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Short Communication

Remarks on the dynamics of random copolymers

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Abstract. — We discuss the dynamics of random AB copolymers, and show that a glassy, quasi-frozen phase is reached as soon as \( \chi_{AB} \sqrt{\frac{N}{N_e^2}} \simeq 1 \) (where \( N \) is the number of monomers, \( N_e \) the entanglement length and \( \chi_{AB} \) the Flory interaction parameter). This criterion is satisfied for much smaller \( \chi_{AB} \) than the value for which segregation occurs: \( \chi_{AB} \simeq 1 \). The relaxation time of weakly disordered chains is furthermore found to take the empirical form \( N^{3+\mu} \), where \( \mu \) can reach significant values for certain choices of \( \chi_{AB} \) and the fraction of B-monomers.

In recent years, several papers have aimed at describing the thermodynamic properties of random copolymers or heteropolymers [1-5]. The motivation for these studies comes from biology (heteropolymers as models of biological molecules) and also from the technological interest of synthetic copolymers. A very interesting work in this respect is the one of Fredrickson and Milner [3], who investigate the phase diagram of random A-B copolymer melts as the Flory parameter \( \chi_{AB} \) and the polymerisation reactivity ratios (i.e. the correlations between A and B sequences along the chains) are varied. Such an equilibrium phase diagram could be helpful for designing copolymers by control of temperature or the polymerisation procedure [3]. From a theoretical point of view, reference [3] also report the appearance of an interesting multicritical ('Lifschitz') point in the phase diagram. All these predictions, however, are only valid if equilibrium can indeed be reached, i.e. if some kind of dynamical freezing does not occur. The aim of this note is to discuss the corresponding dynamical effects, and to show that, because of the randomness, diffusion and relaxation are drastically slowed down for long chains. New reptation laws are derived. In the interesting quasi-homogeneous limit (i.e. when the fraction \( \phi \) of B monomers is small), we show that the disentanglement time grows with the molecular weight \( N \) as roughly \( N^{3+\mu} \), where \( \mu > 0 \) is an effective exponent which depends both on \( \phi \) and \( \chi_{AB} \).

Let us start by discussing the motion of one mobile random copolymer of length \( N \) in a melt of similar, but immobile (for example, much longer) chains. As usual, we assume that the

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chain moves by curvilinear diffusion along its own contour, and suppose for the moment that the entanglement length is $N_e = 1$. If $\phi(1-\phi) \chi_{AB} < 0.5$, the equilibrium state is homogeneous [3], and it is reasonable to assume no particular correlations in the relative positions A's and B's.

The interaction energy of the ‘marked’ chain in a given configuration $C$ is given by $V(C) = \sum_{i=1}^{N} v_i(R_i)$, where $R_i$ is the position of the $i^{th}$ monomer and $v_i(R)$ is the potential created by all other chains at site $R$, which also depends on the nature of the $i^{th}$ monomer (A or B). One can always write $v_i(R) \equiv v(R) + \sigma_i w(R)$, where $\sigma_i = +1$ if the $i^{th}$ monomer is of type A, and $-1$ if it is of type B. Now let us bring the polymer to a new configuration $C'[s]$ by translating the whole chain along its tube by a curvilinear length $s$. Defining $\Delta V(s) = V(C) - V(C'[s])$ and using $< \ldots >$ to mean averaging over the 'chemical' disorder (not the Boltzmann average), the averages $< \Delta V(s) >$ and $< \Delta V(s)^2 >$ are given by: $< \Delta V(s) > = 0$ (the problem is statistically translational invariant) and, for $0 < s \leq N$,

$$< \Delta V(s)^2 >= 2s \overline{v^2} + 2N \overline{w^2} \tag{1}$$

We have assumed for simplicity complete chemical randomness along the chain, i.e. $< \sigma_i > = 1 - 2\phi \equiv m$ and $< \sigma_i \sigma_j > = m^2 = \delta_{ij}$. In equation (1), $\overline{v^2} = < v^2 > - < v >^2$ and $\overline{w^2} = < w^2 > - < w >^2$ measure the fluctuations in potential energy. In order of magnitude,

$$\overline{v} \sim \overline{w} \sim \sqrt{\phi(1-\phi)\overline{z^2}} \chi_{AB} V T \tag{2}$$

where $z^*$ is the effective number of neighbours to a given monomer (2 of which belong to the same chain and hence cannot contribute to the fluctuation of potential energy). For $s > N$, the tubelike environment of the chain is completely replaced and equation (1) saturates at the value $< \Delta V(s \geq N)^2 >= 2N(\overline{v^2} + \overline{w^2})$.

![Diagram](image)

Fig. 1. — Typical variation of the potential energy $V(s)$ seen by an random copolymer as a function of the ‘distance’ travelled along the chain, $s : V(s) \simeq \overline{v} \sqrt{N + s}$.

