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Dynamical Renormalization of Polymers in Quenched Disorder: Long-Time Diffusion and Short-Time Anomalies.

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Abstract. – A single self-repelling polymer chain embedded in ($2 < d \leq 4$)-dimensional space and moving in a quenched short-ranged random potential is analysed with the help of the dynamical renormalization group. The renormalization group flow of the time scale is discussed for the first time. The results allow for the evaluation of the mean-squared displacement of the centre of mass in the limit of weak disorder. In contrast to the linear time dependence of a Markovian process, we find a strong acceleration of the motion on short time scales, represented by some anomalous chain-length–dependent power law. For long times we recover normal diffusion with some drastically reduced chain-length–dependent diffusion coefficient.

The behaviour of long-isolated-chain molecules in a random environment poses a challenging problem, which has found some interest recently. Most work [1, 2] concentrates on static properties like the size or the free energy of a single chain. Investigations of dynamical properties [2-4] are rare, even though these properties are most strongly affected by a spatially random (but time-independent, *i.e.* «quenched») external potential V. To explain the relevance of an analysis of dynamical phenomena, let us recall that the partition function of a finite chain per unit volume

$$\mathcal{Z}[V] = \lim_{\Omega \to \infty} \frac{1}{\Omega} \mathcal{Z}[V, \Omega] \tag{1}$$

is self-averaging. (Ω is the volume of the embedding space.) This is a strict consequence of the ergodic theorem. In standard terms it implies that the quenched average, *i.e.* the average over $F = -\ln \mathcal{Z}[V]$, is equivalent to the annealed average, *i.e.* the average over $\mathcal{Z}$. Now, the annealed average has been analysed in great detail [5]. It has been found that for weakly fluctuating potentials correlated over some finite distance, only the second moment v_0 of the local potential fluctuations is relevant. The only effect of disorder consists in reducing the excluded-volume constant u_0, which measures the self-repulsion of chain segments. u_0 is to be replaced by $w_0 = u_0 - v_0$. This argument holds for all quantities which are defined as an average over the (infinite) volume. For instance, the end-to-end distance R_{E} of a chain of polymerization index («length») N_0 behaves as $R_E^2 \underset{N_0 \to \infty}{\sim} N_0^{2\nu}$, $\nu \approx 0.588$ in three dimensions, irrespective of disorder, as long as w_0 stays positive.

To outwit this argument, one either

i) increases the disorder so that w_0 becomes negative and the polymer chain collapses,

or

ii) fixes the position of the chain in the volume, thus breaking ergodicity.

Both possibilities have been discussed to some extent, but we do not expect the result to be universal. They will depend on the type of disorder or the polymer model used.

In contrast, in dynamics we find interesting effects of weak disorder also for freely moving chains embedded in an infinite volume. These effects are new, universal and non-trivial. Consider, for instance, the diffusion coefficient $D(N_0)$. In the absence of a random potential, the polymer coil diffuses like a Brownian particle of the same mass, the diffusion coefficient being given as

$$D_0(N_0) = 2d \frac{\gamma_0}{N_0}, \tag{2}$$

where γ_0 is some microscopic friction coefficient and d denotes the dimension of the system. The self-repulsion alone does not affect the centre-of-mass motion. (We ignore hydrodynamic interactions.) On the other hand, diffusion is clearly slowed down by a random external potential. The effect should be more pronounced for longer chains, since these are more strongly bound to favourable regions of the potential. Indeed, a rough hopping-type model including the statistics of large potential fluctuations [3] suggests an exponential decrease of $D(N_0)$, proportional to $\exp[-\mathrm{const}\, v_0 N_0^{2-\nu d}]$.

