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1990 J. Phys. A: Math. Gen. 23 L1003

(http://iopscience.iop.org/0305-4470/23/18/011)

J. Phys. A: Math. Gen. **23** (1990) L1003-L1008. Printed in the UK

**LETTER TO THE EDITOR**

# Pulsed electrophoresis of point particles in random media

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Received 15 June 1990

**Abstract.** We investigate the motion of a point particle moving on a random substrate and subject to an oscillating electric field. Several situations are explored and interesting scaling laws are obtained. In particular, non-monotonic behaviour of the mobility against applied field is found.

There is a growing interest in the problem of (charged) polymer chains driven by an oscillating electric field [1-6]. This problem is of tremendous practical importance, since it was realized [1-2] that the separation of chains of different molecular weights is much more efficient in an oscillating field than in a constant field. Non-monotonic dependence of the chains mobility with molecular weight have also been reported [3]. Some models aiming to understand these facts have been proposed and studied [3-6].

The aim of this work is more modest since we study the motion of point particles on a disordered substrate; hence we completely neglect the internal degrees of freedom of the polymer—which are in fact argued [5, 6] to play an important role. Rather, we investigate the rather rich situation arising from the intertwining of disorder and oscillating driving field, on model 'substrates'. Two particular models will be specifically mentioned: the percolation cluster—at ($p = p_c$) and away from the critical point, and the 'random walk' substrate—which is simply an internally linear structure, which has the geometrical properties of a random walk. New and rather general results are obtained; in particular, we find that the amplitude of motion $A$ is always a decreasing function of the applied field $F(A \sim F^{-\alpha})$ for strong bias. This results from the trapping of the particles in 'fjords' or in backbents (figure 1). Our arguments nicely account for the numerical results of Harder *et al* [7], who precisely studied the motion of a random walker on the percolation cluster ($p = p_c$) in the presence of an oscillating bias. Further numerical work is suggested, in particular off-criticality.

This paper is organized as follows. We first recall the general results pertaining to a static field. Then we show how in the AC case, a period of oscillation may be decomposed into an active phase, where the particle may move, and a passive phase, during which the field is too strong, and the particle trapped. Simple arguments then lead to the field and frequency dependence of the amplitude $A$. We finally discuss the important case where both a small static field and a stronger oscillating field are present.

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0305-4470/90/181003+06$03.50  

We thus first consider the case of a particle evolving on a disordered isotropic subtrate, (not necessarily fractal), of mass dimension $d_f$ and spectra dimension $d_s$. In the absence of an external field, the particle diffuses with an exponent $\nu = d_s/2d_f$: $R \sim a(\omega_0 t)^\nu$ ($a$ is a microscopic length and $\omega_0$ a microscopic frequency). When a static external field $F$ is applied, a very general relation holds for 'short' times, which echoes the fluctuation dissipation theorem in statistical mechanics: it reads (see e.g. [8, ch 5]):

$$\bar{R}(t)_F = \frac{\bar{R}^2(t)_{F=0}}{\mathrm{d}kT} F \tag{1}$$

where the bar denotes thermal averaging, and $d$ is the dimension of space. Note in particular that it is valid for a given disordered sample (no average over samples). The derivation of (1) only assumes that the total energy gain due to the presence of the field is small compared to $kT$, that is: $\bar{R}(t)_F F \leqslant kT$, or $t \leqslant t^* = \omega_0^{-1}(kT/Fa)^{1/\nu}$.

For longer times, no general expression exists. However, for certain classes of disordered lattices on which diffusion is normal [8], one has (for weak fields) $\bar{R}(t)_F = (D/kT)Ft$, which is Einstein's relation ($D$ is the diffusion constant). In contrast, a stretched polymer made of $t$ monomers has an extension given by [9] $\bar{R}(t)_F \sim tF^{(1-\nu)/\nu}$.