Equation (1) has a simple meaning: the mobile chain evolves in a random potential landscape schematically represented in figure 1. In fact, this problem is very close to the 'one dimensional random force model' [6-9] for which quite a number of results are known. For our purpose, however, it is sufficient to understand from (1) that the characteristic energy barrier, which the chain will have to overcome in order to travel a distance $s < N$, grows roughly like
Fig. 2. — Phase diagram in the plane \((N, \chi_{AB})\). The dot-dashed line corresponds to the segregation line for homopolymers, the thick dashed line is the dynamical crossover line above which freezing occurs, while the plain horizontal line is the equilibrium segregation line [3].

\[ \varepsilon(s) \sim \tilde{\sigma}\sqrt{(s + N)} \]

Hence, a simple Arrhenius-Kramers argument (see e.g. [9]) leads to the following law for time \(t(s)\) required for the polymer to move a distance \(s\) along its tube:

\[ t(s) \sim \left\{ \frac{s^2}{2D} \right\} \exp \left[ \frac{\sqrt{2N\tilde{\sigma}^2 + 2s\tilde{\sigma}^2}}{kT} \right] \]

(3)

where \(D\) is the usual curvilinear diffusion constant of the whole chain \((D \propto N^{-1})\), and the expression between curly braces is the inverse 'trial frequency' on scale \(s\). From equations (2, 3), one sees that a dynamical crossover line appears in the plane \(N, \chi_{AB}\) (see Fig. 2) for \(\chi_{AB} \approx N^{-1/2}\), i.e., much below the equilibrium segregation line \(\chi_{AB} \approx 1\) [3]. Below this crossover line, the usual reptation laws are only slightly affected, whereas above this line, the chain is trapped in deep energy valleys, which drastically slows down its progression.

It is possible to understand this crossover line as an 'aborted segregation line' in the following sense: if a chain is divided into segments of length \(P\), each segment will present (through statistical fluctuations) a relative excess of A (or B) monomers, of order \(P^{-1/2}\). One could think to arrange the chains in such a way that the 'A-rich' segments sit together in regions of size \(\sim \sqrt{P}\) (and similarly for the 'B-rich' segments), leading to a micro phase separation. This sorting out of segments costs an entropy \(\sim P^{-1}\) per monomer, while the resulting energy gain is of order \(\chi_{AB}kTP^{-1/2}\) per monomer. The optimal \(P\) would thus be of order \(P^* \sim \chi_{AB}^2\), and the condition \(P^* \leq N\) would coincide with \(\chi_{AB} \geq N^{-1/2}\). The reason why the system does not phase separate is because a local increase of density of A must by exactly compensated by a decrease of density elsewhere, so that the total energy gain per monomer is in fact of order \(\chi_{AB}kTP^{-1}\) and not \(\chi_{AB}kTP^{-1/2}\). Hence, the fluctuation energy \(\chi_{AB}\sqrt{N}\) cannot induce strong static correlations. However, it does lead to important dynamical effects.
In the case where \( \tilde{w} = 0 \) (corresponding to a homopolymer in a sea of heteropolymers), one finds from equation (3) that the chain 'creeps' logarithmically [7, 9] – rather than reptates – along its tube:

\[
s \propto \begin{cases} 
\sqrt{2Dt} & \text{for } t \ll t^* \\
\delta^* \log^2 \left( \frac{t}{t^*} \right) & \text{for } t^* \ll t \ll t^{**}
\end{cases}
\]  

(4)

where \( \delta^* = \left( \frac{kT}{u} \right)^2 \) is the length such that the energy barrier \( e(s) \) is of order \( kT = t^* = \frac{s^*}{2D} \) is the time needed to diffuse a distance \( s^* \) along the tube. Finally the escape time from the tube \( t^{**} \) obeys \( s(t^{**}) = N \), which gives:

\[
t^{**} = \frac{N^2}{D} \exp \left[ \sqrt{2N \tilde{v}} \right]
\]  

(5)

Note that the condition \( s^* \ll N \) for the existence of the logarithmic regime in equation (4) is equivalent to \( \chi_{\text{AB}} \gg N^{-1/2} \), as described above. For time scales longer than \( t^{**} \), the tube configuration is completely renewed and the effective energy barrier ceases to grow (see Fig. 1). Assuming Brownian statistics for the chain in real space (though see remark (a) below), the center of mass motion then reads:

\[
R(t) \propto \begin{cases} 
(2Dt)^{1/4} & \text{for } t \ll t^* \\
\sqrt{s^* \log \left( \frac{t}{t^*} \right)} & \text{for } t^* \ll t \ll t^{**}
\end{cases}
\]  

(6)

with the asymptotic real space chain diffusion constant \( D_{\text{creep}} \) is given by:

\[
D_{\text{creep}} = D_{\text{rep}} \exp \left[ \sqrt{2N \tilde{v}} \right]
\]  

(7)

where \( D_{\text{rep}} \propto N^{-2} \) is the diffusion constant obtained from the usual reptation theory [10, 11]. When \( \tilde{w} \neq 0 \), the logarithmic regime in equation (6) is only observable for \( N > s > N_{\text{co}} \), and the asymptotic diffusion constant is obtained by replacing \( \tilde{v}^2 \) with \( \tilde{v}^2 + \tilde{w}^2 \) in equation (7).

