

Hydrodynamic interactions in self similar structures, such as polymers

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Abstract. We study the hydrodynamic properties of polymers and more generally self-similar structures using a new recursion model. The hydrodynamic interaction between monomers is modeled by the standard Green's function of Stokes flow in which an ultrametric distance is substituted for the usual Euclidean distance. This leads to a model where the long-range hydrodynamic interactions and the long-range correlations of the polymer conformation can both be accounted for and yet allow for analytical solutions. We explore the asymptotic as well as the finite size corrections to the scaling behavior with this model. In order to compare the results of the present scheme with more conventional techniques a generalized version of the existing mean field results by Kirkwood and Riseman for the hydrodynamic drag is introduced.

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1 Introduction

Extensive theoretical and experimental work has been reported on the hydrodynamic properties of linear polymers in solvents of varying thermodynamic quality. In dilute solutions the hydrodynamic properties can be characterized by experimental quantities such as the intrinsic viscosity or the effective Stokes radius, R_h . These properties can be compared to static properties like the thermodynamic second virial coefficient or the radius of gyration, R_g . Comparison of theory with experimental results show serious discrepancies (see Ref. [1] for a review of the existing theory and the different attempts to deal with these discrepancies). An important test for the theory is the dependence of $\rho \equiv R_g/R_h$ on the number of segments, N . R_g and R_h are relatively easy to determine using scattering techniques. Both the Kirkwood-Riseman (K-R) approach [2–4] and more recent renormalization group (RG) theory calculations [5,6] predict ρ to be independent of N and independent of the particular polymer solvent combination. For polymers in theta solvents, ρ is indeed observed to be independent of N for sufficiently large polymers. However, the experimental value varies somewhat from system to system and differs from the values predicted by the K-R and RG theory. In good solvents the experimental value of ρ increases with increasing N even

for the largest polymers which have been measured up to date. In good solvents flexible linear polymers are less dense than in theta solvents and partial draining is more important. In theta solvents the fractal dimension, D , is 2 while in good solvents it is 5/3 [7–9]. Experimentally, D can be obtained from the dependence of R_g on N : $R_g \propto N^{1/D}$ or the scattering wave vector dependence of the scattering intensity $I \propto q^{-D}$ [10,12]. Experimentally, R_h is observed to scale with N even in good solvents, but with an exponent smaller than D which leads to a dependence of ρ on N . Different possible causes for the observed discrepancies are discussed in reference [1].

Relatively little attention is given to the dynamic properties of fractal objects in general, of which flexible linear polymers are an example and aggregates of small particles [11] are another. The structure of these particles depends on the growth process, *e.g.* reaction controlled cluster-cluster aggregation leads to objects with a fractal dimension close to two, but has a different cutoff at small and large scales than fractals formed by a random walk [12]. Another important class of examples are particles formed by a percolation process close to the sol-gel transition which have a fractal dimension of 2.5 [13]. In general it is feasible that by some specific aggregation process particles can be formed with any fractal dimension between 1 and 3. Here we introduce an approach to calculate the friction of fractal objects. The emphasis is however, still on polymers, and we verify that the hydrodynamic properties of our fractals are indeed very close

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to results for ρ obtained by Zimm [14] for the case where $D = 2$. Hence, for concreteness we will, in the following, use the term polymer even for these more general fractals.

The basic idea of our approach is to calculate friction coefficients recursively for ever bigger chunks of space: If the drag or friction of a representative element in space is known, the drag of a collection of such chunks may be computed by a recursion relation. In this way the friction coefficient is obtained by mapping small scale information to larger scale information. In this sense it is a renormalization group approach – although it does not employ the ϵ expansion-technique. Using this strategy we investigate an approximation to the long range hydrodynamic interactions which preserves the basic scaling with distance but otherwise represents a discretization. This is achieved by using an ultrametric distance instead of the standard Euclidean one.

While ϵ -expansion techniques [5, 6, 15] ($\epsilon = 4 - d$, where d is the spatial dimension) and the present model both belong within the same general conceptual framework, they are distinctly different in the questions they address, their theoretical structure and the level of mathematical complexity. The present aim is not to add to the numerical precision or sophistication of the ϵ -expansion methods, but rather to add a new and conceptually simple tool to understand scaling properties. The present relatively simple recursion scheme only addresses the pre-averaged case. This is in contrast to the ϵ expansion techniques, which must be employed to show that the pre-averaged results receive corrections of order ϵ .

We compare the results of our approach with the K-R model in the mean field approximation generalized for objects with arbitrary fractal dimension. Good agreement of the scaling properties of the friction coefficient and the finite size correction of ρ is obtained. In particular the finite size scaling results are consistent with previous calculations done by Bernal *et al.* [16]. Bernal *et al.* found a correction term scaling as $M^{-1/2}$ in slight contrast to the scaling $M^{-0.4}$ which results from the present study in the good solvent case.

From a numerical point of view it is of central interest to investigate models that single out key aspects of the underlying physics in order to simplify the computation. Computer simulations like those of Zimm and de la Torre *et al.* [14, 17] have been successful in capturing the quantitative aspects of polymers in theta-solvents. These results and related numerical work [16, 18, 19] focus on constructing realistic polymer geometries using Monte-Carlo simulations with a Lennard Jones potential. Compared to these computational techniques the simulations based on the present model ignores much of the hydrodynamic detail and can therefore handle much larger systems.