For a general disordered substrate, the long time drift in a static field depends upon the value of the 'skewness exponent' $\zeta$ of the structure, defined in the following way: Consider two points $A$, $B$ belonging to the structure, such that $|AB| = r$. As the paths going from $A$ to $B$ on the structure are not necessarily straight, the walker will occasionally have to struggle against the field and wait for sufficient thermal energy to carry its way through. If the longest unfavourable sequence of steps the particle has a finite probability to make to reach $B$ is $l$ long, $\zeta$ is defined as

$$l \underset{r\to\infty}{\sim} r^\zeta. \tag{2}$$

For example, if the substrate is an isotropic random walk, $\zeta = 1$. This is also expected to be the case for the percolation cluster since dead ends of all length scales and random orientations are known to exist.

The drift behaviour is then obtained by writing Arrhenius's law: by definition of $l$, one has $t \sim t^* \exp(Fl/kT)$, which is valid if $t \gg t^*$. Hence:

$$R \sim \frac{kT}{F} \ln^{1/\zeta}\left(\frac{t}{t^*}\right) \tag{3}$$

($t \gg t^*$). This behaviour, with $\zeta = 1$, has indeed been observed numerically [10, 11] on the percolation cluster. The same result was argued to hold for general isotropic linear structures† [8, 12, 13].

The case $\zeta = 0$ (which arises e.g. if a finite length scale exists in the problem) is more subtle. The biased random walk structure is amenable to an exact treatment: it is easy to show [8, 13] that this situation is equivalent to the problem of a one-dimensional particle in a random (biased) force field. Following [8, 13], one may thus show that the relevant parameter is $\mu = kT/Fl_d$, where $l_d$ is the 'diffusion length' of the structure (see figure 1). For $\mu < 1$, on finds‡ [8, 13, 14]:

$$x \sim x_1 \left(\frac{t}{t_1}\right)^\mu. \tag{4}$$

† The derivation given in [12] is somewhat more involved than the simple argument given above.
‡ $x_1 = kT^2/E^2a$, $t_1 = x_1^2/D$.

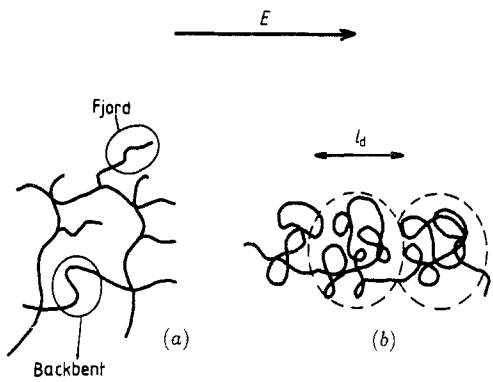


**Figure 1.** Typical substrates considered in this work. Figure 1(*a*) shows 'fjords' and 'backbents', which act as traps when an external field is present. Figure 1(*b*) shows the stretched 'random walk' structure, which is isotropic for scales smaller than $l_d$ and one dimensional for larger length scales.

We believe that the same mechanism which underlies (4) (i.e. the appearance of a broad distribution of local trapping times [8, 11, 13, 15]) is present in the case of the percolation cluster with a finite correlation length $\xi$. Thus (4) should hold in that case, with $\mu \simeq kT/F\xi$. A continuously varying exponent, decreasing with increasing bias, was also found in [15], for the percolation cluster in the presence of a 'topological' bias (we only consider 'Pythagorean' [15] bias).

The main point to be emphasized is that, due to randomness, the external field indeed drives the particle for short times, but that its main effect is to virtually freeze the particle in a deep induced potential well—or more precisely only allow logarithmic progression for longer times.

We shall first study the case of a structure with no characteristic scale, such as the percolation cluster at $p = p_c$, or the isotropic random walk. The crossovers induced by a finite correlation length will be explored below.

The external field oscillates at a frequency $\omega$, and we shall write:

$$E(t) = E_0 \sin \omega t. \tag{5}$$

Let us focus on the first half of period, $0 \leqslant t \leqslant \pi/\omega$. For short times, the field $E(t)$ is also small and is equal to $E_0\omega t$. Linear response applies, leading to† [16] $R(t) \sim E(t)\bar{R}^2(t)_0 \sim E_0\omega t^{1+2\nu}$. This is valid as long as typical energy barriers are smaller than $kT$, or for times less than $t^*$ (active phase) such that

$$\bar{R}(t^*)E(t^*) \sim E_0^2\omega^2 t^{*2+2\nu} \sim kT \tag{6}$$

or

$$t^* \sim (E_0\omega)^{-1/(1+\nu)}. \tag{7}$$

If $t^*$ is larger than $1/\omega$ (corresponding to $E_0 < \omega^\nu$), linear response is always valid, and the amplitude of motion simply reads $A(\omega, E_0) \sim \bar{R}(\omega^{-1}) \sim E\omega^{-2\nu}$.