In this communication we report the results of a dynamical renormalization group (RG) calculation of the centre-of-mass motion, discussing both short- and long-time scales. We use the standard model of polymer dynamics (see [2], for instance). Its equilibrium properties are governed by the dimensionless effective potential

$$\mathscr{H} = \frac{1}{4l_0^2} \sum_{j=1}^{N_0} (\boldsymbol{r}_j - \boldsymbol{r}_{j-1})^2 + u_0 l_0^d \sum_{0 \leqslant i < j \leqslant N_0} \delta^d(\boldsymbol{r}_i - \boldsymbol{r}_j) + \sum_{j=0}^{N_0} V(\boldsymbol{r}_j). \tag{3}$$

The segment coordinates $\boldsymbol{r}_j = \boldsymbol{r}_j(t)$ fix the polymer configuration. The first part of $\mathscr{H}$ incorporates chain connectedness, involving the microscopic length l_0 which determines the average size of the segments. The second part represents the excluded-volume interaction of strength $u_0 > 0$. The last part is a one-body potential, which is taken to be a Gaussian-distributed random variable of second moment $\overline{V(\boldsymbol{r})\, V(\boldsymbol{r}')} = v_0 l_0^d \delta^d(\boldsymbol{r} - \boldsymbol{r}')$. (The bar denotes averaging over disorder.) Dynamics is incorporated via the Langevin equation

$$\frac{\partial}{\partial t} r_{j\alpha} = -\gamma_0 \frac{\partial}{\partial r_{j\alpha}} \mathscr{H} + \xi_{j\alpha}, \qquad j = 0, \dots, N_0, \quad \alpha = 1, \dots, d, \tag{4}$$

where the noise $\xi_{j\alpha}(t)$ is Gaussian distributed with second moment $2\gamma_0 \delta_{jj'} \delta_{\alpha\alpha'} \delta(t - t')$. Except for possible long-range forces due to solvent effects, or long-range correlations in the potential distribution, which we ignore, this model contains all terms which near $d = 4$ are relevant or marginal in the RG sense. In the limit of large N_0, the results can therefore be expected to be universal, provided the model is renormalizable. We should note, however, that in any physical realization of three-dimensional quenched disorder the connectedness of the disordered medium introduces long-range correlations, which might limit the applicability of our results.

To evaluate the model we use standard methods of critical dynamics as derived in ref. [6] and applied to polymer dynamics in ref. [7]. We calculate the Green's functions

$$G_{ab}(\boldsymbol{q}, t) = \overline{\langle \exp[-i\boldsymbol{q}(\boldsymbol{R}^{(a)}_{\text{c.m.}}(t) - \boldsymbol{R}^{(b)}_{\text{c.m.}}(0))]\rangle} \qquad (a, b = 1, 2) \tag{5}$$

giving the time dependence of the correlations among the centre-of-mass $\boldsymbol{R}_{\text{c.m.}}(t)$ of the same ($a = b$) or two different ($a \neq b$) polymers. (As usual the pointed brackets stand for the average over the random force $\xi_{j\alpha}(t)$, and the time interval is extended to $-\infty < \tau < \infty$ so that the system equilibrates before the first measurement occurring at $\tau = 0$.) The free theory ($u_0 = v_0 = 0$) is easily solved by introducing Rouse coordinates. We then perform perturbation theory in u_0 and v_0 up to one-loop order. To exemplify the typical structure we give the expression for the centre-of-mass motion

$$R^2(t, N_0) = \overline{\langle (\boldsymbol{R}^{(1)}_{\text{c.m.}}(t) - \boldsymbol{R}^{(1)}_{\text{c.m.}}(0))^2\rangle} = -\Delta_q |_0 G_{11}(\boldsymbol{q}, t) =$$

$$= 2d\frac{\gamma_0}{N_0}\left(1 - \frac{1}{2}(4\pi)^{-d/2} v_0 N_0^{(4-d)/2}\int_0^T \mathrm{d}\tau \frac{T-\tau}{\tau} F(\tau)\right), \tag{6}$$

where

$$F(\tau) = \int_{-1/2}^{+1/2} \mathrm{d}x\,\mathrm{d}y[\tau + (x - y) + A(\tau, x - y) + A(\tau, x + y)]^{-(d+2)/2}, \tag{7}$$

$$A(\tau, x) = \int_0^{\tau} \mathrm{d}\tau' \sum_{k=1}^{\infty} \cos(\pi k x) \exp[-\pi^2 k^2 \tau'/2], \tag{8}$$

and $T = \gamma_0 t/N_0^2 l^2$. The function $A(\tau, x)$ contains the effect of the internal relaxation modes of the chain and x or y fix the position of the interacting segments j, j' along the chain ($x = j/N_0 - 1/2$, etc.). The detailed derivation of such one-loop (and some two-loop) results will be given elsewhere.