The (standard) pre-averaging step performed in the present model averages the Green's function (the Oseen tensor), which gives the hydrodynamic response to a point force. However, the fluctuations resulting from the random location of this point force are kept. This allows us to study, at least qualitatively, the effect of density fluctuations, which cannot be handled by mean field theories. We

show that within an ensemble of polymers characterized by a given D , drag fluctuations are much larger among dilute than among the dense polymers. For a given D the variance of the drag is found to decrease exponentially with mass.

Generally, it is clear that we can only address the scaling properties since the prefactors depend on the internal and external cutoff of the pair correlation function. These quantities depend on the particular system and are in our case determined by the way the fractals are generated in the simulation. A crossover dimension $D = 1$ between the non-draining and free draining regime is predicted. However, a more detailed description is needed to resolve the magnitude of the partial draining through the fractal.

The paper is organized as follows: in Section 2 we briefly review the K-R approach using the mean field approximation extended to fractal objects in general. In Section 3 we introduce the present ultrametric recursion model and compare the results of numerical simulations to the K-R theory. In Section 4 we discuss the effect of density fluctuations.

2 The Kirkwood sum – a mean field result

In this section we review the standard Kirkwood-Riseman theory for the drag on a single polymer and generalize it to the case of an arbitrary fractal. We consider a rigid polymer moving with a velocity \mathbf{v} in a fluid which is at rest at large distances from the polymer. One individual monomer will exert a force on the fluid and perturb the velocity field around all other monomers, giving rise to a coupling between the frictional forces. When the Reynolds number is small, a typical situation, the fluid flow is governed by the Stokes equations. Hence the problem is linear and the flow fields caused by each single monomer can simply be added to give the total flow field.

Let ζ be the friction coefficient of the monomers, then the force on the i th monomer is given by the Stokes law

$$\mathbf{f}_i = \zeta(\mathbf{v} - \sum_{j \neq i} \mathbf{T}_{ij} \mathbf{f}_j) \quad (1)$$

where the Oseen interaction tensor \mathbf{T}_{ij} gives the velocity at the relative position \mathbf{r}_{ij} resulting from a force \mathbf{f}_j at \mathbf{r}_j . It has the form [20]

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta r_{ij}} \left[\mathbf{I} + \frac{\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}}{r_{ij}^2} \right] \quad (2)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, η is the dynamic viscosity of the solvent and \mathbf{I} the unit tensor in three dimensions. The Oseen tensor represents a good approximation when inter-monomer distances are significantly larger than the monomer diameter, *i.e.* the approximation will be well-justified when the long range nature of the interactions dominate short range effects.

If there are N monomers in the chain and we let \mathbf{v} be the translational velocity of the polymer, equation (1)

yields $3N$ linear equations for the forces \mathbf{f}_i . The translational friction constant for the whole chain is then given by the sum

$$\Xi = \frac{1}{v} \sum_{i=1}^N \mathbf{f}_i \equiv 6\pi\eta R_h. \quad (3)$$

If we have strong hydrodynamic interactions, the flow velocity around each monomer will be small and the left hand side of equation (1) will be small compared to each of the two terms on the right hand side. Hence, if the left hand side is set to zero, the friction coefficient will drop out of the equation and Ξ will be ζ independent. This corresponds to the *non-draining* regime.

2.1 The Kirkwood-Riseman approximation

Kirkwood and Riseman simplified the above model by replacing the interaction tensor in equation (1) by its ensemble- and direction average, the pre-averaging approximation [2]. The complicated tensor problem is then reduced to a scalar problem. If u is the relative velocity between polymer and solvent, the scalar forces are related by the Kirkwood-Riseman equations

$$f_i = \zeta \left(u - \sum_{j \neq i}^N G_{ij} f_j \right) \quad (4)$$

where G_{ij} is the pre-averaged Oseen tensor

$$G_{ij} = \frac{1}{3} \langle \text{Tr}(\mathbf{T}_{ij}) \rangle = \left\langle \frac{1}{6\pi\eta r_{ij}} \right\rangle. \quad (5)$$

By solving a generalized diffusion equation, Kirkwood obtained an approximate solution to the total friction coefficient [3]. However, applying a mean-field approach directly to the linear equation (4) the same result is obtained. We replace f_j by its mean value $\langle f \rangle = F/N$ where F is the total force $F = \sum_{i=1}^N f_i$ and so equation (4) becomes

$$f_i = \zeta \left(u - \langle f \rangle \sum_{j=1}^N G_{ij} \right). \quad (6)$$

It is now straightforward to find the total force F . We compute the sum of the f_i in equation (6), solving for F yields

$$F = \frac{N\zeta u}{1 + \frac{\zeta}{N} \sum_{i \neq j} G_{ij}} \quad (7)$$

where the sum is now over both i and j . When G_{ij} is given by the pre-averaged Oseen tensor in equation (5) we find the Kirkwood double sum formula for the total friction coefficient of the polymer $\Xi = F/u$

$$\Xi = \frac{N\zeta}{1 + \frac{\zeta}{N} \sum_{i \neq j} \left\langle \frac{1}{6\pi\eta r_{ij}} \right\rangle}. \quad (8)$$

2.2 Kirkwood sum for an arbitrary fractal dimension

The original KR treatment considers Gaussian distributed particle separations with variance $|i-j|b^2$, this corresponds to a fractal dimension $D = 2$. We use a simple generalization of the Kirkwood double sum formula so as to account for any fractal dimension.