Several important remarks are now necessary:

a) **The motion of the other chains.** Of course, our assumption that the other chains are immobile is incorrect if one is to discuss a situation where all chains have approximately the same size. The disorder is thus 'annealed' rather than 'quenched', and the potential seen by a given chain becomes time dependent: \( V(C, t) \). The slow motion of all the chains, however, induces strong time correlations in \( V(C, t) \). A self consistent argument, in the spirit of those developed in [9, 12] shows that in fact the Sinai diffusion in \( \log^2 t \) is unchanged (although the prefactors will change). The basic idea is that since the correlation time of the medium is the renewal time \( t^{**} \) itself, the energy barriers hindering the motion of the chains will persist until \( t^{**} \). Hence we believe that equations (4-7) are qualitatively correct, although possibly with a smaller coefficient of the chain length \( N \). The fact that the disorder is annealed rather than quenched was thus implicitly assumed in obtaining equation (6). Indeed, in the case of a quenched disorder, the configuration of a chain is no longer Gaussian (\( R \propto \sqrt{N} \)) but is characterized by \( R \propto N^\nu \) (with \( \nu \neq 1/2 \), the precise value of which is still the matter of some debate [13]) [14].
b) **Chain contour length fluctuations.** Above we have assumed that reptation occurs only by rigid translation of the chain as a whole along the tube. This is the conventional reptation description and omits fluctuations in both the tube length and the local monomer density within the tube, arising from the internal dynamical modes of the chain [11]. However, we believe that the above results are more general: indeed suppose one moves the chain from configuration \( C \) to configuration \( C' \) such that \( s_1 \) monomers do not change position at all, \( s_2 \) monomers occupy positions already taken by different monomers of the same chain in \( C \). In this case

\[
< \Delta V (s_1, s_2)^2 > = 2s_2 \tilde{\omega}^2 + 2(N - s_1) \tilde{\omega}^2
\]

which in effect does not differ greatly from equation (1).

c) **The entanglement blobs.** If the entanglement length \( N_e \) is not equal to one, then \( N \) should presumably be replaced by \( \frac{N}{N_e} \) in the above formulae. However, one should also replace the strength of the fluctuating potentials \( \tilde{\omega}, \tilde{\nu} \) by effective potentials \( \tilde{\nu}_e, \tilde{\omega}_e \) acting on a 'blob' of size \( N_e \). If no strong correlations exist on the scale of the blob (which is certainly likely as long as \( \chi_{AB}N_e^{1/2} \ll 1 \)), these effective potentials can be estimated using the replica method and perturbation theory, and noting that within each blob, the chain behaves as a ideal polymer. One finds that the effective \( \tilde{\nu}_e, \tilde{\omega}_e \) are given by \( N_e^{1/4} \tilde{\nu}, \tilde{\omega} \). This differs from the result \( N_e^{1/2} \tilde{\nu}, \tilde{\omega} \) found by assuming that the potential energy is the sum of \( N_e \) independent random variables [15]. In other words, the thermal motion preaverages the random potential and reduces the fluctuations. [This preaveraging cannot take place at scales \( > N_e \) because of the tube constraint.]

We thus find that equation (7) must be modified to:

\[
D_{\text{creep}} = D_{\text{rep}} \exp - \left[ 2N \frac{\tilde{\omega}}{N_e^{1/4}kT} \right]
\]

d) **The semi-dilute case.** As is well known [10], the role of the monomers is in this case played by the ‘concentration blobs’, each of which contains \( g \simeq c^{-5/4} \) monomers (where \( c \) is the concentration). Contrarily to the above case, however, the number of contacts per blob is a order one, and thus the fluctuating potentials do not get multiplied by \( g^{1-d/4} \). One thus expect that \( D_{\text{creep}}(N,c) \equiv D_{\text{creep}}(N^{e^{5/4}},1) \) as is the case for ordinary reptation (see [16] for a recent experimental discussion).

e) **The quasi-homogeneous limit.** Let us finally consider in slightly more detail the case of a melt of random copolymers such that the fraction of B is very small: \( \phi \ll 1 \). Then the above arguments suggest that the renewal time grows as \( t^{**} \propto N^3 \exp(q\sqrt{N}) \), where \( q = \eta \sqrt{\phi(z^* - 2)}\chi_{ab}N_e^{-1/4} \), with \( \chi_{ab} = \frac{\chi_{AA} - \chi_{AB}}{kT} \) the difference between the reduced interaction energy of AA contact and that of an AB contact, and \( \eta \) a number of order one (the calculation of which would require a more precise model). We have plotted the above prediction in log-log coordinates, for \( z^* = 6 \), and different values of \( \phi \) and \( \eta \chi_{ab} N_e^{-1/4} \). The range of \( N \) was the experimental one, i.e. \( 10^2 - 10^5 \).