The result (6) exhibits the typical problems of the unrenormalized perturbation theory: the one-loop correction is proportional to $N_0^{(4-d)/2}$ and thus diverges in the limit of long chains. This problem can be solved by renormalization which amounts to studying the behaviour of the theory under a change of the microscopic length scale. We map the original theory defined by l_0, $w_0 = u_0 - v_0$, v_0, N_0, γ_0 to a renormalized counterpart l_{R}, w_{R}, v_{R}, N_{R}, γ_{R}, constructed such that all macroscopic observables stay invariant. The scale invariance of the theory allows us to determine the change of w_{R}, v_{R}, N_{R}, γ_{R} under an infinitesimal change of l_{R}. These «RG equations» can be integrated from $l_{\text{R}} \sim l_0$, where $w_{\text{R}} \sim w_0$ etc. to $l_{\text{R}} \sim R_{\text{E}}$, where the renormalized chain essentially consists of a single segment: $N_{\text{R}} = 1$. With $N_{\text{R}} = 1$, the coefficients of the renormalized perturbation theory are of order 1, and the problem is solved, provided that integrating the flow equations up to $l_{\text{R}} \sim R_{\text{E}}$ yields renormalized couplings which are not too large. This in particular is guaranteed if the couplings for $l_{\text{R}}/l_0 \gg 1$ tend to some small fixed-point value.

Since renormalization of polymer theory has been extensively discussed in the literature (see, for instance, [8], we omit all technical details except for stating that we use the method of dimensional regularization and minimal subtraction, implying the expansion of all quantities in powers of $\varepsilon = 4 - d$. With $G_{ab}(\boldsymbol{q}, t)$, $a, b = 1, 2$, we have sufficient observables to uniquely extract the renormalization of all parameters. An important difference to the static problem should be noted. As pointed out above the static theory involves only the combination $w_0 = u_0 - v_0$. In contrast, in dynamics u_0 and v_0 can be disentangled by their different time dependence. The self-repulsion $u_0 \delta^d(\boldsymbol{r}_i(t) - \boldsymbol{r}_j(t))$ is strictly local in time, whereas the quenched average over the random potential yields an effective attraction which is strictly independent of time, involving a factor $\int \mathrm{d}t\, \mathrm{d}t'\, \delta^d(\boldsymbol{r}_j(t) - \boldsymbol{r}_i(t'))$. This allows for a unique derivation of the flow equations for w_R, v_R and should be contrasted to a previous attempt [2] to calculate the diffusion coefficient, where the flow of the couplings was deduced from a static «replica» approach, without exhibiting a relation of replica theory to the dynamic problems. Still, the dynamical method happens to reproduce the replica equations.

The RG equations suffer from the lack of a stable fixed point for v_R: for $l_\mathrm{R}/l_0 \gg 1$, v_R runs away to infinity. As a result, dynamical correlations do not obey standard power laws like $R_\mathrm{E} \sim N_0^\nu$. Presumably due to this result, the approach [2] has not been pursued further. However, even though this feature keeps us from treating the strong disorder limit $v_0 > 0$, $N_0 \to \infty$, *i.e.* $v_\mathrm{R} \to \infty$, we still can use renormalized perturbation theory to get non-trivial results in the region $v_\mathrm{R} \ll 1$.