For an arbitrary fractal the difference $|i-j|$ is proportional to the mass M between i and j [21]. If the fractal has dimension D , the average length between i and j will then be proportional to $|i-j|^{1/D}$. This leads to the formulas

$$R_G^2 = \kappa^2 b^2 N^{2/D} \\ \left\langle \frac{1}{r_{ij}} \right\rangle = \frac{\lambda}{b} \frac{1}{|i-j|^{1/D}} \quad (9)$$

where κ and λ are constants depending on the specific distribution (which in turn depends on D). In writing the last of the above relations it has been assumed that the spatial monomer distribution is reasonable in the sense that $\langle r_{ij} \rangle \langle 1/r_{ij} \rangle$ does not depend on $\langle r_{ij} \rangle$ for large separations. This is true provided the distribution of lengths r_{ij} goes to zero as $r_{ij} \rightarrow 0$. This is certainly the case for a Gaussian distribution peaked around $\langle r_{ij} \rangle$. Then $\kappa = 1$ and $\lambda = \sqrt{6/\pi}$.

The factors κ and λ depend on the shape of the pair correlation function, *i.e.* the internal and external cutoff of the fractal domain. As κ and λ depend differently on these cutoff functions, ρ_K will not necessarily be the same for objects with the same fractal dimension even if we consider only geometrical properties. In a real system the external cutoff will enter at some characteristic size close to R_g , and the internal cutoff will enter at some length larger than b [22]. Often a single exponential is taken to describe the external density decay, but a random walk for instance has a weaker cutoff and the cutoff of a self avoiding walk is again different. In the simulation the cutoff at L has not been characterized. The sum in equation (8) becomes

$$\sum_{i,j} \left\langle \frac{1}{r_{ij}} \right\rangle = \frac{\lambda}{b} \sum_{i,j} \frac{1}{|i-j|^{1/D}}. \quad (10)$$

Integration to obtain the asymptotic behavior gives the new friction coefficient

$$\Xi = \frac{3\pi\eta b(D-1)(2D-1)}{\lambda D^2} \frac{N^{1/D}}{1 + \frac{b(D-1)(2D-1)}{\lambda^2 D^2 \zeta} N^{(1/D)-1}} \quad (11)$$

to leading order in N^{-1} . For large N the ratio $\rho_K(D) = R_G/R_H$ ratio tends toward the constant

$$\rho_K = \frac{2\kappa\lambda D^2}{(D-1)(2D-1)}. \quad (12)$$

RG theory calculations to the first order in ϵ give the same finite size scaling [5]. For finite N the ratio ρ_K has the same scaling factor as the last factor in equation (11). When

$D = 1$ the Kirkwood sum becomes logarithmically divergent and ρ_K depends on N . This simply means that an extended chain (rod-like) displays logarithmic corrections to the trivial $\Xi = N\zeta$. The finite size scaling in equation (11) is a principal result which will reappear from the recursion model. Note that only the correction term which is proportional to $N^{(1/D)-1}$, depends on the individual friction coefficient ζ . This again reflects non-drainage, *i.e.* the screening that results from a long range Green's function.

In order to verify the scaling predicted in equation (11) we carried out a conventional simulation of polymers in good solvents. These were done by generating the polymers as self avoiding random walks of $D = 5/3$, using standard algorithms [23]. With all the monomer positions given, the linear set of equations given by equation (1) was then solved numerically for the \mathbf{f}_i 's, thus giving the drag and ρ . It was observed that ρ_K indeed scaled linearly with $N^{1/D-1}$, as predicted by equation (11). These results are consistent with those obtained by Bernal *et al.* [16], who instead of the $N^{1/D-1}$ scaling used the argument $N^{-1/2}$. However, the limited range of the data (the number of monomers is between 5 and 50 in both Bernal and our case) make a clear distinction between the two simulation results impossible.

3 The hierarchical model

The understanding of self-similar systems with long-range interaction (described by a Green's function) is a general problem. For instance, the determination of the elastic properties of solids that have a fractal distribution of cracks, is a problem that can be cast in this form [24]. The above mentioned work by Kirkwood and Riseman which was carried out long before the term *fractal* was invented, represents another example.

The recursion model exploits the self similarity, *i.e.* the scale invariance of the problem: the Green's function that describes the dynamic response of the fluid to a point force, is a power law. Hence, in addition to the fractal character of the polymer, the hydrodynamic interactions themselves lack a characteristic scale.

3.1 Hierarchical fractal set

The recursion scheme that we shall use is based on an ultradistance defined on our fractal structure. This distance is described more closely in the next section. The two figures, Figures 1 and 2, show the deterministic and random versions respectively of the fractals we will use to model the polymer geometry.

The deterministic fractal can be constructed by an iteration procedure consisting in assembling small cells into larger cells. We distribute k cubes of unit size on a d -dimensional lattice with N^d sites. This we call the 1st order hierarchical lattice, HL. It will have mass $M = k$ and size $L = N$. A HL of n th order consists of k ($n - 1$)th

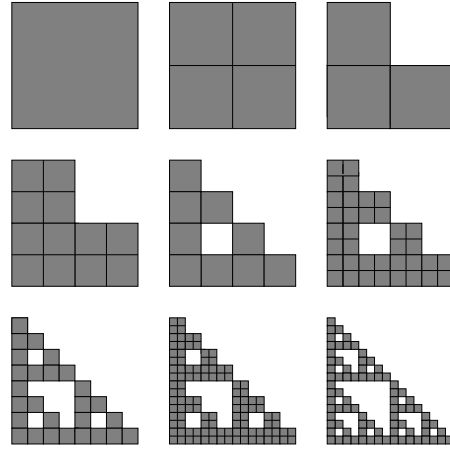


Fig. 1. Deterministic hierarchical lattice with $N = 2$ and $k = 3$. For this particular choice the fractal dimension is $D = \log 3 / \log 2 \approx 1.58$, and we get the famous Sierpinski gasket.