As can be seen in figure 3, one observes in general quite a good straight line, with an effective exponent slightly greater than 3. Hence, empirically one has: \( t^{**}(N) \propto N^{3+\mu} \), where the value of \( \mu \) for different choices of \( \phi \) and \( \chi_{ab} \) is reported in table I. These values are obviously only indicative, since \( \mu \) is quite sensitive to the range of \( N \) chosen for the linear fit. Nevertheless, the interesting conclusion of this ‘toy-model’ is that a very small proportion of monomers of a different chemical nature is enough to increase the effective exponent for the terminal relaxation time. It is conceivable that residual ‘impurities’ in the chemical sequence of homopolymers might play an important role in melts at large molecular weight, and interfere with attempts to
Fig. 3. — Log-log plot of the relaxation time $t^{**}$ versus $N$ for a rather small proportion of B monomers ($\phi = 10^{-4}$), and $\eta'_{AB}N_e^{-1/4} = 0.5$. The best power law fit for $100 \leq N \leq 10^5$ is found to be $t^{**} \propto N^{3.41}$.

Table I. — Values of the effective exponent $\mu$ for different choices of $\phi$ and $\eta'_{AB}N_e^{-1/4} = 0.05$. The * corresponds to values of $\mu$ less than 0.05, while the – corresponds to cases where the power law fit it unacceptable. The range of $N$ chosen for the fit is $100 \leq N \leq 10^5$, although formula (7) only makes sense for $\phi N > 1$.

<table>
<thead>
<tr>
<th>$\eta'_{AB}N_e^{-1/4}$</th>
<th>$f$</th>
<th>$10^{-4}$</th>
<th>$10^{-3}$</th>
<th>$10^{-2}$</th>
<th>$10^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.5$</td>
<td></td>
<td>0.41</td>
<td>1.29</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$0.1$</td>
<td></td>
<td>0.08</td>
<td>0.26</td>
<td>0.82</td>
<td>–</td>
</tr>
<tr>
<td>$0.05$</td>
<td></td>
<td>0.04</td>
<td>0.13</td>
<td>0.41</td>
<td>1.29</td>
</tr>
<tr>
<td>$0.01$</td>
<td>*</td>
<td>*</td>
<td>0.08</td>
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<tr>
<td>$0.005$</td>
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<td>*</td>
<td>0.04</td>
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precisely determine this exponent (see e.g. [17]). The fact that the viscosity exponent could be increased by trapping effects was already advocated in several papers [18-21], although with underlying mechanisms quite different from the one proposed here.

In conclusion, let us emphasize the two main points of this paper:

i) The dynamics of random copolymers melts should be extremely slow as soon as $\phi_{AB}N_e^{1/4} > 1$, i.e. for values of $\phi_{AB}$ much smaller (for long chains) than the one corresponding to the equilibrium segregation line $\phi_{AB} \approx 1$. The dynamics of a labelled chain could reveal an
interesting logarithmic diffusion behaviour for intermediate times.

ii) Even in the case of very weakly disordered copolymers, one may expect significant departures from the ‘ideal’ reptation theory - with effective exponents for the renewal time significantly greater than 3.

We hope that these remarks will trigger some experiments on this subject. In particular, it would be extremely interesting to monitor the fraction $\phi$ of ‘foreign’ atoms in order to check that the effective viscosity or diffusion exponent shows a systematic dependance on this quantity, as predicted above.

Acknowledgements.

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References

[14] The dynamics of shorter chain in a effectively quenched random medium made up of long chains would require the knowledge of the exponent $\nu$ mentioned above, and also of the ‘energy’ exponent $\omega$ describing the scaling of the energy fluctuations with $N$ [13]. One may conjecture that the Sinai regime in equation (6) will be modified as $s \propto \log^\nu t$ and the renewal time $t^*$ will grow as $N^3 \exp \left[ \frac{\nu}{\epsilon t} N^\omega \right]$ (but see [22]).
[15] Note that the average free energy is, in $d$ dimensions and for a swelling exponent $\nu$, or order $\frac{\nu}{\epsilon t} N^2 - \nu d$ [18, 21]. This is however not the quantity which enters the calculation of the barrier heights, but rather its fluctuations, which are found to be $\sim N^{1-\nu d/2}$