This corresponds to a current $J(\omega, E_0) = \omega A(\omega, E_0) \sim E_0\omega^{1-2\nu}$: the conductivity is frequency dependent. This is a well known result: see e.g. [16, 18].

† We shall omit in the following 'trivial' dependences on $a$, $kT$, $\omega_0$.

In the opposite case, for times between $t^*$ and $\pi/\omega - t^*$, the field is too strong for the particle to move (passive phase), and the total amplitude of motion $A$ is fixed at

$$A(\omega, E_0) = \bar{R}(t^*) \sim (E_0\omega)^{-\nu/(1+\nu)} \tag{8}$$

hence corresponding to a current $J(\omega, E_0) \sim E_0^{-\nu/(1+\nu)}\omega^{1/(1+\nu)}$ which, although increasing with frequency, is a decreasing function of the field.

The two regimes described above can be summarized in a single scaled expression: introducing the crossover field $E^* = \omega^{\nu}$, one has

$$A(\omega, E_0) \equiv E_0\omega^{-2\nu} f\left(\frac{E_0}{E^*}\right) \tag{9}$$

with $f(0) = 1$ and $f(x) \sim x^{-\alpha}$ with $\alpha = (1+2\nu)/(1+\nu)$.

Harder *et al* [7] proposed precisely such a scaling expression to rationalize their numerical data concerning a biased particle on the two-dimensional precolation cluster at $p = p_c$. The found $E^* = \omega^{0.35}$, which is in very good agreement with the accepted value of $\nu = d_s/2d_f$. Their numerical determination of the scaling function $f$ is given in figure 2, and its asymptotic behaviour compared with our prediction of $\alpha \sim 1.26$. Again, agreement is rather good. It would be interesting to investigate this problem on other structures, such as the random walk substrate, where $\nu = \frac{1}{4}$ and $\alpha = \frac{6}{5}$ in any dimension.

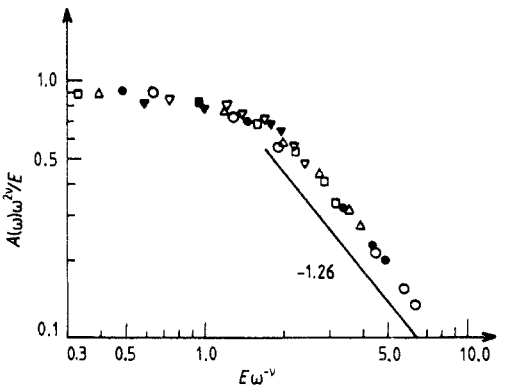


**Figure 2.** The numerical results of [7], showing $A(\omega, E_0)/E_0\omega^{-2\nu}$ as a function of $E_0/\omega^{\nu}$. The bold line is our prediction for the large argument behaviour of the scaling function: $f(x) \sim x^{-1.26}$.

It is rather easy to extend the previous arguments to the case where a length scale $\xi$ separates a fractal behaviour at small scales from a Euclidean behaviour (characterized by normal diffusion $\nu = \frac{1}{2}$) at large scales. Essentially, one must compare $\bar{R}(t^*)$ and $\xi$. Nevertheless, a slight subtlety is associated with the fact that, for $\zeta = 0$ (as is the case for the percolation cluster for $p \neq p_c$), one may not decompose very neatly the period of oscillation into an active phase and a passive phase: even in the strong field period, the particle may still creep according to $x \simeq t^{\mu}$ (with $\mu = kT/E_0\xi$). Hence, the 'phase diagram' represented in figure 3 only gives the different asymptotic regimes in the plane $(E_0, \omega)$; however, the shaded region requires a more precise treatment to obtain subdominant terms. The most interesting point is that, for sufficiently strong fields, the amplitude of motion always decreases with the field. For low frequencies,