In our further discussion we set $N_\mathrm{R} = 1$, and we restrict ourselves to the fixed point $w_\mathrm{R} = w^*$, which governs the polymer chain in the excluded-volume limit. The well-known static result $l_\mathrm{R} = l_0 (bN_0)^\nu$ follows, where b is some non-universal constant. The RG flow of the disorder coupling takes the form

$$c v_0 (bN_0)^{-\nu\omega_{12}} = \frac{v_\mathrm{R}}{1 + v_\mathrm{R}/\bar{v}} (1 + O(v_\mathrm{R})), \tag{9}$$

where $\bar{v} = \varepsilon/4 + O(\varepsilon^2)$, $\omega_{12} = -\varepsilon/2 + O(\varepsilon^2)$, $\varepsilon = 4 - d$. The non-universal constant c relates $v_\mathrm{R}(l_\mathrm{R} = l_0)$ to v_0. Note that the same result follows from the replica formalism [2].

Some comments on eq. (9) are appropriate:

i) To leading order in ε the identity $-\nu\omega_{12} = 2 - \nu d = \alpha$ is valid. We believe that this result holds generally: α/ν is the Hausdorff dimension of the set of points common to two uncorrelated self-avoiding walks. The expansion in the (weak) interaction among the walks should thus proceed in powers of $v_0 N_0^\alpha$. It is amusing to note that the occurrence of α is consistent with the Harris criterion [9], though the argument is completely different.

ii) v_R depends on v_0, N_0 only via the combination $v_0 N_0^{-\nu\omega_{12}} = v_0 N_0^\alpha$. It may be shown that this holds to all orders in v_R, provided $v_0 \ll 1$.

iii) Equation (9) is valid only for $v_\mathrm{R} \ll 1$, implying the limit of weak disorder: $c v_0 (bN_0)^\alpha \ll 1$. It does not imply that we may neglect the denominator on the r.h.s. In the sense of the ε-expansion the range of v_R is bounded by $v_\mathrm{R} \sim \varepsilon$, implying $v_\mathrm{R}/\bar{v} = O(1)$.

The completely new aspect of the present problem is the renormalization of γ_0. We find the RG flow

$$\gamma_\mathrm{R} \equiv \frac{\gamma_\mathrm{R}}{N_\mathrm{R}} = \frac{\gamma_0}{N_0}\left(1 + \frac{v_\mathrm{R}}{\bar{v}}\right)^{-I/2 + O(\varepsilon)} (1 + O(v_\mathrm{R})), \tag{10}$$

where $I = \int\limits_0^\infty \mathrm{d}\tau \left(1 + \int\limits_0^\tau \mathrm{d}t (2\pi t)^{-1/2} \exp[-1/2t]\right)^{-3} = 3.587$ is the remainder of the short segment—short time—singularity of the Rouse modes, which can be isolated from eq. (6) by a Poisson transform on $A(\tau, x)$. Equation (10) shows that γ_R decreases rapidly with increasing v_R.

The renormalized counterpart of eq. (6) to first order of the ε-expansion reads

$$\frac{R^2(t, N_0)}{2\,dl_R^2} = (1 + 2.218 v_R)\,\bar{t} + \frac{v_R}{4}\int_0^\infty d\tau[\bar{t}\Theta(\tau - \bar{t}) + \tau\Theta(\bar{t} - \tau)]\,F(\tau), \tag{11}$$

where $\bar{t} = \gamma_R t/l_R^2$. For $\bar{t} \sim 1$ the chain has moved a distance of the order of its mean-squared end-end distance $R_E^2 \sim 2\,dl_R^2$. This time also coincides with the longest internal relaxation time.

Evaluating eq. (11) for $\bar{t} \rightarrow \infty$, we find normal diffusion ($R^2(t) \sim t$) with the diffusion coefficient

$$D(N_0) = \lim_{t \rightarrow \infty} \frac{R^2(t, N_0)}{t} = 2d\gamma_R(1 + 2.218 v_R) = D_0(N_0)\frac{1 + 2.218 v_R}{(1 + v_R/\bar{v})^{l/2}}. \tag{12}$$

As a result $D(N_0)/D_0(N_0)$ only depends on $v_R = v_R(v_0 N_0^\alpha)$. If evaluated for $d = 3$, in the interval $0 \leqslant c v_0 (b N_0)^\alpha \leqslant 0.2$, corresponding to $0 \leqslant v_R \leqslant 1$, $D(N_0)/D_0(N_0)$ almost linearly drops down from 1 to 0.18. So at least for the initial decrease of the diffusion constant, we do not recover the exponential law of ref. [3].