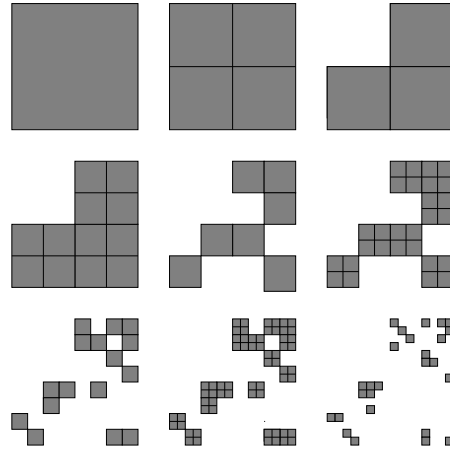


Fig. 2. A stochastic hierarchical lattice with $N = 2$.

order HL. The total mass is $M = k^n$ and the size $L = N^n$, hence $M = L^D$, where $D = \log(k) / \log(N)$ is the fractal dimension.

The same procedure may be used to construct a stochastic fractal. A cube is occupied with probability p and vacant with probability $1 - p$. Thus the average number of sub-units on each level becomes $\langle k \rangle = pN^d$ and average mass $\langle M \rangle = L^D$, where D is given by

$$D = d + \frac{\log(p)}{\log(N)}. \quad (13)$$

The fractal dimension of the stochastic HL has the merit of being continuously tunable, by simply choosing an appropriate p -value. We also notice that there is a critical probability $p_c = N^{-d}$ where $D = 0$, when $p < p_c$ the iteration process terminates since the average number of particles within one cell is less than one.

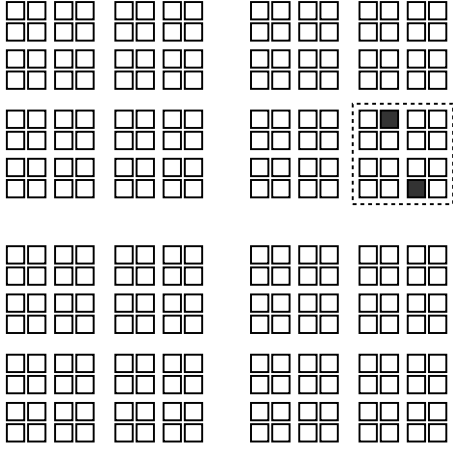


Fig. 3. Two-dimensional square lattice. To clarify the hierarchical structure, we have artificially separated the different generations. The structure shown here has a scale factor $N = 2$. The distance used on top of this lattice is based on the hierarchical structure. The distance between the two grey sites on the figure is found by considering the smallest group (shown as a dotted line) which contains both sites. The generation order of this group (here $n = 2$) defines the distance $r = N^n - 1$ ($r = 3$ in this example).

3.2 Ultra metric distance

The hierarchical lattice is naturally endowed with a metric structure which will constitute the essential brick of our procedure. This distance is indeed directly constructed from a coarse-graining of the structure, and is thus well suited for a recursion approach.

The definition of the distance is illustrated in Figure 3. We let the distance between two “monomers” i and j be $r(i, j) = N^n - 1$, where n is the order of the smallest HL that contains both i and j . The generation n is the number of coarse-graining steps necessary to merge the two sites into a single unit. It is trivial to show that this defines a distance in the mathematical sense. However, this distance is particular. It displays a property stronger than the “triangular” inequality: for any triplet of points i , j and k , at least two of the three distances $r(i, j)$, $r(i, k)$ and $r(j, k)$ are equal. This property makes r an ultra-distance.

3.3 Ultra metric interaction equations

The HL provides us with a self similar set of particles with a tunable fractal dimension. We want to examine the hydrodynamic interactions between these particles and calculate the resulting friction coefficient. We assume a scalar Green’s function G in the same spirit as in the pre-averaging introduced by Kirkwood and Riseman. The force, f_i on one particle is then given by equation (4). Let us note at this stage that the pre-averaging is not a compulsory step in the process of computing the drag of a cube from the drag of the sub-cubes. A full tensor interaction could be considered in an elementary cell and then using

the similarity of the interaction term, the Green’s function could be extended in the entire space. This however induces much more cumbersome algebra and little more physics, thus we will in the present article solely focus on this scalar approximation.