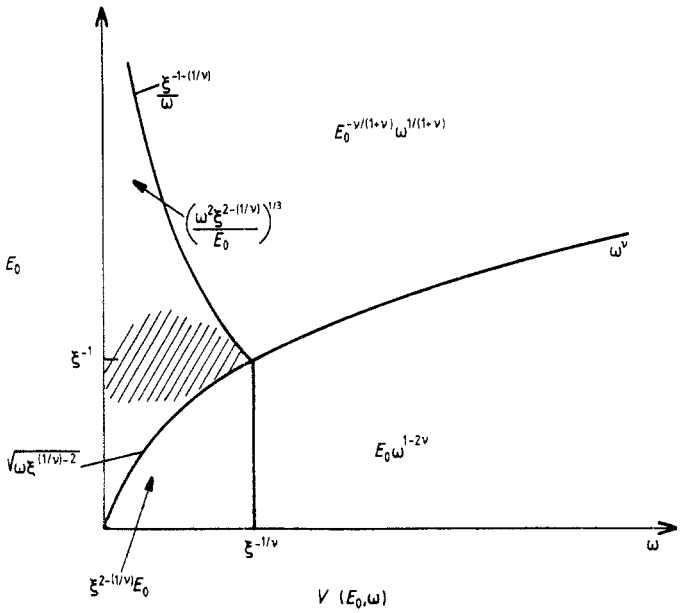


**Figure 3.** The 'phase diagram' in the plane $E_0$, $\omega$ for a fractal with a finite correlation length $\xi$. The behaviour of the 'itensity' ($\sim\omega A(\omega, E_0)$) is shown in each region (the plain lines are in fact crossover lines). At low frequencies and low field, one observes the usual linear response. At higher frequencies, the fractal diffusion law appears ($\nu \neq \frac{1}{2}$), but the current is still linear in applied field. The high-frequency, high-field region corresponds to (8): the particle moves only during a small fraction of the field period, and it moves sufficiently little to probe only the 'fractal' region. Finally, in the high-field, low-frequency region, the particle is basically trapped, but it moves sufficiently far to enter the 'Euclidean' diffusion regime.

this decay is governed by Euclidean diffusion and one has:

$$A(\omega, E_0) \sim \left(\frac{\xi^{2-1/\nu}}{E_0\omega}\right)^{1/3}. \tag{10}$$

In a practical situation, one hopes to separate different particles simply by applying a static field. Different particles with different mobilities would, after a sufficiently long time, evolve in well-resolved packets. As we have emphasized, a constant field on a random substrate is most inconvenient since it leads not only to trapping but also to clustering (as shown by Golosov [19; see also 8] for the isotropic random walk substrate). If one superimposes a sufficiently strong oscillating field, the particle may escape deep trapping regions: that is the experimental situation of [17]. The problem is now to determine the static mobility $m$ of the particle (defined as $\bar{R}(t) = mE_s t$, where $E_s$ stands for the static field), as a function of the frequency and amplitude of the AC field.

Again applying simple crossover and scaling arguments, one finds—restricting for simplicity to $\xi = \infty$—the following regimes:

$E_s > E_0$: strong trapping, $m = 0$

$E_s \ll E_0$: three timescales must be compared: $t^*$, $\omega^{-1}$ and $t_s^* = \omega_0^{-1}(kT/E_s)^{1/\nu}$. This leads to three regimes:

I. $E_0 < \omega^\nu$. In this case, the 'blocking' times $t^*$, $t_s^*$ are larger than the period of the field; usual linear response thus holds unperturbed: $m \simeq \omega^{1-2\nu}$.

II. $E_0 > \omega^{\nu}$, but $E_s < (E_0\omega)^{\nu/(1+\nu)}$. Now the 'blocking' time associated with the AC field is shorter than both $1/\omega$ and $t_s^*$. For each period, the average displacement is thus $(E_s/kT)\bar{R}^2(t^*)_0$. Hence, using (7), one obtains: $m \simeq E_0^{-(2\nu/(1+\nu)}\omega^{(1-\nu)/(1+\omega)}$.

