Equations (39) and (40) should cross over at $d_s = 2$ to $\nu = d_f^{-1}$, $\mu = 0$. The argument for this comes from $d_w = d_f + w$, where w describes the scaling of R , $R \approx L^w$. $w < 0$ implies the availability, to a random walker, of alternate paths that let it revisit regions of space where it has been previously. Thus, when limited by the requirements of self-avoidance, a random walker is not compelled to simply walk forward as it is, for example, in the case of a hierarchical lattice; for a hierarchical lattice $d_f = 1.262$, $w = 0.834$, $d_w = 2.096$ and $d_s = 1.204$.

Acknowledgments

This work was supported by the National Science Foundation (DMR-84-20902), the Materials Research Laboratory at the University of Massachusetts and SERC.

† The treatment of diffusion on a fractal due to O'Shaughnessy and Procaccia yields a Green function different from that of Guyer [10]. The Green function of Guyer, valid for $r^2 \gg N^{2/d_w}$, is not appropriate for our calculation, in which $r \ll N$ is important.

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