The first-order term of the short-time behaviour of eq. (11) is dominated by a $\bar{t} \ln \bar{t}$ contribution. Following the standard philosophy of exponentiating logarithmic singularities, we find the following equivalent form:

$$\frac{R^2(t, N_0)}{2\,dl_R^2} = \bar{t}^{\,1 - v_R l/4}(1 + 0.806 v_R + O(v_R^2)). \tag{13}$$

So on times $\bar{t} \ll 1$, the chain on the average moves faster than without disorder, the diffusion being anomalous. In fig. 1 we plot $r^2 = R^2(t, N_0)/(2\,dl_R^2)$ as a function of $T = D_0(N_0)\,t/(2\,dl_R^2)$. To get an impression of the overall behaviour, we have combined the short-time asymptotics (13) and the long-time asymptotics $r^2 = D(N_0)\,T/D_0(N_0) + 0.372 v_R$. Note that the length—or time—scales are independent of the disorder strength. So fig. 1 allows for a direct comparison of the diffusion of chains of the same length N_0 in disorder of different strength v_R,

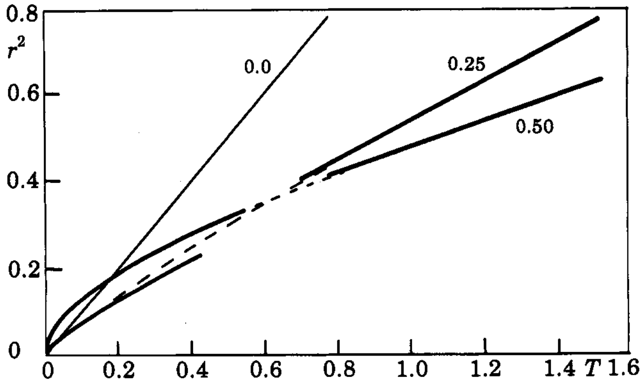

Fig. 1. - $r^2 = R^2(t, N_0)/(2\,dl_R^2)$ as a function of $T = D_0(N_0)\,t/(2\,dl_R^2)$ for $v_R = 0.0$, 0.25, 0.5. The thick lines give the asymptotic behaviour for $v_R = 0.25, 0.5$ as calculated from eq. (9) ff. The broken lines interpolate between the short-time and the long-time behaviour. For comparison we included free diffusion ($v_R = 0.0$).

respectively, v_0. The disorder-induced acceleration of the short-time motion is clearly brought out.

Some final comments on these results may be appropriate:

i) The memory terms effectively introduced by the quenched random potential render the time evaluation of the process non-Markovian. For a Markovian process, $R^2(t, N_0) = \text{const}\cdot t$ necessarily holds on all time scales. In the presence of the potential the diffusion in thermal equilibrium becomes anomalously faster in times $t \ll T_0 \sim l_R^2/\gamma_R$ ($\bar{t} \ll 1$) and it diffuses slower in times $t \gg T_0$.

ii) We interpret the short-time accelerated diffusion as relaxation of subchains from unfavourable regions, which are populated to some extent in thermal equilibrium. We suspect that every extended flexible object in a random potential of shorter coherence length should show a similar effect. For polymers this effect is universal, due to their universal structure on intermediate length scales.

iii) The anomalous short-time diffusion is governed by the disorder- and chain-length-dependent exponent $1 - (I/4)v_R$. Such a behaviour has also been observed in Monte Carlo simulations [10, 11]. (In their terms we discuss the «intermediate» regime after some non-universal short-time regime, which is suppressed by renormalization.) The resource of MC data is best for Gaussian chains [10] ($w^* = 0$, $\nu = 1/2$). It is easy to modify our calculations correspondingly. When analysing the anomalous slopes in the plots of $\log R^2(t, N_0)$ against $\log t$ (p. 3085 in [10]) for different v_0 and N_0, we find results not inconsistent with our calculation.

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