If the interaction only depends on the generation number n , the self similar structure can be exploited. This may be achieved by introducing the ultra metric distance of the previous section. We calculate the total friction coefficient, ζ_n^i of the n th order HL in the i th cell and use this result to find ζ_{n+1} for the $n + 1$ order cell. The key feature used here in the ultrametric distance is the fact that the distance between *any point* inside a cell and a point outside is the same. Therefore it is possible to coarse-grain the total friction since it contains all the necessary information when computing the drag for all subsequent generations in the construction of the self-similar structure. The Green’s function will only depend on the generation number n , and so the force on the i th cell in the $(n + 1)$ th lattice is given by

$$f_i = \zeta_n^i \left(u - G(n) \sum_{j \neq i} f_j \right). \quad (14)$$

We assume a Green’s function of the form

$$G(n) = \frac{a}{r(n)^\alpha} \quad (15)$$

where $r(n) = N^{n-1} - 1$ is the distance introduced in a previous section. In the following, we will be mostly interested in the large scale properties of the system so that we will approximate the distance by $r(n) = N^{n-1}$. The prefactor a can be set to adjust to the monomer size. Comparing with the pre-averaging form of the Oseen tensor, we set $\alpha = 1$ for the hydrodynamic case. It is again noteworthy that other values of α may arise in different contexts where a similar formal approach can be developed, (such as *e.g.* micro-cracks in an elastic matrix where $\alpha = d$).

The friction coefficient on level $n + 1$ is $\zeta_{n+1} = 1/u \sum_i f_i$. Hence,

$$f_i = \zeta_n^i (u - G(n)(u\zeta_{n+1} - f_i)). \quad (16)$$

This equation can be solved for f_i and the result can be written in the form

$$\frac{f_i}{1 - G(n)\zeta_{n+1}} = \frac{\zeta_n^i u}{1 - G(n)\zeta_n^i}. \quad (17)$$

When summed over i the definition of ζ_{n+1} gives

$$\frac{\zeta_{n+1}}{1 - G(n)\zeta_{n+1}} = \sum_i \frac{\zeta_n^i}{1 - G(n)\zeta_n^i}. \quad (18)$$

For the deterministic fractal all the coefficients ζ_n^i on a given level are equal and the sum runs over N^D non-zero elements. The recursion relation can be written as

$$\zeta_{n+1} = \frac{N^D \zeta_n}{1 + (N^D - 1)G(n)\zeta_n}. \quad (19)$$

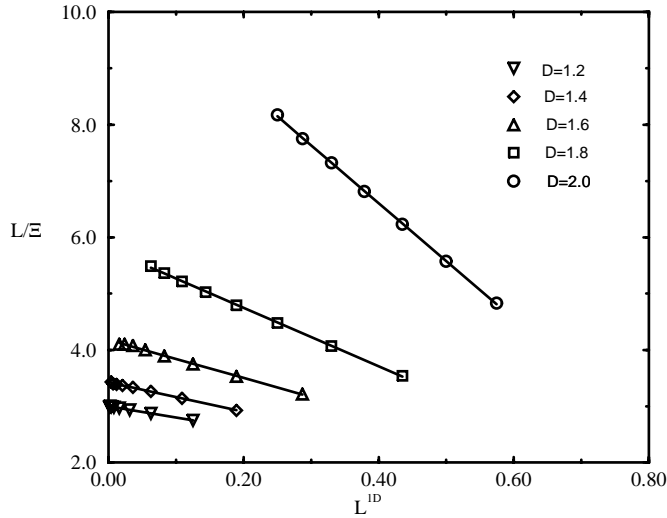


Fig. 4. The inverse friction coefficient Ξ as multiplied by the predicted asymptotic size dependence plotted against the predicted correction term L^{1-D} .

We observe that $1/\zeta_{n+1}$ is the following simple first order polynomial in $1/\zeta_n$

$$\frac{1}{\zeta_{n+1}} = \frac{1}{\zeta_n N^D} + \frac{N^D - 1}{N^D} G(n). \quad (20)$$

This gives us the sum

$$\frac{1}{\zeta_n} = \frac{1}{\zeta N^{nD}} + \frac{(N^D - 1)}{N^{nD}} \sum_{m=0}^{n-1} N^{mD} G(m) \quad (21)$$

where ζ denotes the drag of the initial monomers. Using the form of the Green's function equation (15), the sum appearing in equation (21) is a geometrical series, and the scaling properties of ζ are obtained by evaluating the sum and substituting L for N^n . We get the following mean field expression for total friction coefficient $\Xi = \zeta_n$

$$\Xi = \frac{L^\alpha}{\frac{N^D - 1}{N^{D-\alpha-1}} a + \zeta^{-1} L^{\alpha-D}}. \quad (22)$$

When $\alpha = 1$, *i.e.* the value required for the hydrodynamic interactions studied here, the scaling properties of this equation are exactly those of equation (11).

In Figure 4 the finite size scaling behavior of equation (22) are verified by the results of simulations. The inverse drag L/Ξ is plotted against L^{1-D} for various fractal dimensions and $d = 2$, $\alpha = 1$. In the simulations, stochastic fractal sets were used along with the recursion formula of equation (18). Linear behavior is observed showing that the mean field result given by equation (22) (with $M = L^D$) predicts the correct finite size scaling for the random fractals. In every lattice realization the friction coefficient was computed using the ultra-metric Green's function. Finally the results were averaged. We stress that the simulation results are not mean field result but include directly the fluctuations corresponding to