III. $E_0 \gg E_s > (E_0\omega)^{\nu/(1+\nu)}$. The 'static blocking time' $t_s^*$ is now the shortest time in the problem. Since $E_0\omega t_s^*$ is much smaller than $E_s$ in this regime, the role of the AC field is only to allow the particle to make jumps of size $l \sim kT/E_s$ from a given trapping region to another. Since those jumps are preferentially made in the direction of the static field (since $E_s l \sim kT$) the mobility becomes a decreasing function of the field:

$$m \simeq \omega/E_s^2.$$

The mobility is thus an increasing function of the frequency. For a fixed value of $E_s < E_0$ and for example for $\nu = \frac{1}{3}$, one finds $m(\omega) \sim \omega$ for low frequencies, crossing over to a $\omega^{1/2}$ behaviour for higher frequencies.

We have seen that applying an alternating bias to a point particle diffusing in a random environment leads to a quite complex dependence on the field and frequency. In particular, a general non-monotonic behaviour of the amplitude of motion as a function of the field is found. Electrophoresis of long chains is certainly an even richer situation. We, however, hope that the ideas and methods developed in this letter could be useful to understand some aspects of pulsed electrophoresis. In particular, the experiments described in [17], where a kind of 'hook' is attached to the DNA chains, exhibit trapping and frequency-assisted diffusion quite similar to the phenomena described here.

We wish to thank L Valentin and E Guyon for drawing our attention to the problem of pulsed electrophoresis. Discussions with J L Viovy and J Prost have been most useful.

## References

[1] Schwartz D C 1984 *C.R. Cantor Cell* 7 67
[2] Carle G F and Olson M V 1984 *Nucleic Acid Res.* **12** 5647
Smith C L and Cantor C R 1986 *Nature* **319** 701
Carle G F, Frank M and Olson M V 1986 *Science* **236** 65
Chu G, Vollrath D and Davies R W 1986 *Science* **234** 1582
[3] Noolandi J, Rousseau J, Slater G, Turmel C and Lalande M 1987 *Phys. Rev. Lett.* **58** 2428
[4] Lalande M, Noolandi J, Turmel C, Rousseau J and Slater G 1987 *Proc. Natl. Acad. Sci. USA* **84** 8011
[5] Viovy J L 1988 *Phys. Rev. Lett.* **60** 855; 1988 *Europhys. Lett.* 7 657
[6] Deutsch J M and Madden T L 1989 *J. Chem. Phys.* **90** 2476
[7] Harder H, Bunde A and Havlin S 1986 *J. Phys. A: Math. Gen.* **19** L609
[8] Bouchaud J P and Georges A 1990 *Phys. Rep.* in press
[9] de Gennes P G 1985 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[10] Bunde A 1988 *Random Fluctuations and Pattern Growth* eds H E Stanley and N Ostrowsky (Dordrecht: Kluwer)
Guyon E and Roux, S 1987 *Europhys. Lett.* **4** 175
[11] Havlin S, Bunde A, Glaser A and Stanley H E 1986 *Phys. Rev.* A **34** 3492
Havlin S and Ben-Avraham D 1987 *Adv. Phys.* **36** 695
[12] Roman H E, Schwartz M, Bunde A and Havlin S 1988 *Europhys. Lett.* 7 389
[13] Bouchaud J P, Comtet A, Georges A and Ledoussal P 1990 *Ann. Phys.* in press
[14] Derida B and Pomeau Y 1982 *Phys. Rev. Lett.* **48** 627
[15] Bunde A, Havlin S, Stanley H E, Trus B and Weiss G H 1986 *Phys. Rev.* B **34** 8129
[16] Ohtsuki T and Keyes T 1984 *Phys. Rev. Lett.* **52** 1177
[17] Ulanovsky L, Drouin G and Gilbert W 1990 *Nature* **343** 190
[18] Gefen Y, Aharony A and Alexander S 1983 *Phys. Rev. Lett.* **50** 77
[19] Golosov A 1984 *Comm. Math. Phys.* **92** 491