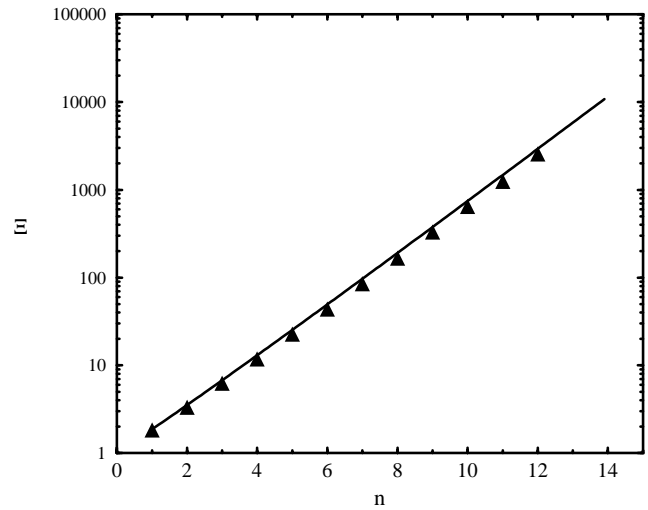


Fig. 5. The triangles show the values of the total friction Ξ calculated for the stochastic HL by use of the recursion relations. The data corresponds to lattice generation from $n = 1$ to $n = 11$ (*i.e.* for the latter the embedding lattice is of size 248×2048). The solid line shows the deterministic HL and the corresponding mean field result. The fractal dimension is $D = 1.25$, the interaction parameter is $a = 0.2$ and the number of samples is 10000.

variations in the lattice geometries. All curves are straight to a good approximation, allowing for the extrapolation to obtain $\Xi(L \rightarrow \infty)$.

In Figure 5 the drag resulting from deterministic fractals is compared with the results from random fractals. In both cases the recursion relation (18) is used. It is seen that the drag computed from the fluctuating structures is smaller than the drag resulting from the deterministic ones. Physically this is due to the fact that in the deterministic fractals the mass is more homogeneously distributed than in the random case. In an ordered homogeneous structure randomness can only increase the clustering of mass which in turn will decrease the drag. The mean field result in equation (11) is exact for the deterministic fractal. In the simulations $D = 1.25$. For larger D the difference between the deterministic fractal, or equivalently the mean field result, and the random fractal are expected to be smaller since in the non-draining regime the interior holes created by fluctuations play a weaker role.

Are arbitrary fractal sets relevant models for real polymers? As has been argued, this question reduces to a question as to the effects of the cutoffs on the fractal domain. As a way to address it we calculated ρ for a random hierarchical fractal in a the same way as was done by Zimm [14]. This procedure allows for direct comparison. We used a fractal of $D = 2$ in a three-dimensional space and calculated the drag by means of the full Oseen tensor, equation (2), using now the Euclidean metric. This requires the solution of a linear set of $3N + 3$ equations, where N is the number of "monomers". Hence, only the geometry is kept from the renormalization scheme. In order to get the asymptotic behavior results extrapolation using the above finite size scaling results was necessary.

The resulting asymptotic value of $\rho = 1.26$ is in striking agreement with the result of Zimm [14] who obtained $\rho = 1.28$ for a connected random walk chain, and also with the results of Freire *et al.* [18] who obtained $\rho = 1.27$ in a model that included long range molecular interactions. This shows that cutoff effects really do not make the random fractal too unrealistic at $D = 2$.

For the fractal dimension $D = 5/3$ corresponding to the good solvent case we did not succeed in getting the necessary asymptotic values based on the full Euclidean tensor calculations. The results indicate though that the correspondence between the hierarchical geometry and the more realistic geometries seems weaker. This suggests that the finite size effects are much stronger for lower D down to the critical dimension $D = 1$ below which a sensitivity to the small scale structure of the medium survives in the thermodynamic limit.

In equation (22), we note that the fractal dimension $D = \alpha$ separates two distinct regimes. In the hydrodynamic case of $\alpha = 1$, and for a connected structure $D > 1$, the inequality $D > \alpha$ always holds, and thus the hydrodynamic drag is controlled by the radius of gyration of the polymer. However, this is no longer true for disconnected structures where the fractal dimension is less than 1. In a different context, *e.g.* for interacting cracks in an elastic medium, $\alpha = d$ and thus all structures are in the other regime $D < \alpha$. In this case it is more instructive to rewrite equation (22) as

$$\Xi = \frac{\zeta L^D}{1 + \frac{N^D - 1}{N^D - N^\alpha} N^\alpha a \zeta L^{D-\alpha}}. \quad (23)$$

We observe that now Ξ is proportional to the mass of the fractal set and ζ . This can be interpreted as *draining*, the flow penetrates the polymer, due to only partial screening the monomers acquire an effective friction coefficient and the total friction coefficient of the polymer is just the sum of these effective friction coefficients. For the realistic case $D > \alpha$, equation (22) depends on ζ only through the correction term.

For hydrodynamic interactions $\alpha = 1$ and, when monomers are described as spheres, $a \sim 1/(6\pi\eta)$ and so the friction coefficient obeys the scaling law $\Xi \sim 6\pi\eta M^{1/D} = 6\pi\eta L$. We see that this is simply a Stokes law, the polymer acquires a hydrodynamic radius $R_H \sim L$. These results are in agreement with the results of the KR theories where the friction force inside the polymer drops to zero due to complete screening. We also note a difference in prefactors in the two regimes: in the draining regime the prefactor depends on ζ , in the non-draining regime this is not the case.

For the special case of $D = \alpha$, the coefficient scales as

$$\Xi = \zeta M \left(1 + \frac{a\zeta(N^D - 1)}{\log N} \log L \right)^{-1} \quad (24)$$

which means that there is only a logarithmic correction to the mass-like scaling, from the interactions.

3.4 Continuous limit

In the previous sections we have worked in a discrete metric space. The division of space was controlled by N . The geometrical interpretation requires that this parameter is an integer number $N \geq 2$. However, the final expression for the friction coefficient can be interpreted as a continuous function of N . The formal limit $N \rightarrow 1^+$ restores a continuous dilation invariance. Evaluating this limit for equation (22) yields

$$\Xi = \frac{\zeta M}{1 + a\zeta \frac{D}{D-\alpha} (M^{1-\alpha/D} - 1)}. \quad (25)$$

We observe that this result is close to that obtained with the mean field approach for polymer chains in Section 2.2. Both theories predict the scaling with mass $\Xi \sim M^{\alpha/D}$ and the same scaling of correction term at small scale $M^{\alpha/D}/\Xi \sim \text{const} + M^{\alpha/D-1}$

It is also possible to compare prefactors. Using the pre-averaged interaction $G = 1/6\pi\eta r$ the asymptotic expression in the non-draining regime for the HL is

$$\Xi = 6\pi\eta \left(1 - \frac{\alpha}{D}\right) M^{\alpha/D} \quad (26)$$

while the mean field Kirkwood result from Section 2.2 is

$$\Xi = 6\pi\eta \lambda \left(2 - \frac{\alpha}{D}\right) \left(1 - \frac{\alpha}{D}\right) M^{\alpha/D} \quad (27)$$

where λ is a constant characteristic of the chain lengths statistical distribution. For both theories the ratio α/D is the relevant parameter and we also notice that the prefactor goes to zero as D approaches α from above. In the HL calculations the lattice constant was set equal to unity and in the mean field chain calculations the bond length was set to unity. This does not amount to the same, so the above two expressions are not directly comparable in magnitude.

3.5 Kirkwood double sum for the HL structure

It is instructive to use the ultra metric distance in the pre-averaged Kirkwood equation (4). The latter can be considered as a mean field theory for scalar interactions just as equation (14). In fact, since the directional averages are taken at the outset in both cases, the subsequent approximations are indeed equivalent: the assumption of a deterministic fractal (with the ultra metric distance) automatically leads to $f = \langle f \rangle$ everywhere. This is nothing but the mean field average assumed in the derivation of equation (4).

As a check we carry out the alternative derivation of equation (11) by evaluating the Kirkwood double sum in the hierarchical lattice. The total friction coefficient is

$$\Xi_{\text{DS}} = \frac{M\zeta}{1 + \frac{a\zeta}{M} \sum_{i \neq j} \frac{1}{r_{ij}^\alpha}} \quad (28)$$

where M is the total mass, *i.e.* number of monomers. We define S at level n as

$$S_n = \sum_{i \neq j} \frac{1}{r_{ij}^\alpha} \quad (29)$$

where the sum runs over all occupied sites of the total HL. The sum on level $n + 1$ is given by the sums on level n

$$S_{n+1} = \sum_{i=1}^{N^d} q_i S_n^i + \sum_{i \neq j} q_i q_j M_n^i M_n^j \frac{1}{r_n^\alpha} \quad (30)$$

where $r(n) = N^{n-1}$, $q = 1$ with probability p and $q = 0$ with probability $1 - p$. The deterministic HL of $n + 1$ th order consists of N^D n th order HL and so the first sum runs over N^D elements, and the second over $N^D(N^D - 1)$ and so

$$S_{n+1} = N^D S_n + N^D(N^D - 1)N^{2nD} \frac{1}{N^{n\alpha}}. \quad (31)$$

Hence,

$$S_n = N^{nD}(N^D - 1) \sum_{m=0}^{n-1} N^{m(D-\alpha)} \quad (32)$$

$$= \frac{N^\alpha(N^D - 1)}{N^D - N^\alpha} (N^{n(D-\alpha)} - 1)N^{nD}. \quad (33)$$

Substituting this in equation (28) and $n = \log(L)/\log(N)$ yields

$$\Xi_{DS} = \frac{L^\alpha}{\frac{N^D - 1}{N^{D-\alpha} - 1} a + \zeta^{-1} L^{\alpha-D}}, \quad (34)$$

which is equation (22). This result makes it explicit that the mean field result is exact for the deterministic fractal.

4 Statistical distribution

As opposed to mean field descriptions such as the KR model, the HL model allows for the study of fluctuation effects. It is possible to study the correlation between the friction coefficient and the (fluctuating) mass within lattices of the same generation number n . The fluctuating mass in these simulations corresponds, at least qualitatively, to size fluctuations caused by conformational polydispersity in real flexible polymers or rigid self-similar structures. In the previous section (see Fig. 5) we considered the relation between the friction coefficient and the average mass at given generation numbers. Here we shall consider the fluctuations in Ξ resulting from the mass fluctuations. Figure 6 shows the result of simulations with three different values of n and a mean value $\langle k \rangle$ corresponding to a fractal dimension $D = 1.25$. The simulations were carried out on the basis of equation (18) and used random fractals. The straight line going through the three clusters of points in the figure shows that the scaling of Ξ with the average mass is consistent with that shown

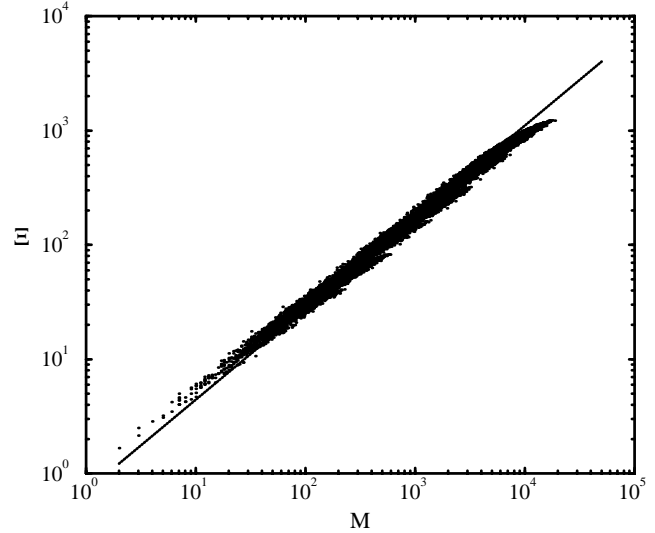


Fig. 6. Joint distribution of friction coefficient Ξ versus mass M for 6, 8, 10 generation lattices, 10 000 statistical realizations. The fractal dimension is to $D = 1.25$. The dotted line has slope $1/D$.

in Figure 5, *i.e.* that on the average $\Xi \propto L$. For each of the three n values the mass is seen to vary over one to two orders of magnitude, corresponding to fluctuations in k at each step in the generation of the HL. For a given n the drag is seen to grow less with mass for large values of the mass. Also, at high masses the clusters are seen to taper off to the right. Physically this is caused by the fact that a dense polymer will increase its drag less than a dilute one upon addition of more mass. Correspondingly there will be smaller fluctuations in the drag with mass at high densities than at lower densities. This effect is quantified in Figure 7 which shows the variance $\sigma_\chi = (\langle \Xi^2 \rangle - \langle \Xi \rangle^2)/L$ as a function of the reduced mass $\mu = M/L^D$, where M is fluctuating and $L = N^n$ is constant. We observe from the figure that $\sigma_\chi \propto \exp(-a_n \mu)$ where the number a_n seems to increase weakly with D . Again, in the high density limit the drag of any object with a given linear extension will be insensitive to the removal of a small fraction of mass. For this reason σ_χ is expected to vanish as μ increases. Hence, when μ approaches its maximum value $\mu_{\max} = 2^{(2-D)n}$ we must have $\sigma_\chi = 0$. However, it is not presently understood why the decay of σ_χ is exponential.

5 Conclusion

We have introduced a hierarchical model for the computation of hydrodynamic properties of polymers modeled as fractals and demonstrated the numerical efficiency of this scheme. Although this model does not employ the sophisticated ϵ -expansion technique it uses a hierarchical renormalization technique in the sense that the results are obtained by mapping small scale structure to larger scale structure. The recursion relations with which this mapping is carried out has been solved exactly for deterministic fractal structures. We have shown that on the mean

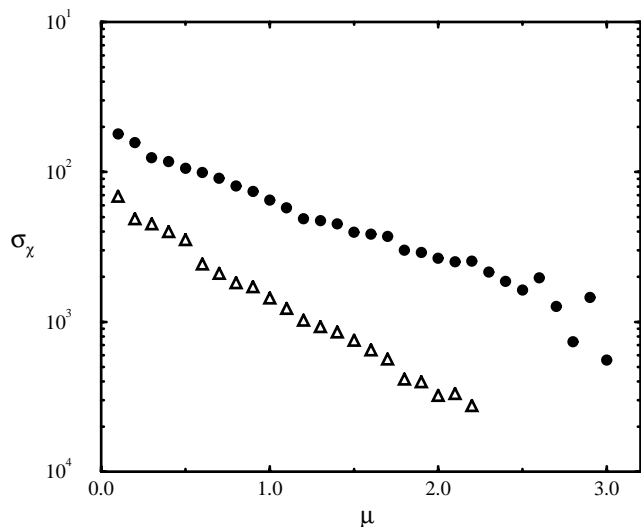


Fig. 7. Standard deviation σ_χ to reduced mass μ , $\chi = \Xi/M^{1/D}$ in a semi-log plot for fractal dimension $D = 1.25$ (sphere) and $D = 1.5$ (triangle).

field level the scaling aspects of this theory coincides with a Kirkwood Riseman type theory for polymers of arbitrary fractal dimension. The recursion relations of the hierarchical procedure based on the ultra metric can be used as a general means of computing the drag of any mass distribution. Hence they can be used to study fractals where the density fluctuations are tuned more systematically than in the present context. This would be of interest for the study of the level of drainage in polymers of smaller fractal dimension where the fluctuation dependence is expected to increase.

We have used the hierarchical model to compare the drag of fluctuating and deterministic structures, and we have used it to obtain the dependence of drag fluctuations on density fluctuations.

In the pre-averaged KR theory the coupling between vector components of the forces are totally neglected, *i.e.* the non-diagonal terms of the Oseen tensor are set to zero. It is possible that these terms may be taken into account in the ultra metric distance construction, leading to a set of coupled recursion relations. The HL model permits the study of fluctuations in the polymer drag for any distribution of polymer masses. While the present study demonstrates the ability of the HL model as a tool for studies of fluctuations in Ξ , a more systematic study with more realistic polymer mass histograms would be of great interest. This, as well as a study of full vectorial interactions, is likely to lead to further insight into the unsolved and

complicated problem of non pre-averaged hydrodynamic interactions.

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