

# Mechanical properties of dynamically disordered networks

Abraham Nitzan<sup>1</sup>

*Department of Chemical Physics, the Weizmann Institute of Science, Rehovot, 76100, Israel*

Rony Granek

*School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv, 69978, Israel*

Mark Ratner

*Department of Chemistry, Northwestern University, Evanston, IL 60208, USA*

Ionic motion in polymeric ionic conductors has been recently described in the framework of dynamic percolation theory (DPT) or, more generally, dynamic disorder hopping (DDH). In these models the polymer network above the glass transition is modelled as a random bond network in which the random bond distribution evolves in time with rate characteristic to the polymer motion. The present paper deals with the mechanical properties of such networks. We present a simple analysis of the viscosity of such dynamically disordered networks, thus relating a characteristic network relaxation time to the local (microscopic) viscosity of the polymer. If the same time is assumed to govern ionic transport, we obtain a relation between the ionic diffusion rate and the polymer viscosity. Estimates of the ionic diffusion based on this model are consistent with experimental observations.

## 1. Introduction

In a recent series of articles [1] we have developed a dynamic bond percolation model for ionic motion in polymeric ionic conductors and, more generally, for diffusion in strongly interacting systems. Such an approach has been also taken by other workers in a similar context [2]. In polymeric ionic conductors, ionic salts are dissolved in the polymer, usually polyether, network, forming systems with relatively high ionic mobilities above their glass transition temperatures [3]. Unlike in crystalline or glassy ionic conductors, these systems are characterized by strong correlations between the ionic motion and between the segmental motion of the underlying host polymer. Dynamic

bond percolation theory models this segmental motion by the dynamics of the randomly assigned bonds, whereupon available and broken bonds interchange, creating transient pathways and blocks for the ionic motion. These bond dynamics freeze at and below the glass transition temperature, freezing also long-range ionic motion if the density of available bonds (pathways) is below the percolation threshold of the random network. This is the glass limit of the model.

It is intuitively clear that the same motions that enable the ionic diffusion are also associated with the mechanical properties of the polymer above glass transition temperature. It is therefore tempting to try to relate the bond renewal dynamics to the mechanical properties of this model. The aim of this paper is to make this connection by providing a simple calculation of the viscosity of the same network.

<sup>1</sup> On leave from Tel Aviv University, Tel Aviv, Israel.

**DC viscosity in the dynamic bond percolation model**

For simplicity, we limit our discussion to simple square or cubic networks in which an average fraction  $q = 1 - p$  of the bonds are broken. Each bond is fluctuating between its 'on' and 'off' states according to the simple kinetic equation [4]

$$\begin{aligned} \frac{df_\alpha(1, t)}{dt} &= \frac{1}{\tau} [pf_\alpha(0, t) - qf_\alpha(1, t)], \\ \frac{df_\alpha(0, t)}{dt} &= \frac{1}{\tau} [qf_\alpha(1, t) - pf_\alpha(0, t)], \end{aligned} \quad (1)$$

where  $f_\alpha(i, t)$  is the probability to find bond  $\alpha$  in state  $i$  (available,  $i = 1$ , or unavailable,  $i = 0$ ) at time  $t$ .  $\tau$  is the characteristic evolution time of the random network. The bond length,  $a$ , is taken as the characteristic segment size.

To make the connection of this picture to mechanics, we assume that mechanical relaxation is associated with the same bond fluctuation dynamics as described by eq. (1). Below the glass transition temperature,  $T_g$ , the (existing) bonds are elastic and are characterized by a frequency,  $\omega$ . Above  $T_g$ , the additional renewal dynamics expressed by eq. (1) become possible. Only then can an external force cause a permanent macroscopic distortion. Consider our network above  $T_g$  under shear (fig. 1) with velocity gradient  $v/a$ . The shear adds an additional mechanism for bond breaking. We assume that a bond connecting two nodes breaks when the relative distortion of the two

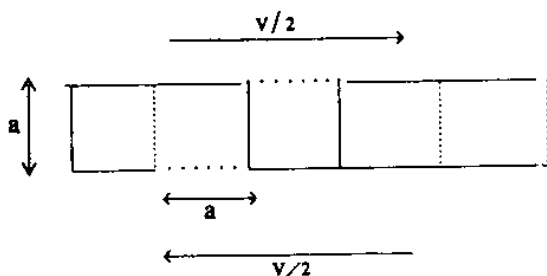


Fig. 1. A schematic representation of shear in the random network. Parameters are defined in the text.

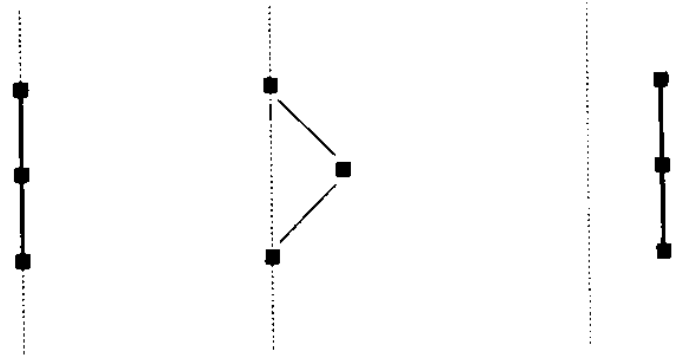


Fig. 2. Relaxation of local distortions in a dynamic random network.

nodes is equal to  $a$ . Thus, in the presence of shear, eqs. (1) take the new form

$$\begin{aligned} \frac{df_\alpha(1, t)}{dt} &= \frac{1}{\tau} [pf_\alpha(0, t) - qf_\alpha(1, t)] \\ &\quad - \frac{v}{a} f_\alpha(1, t), \\ \frac{df_\alpha(0, t)}{dt} &= \frac{1}{\tau} [qf_\alpha(1, t) - pf_\alpha(0, t)] \\ &\quad + \frac{v}{a} f_\alpha(1, t). \end{aligned} \quad (2)$$

This implies that the steady state density of intact bonds ( $p(v) = f_\alpha^{ss}(1)$ ) is

$$p(v) = \frac{p}{1 + (v\tau/a)}. \quad (3)$$

For small shear velocities ( $\ll 1$  cm/s) the denominator in eq. (3) is close to 1 and  $p(v) = p$ . This is the limit of interest in the present discussion.

It is important to realise that this extremely simple model is characterized by only two timescales. If a sudden force is applied to a given node, the suddenly formed distortion is associated with the local elastic force constant or the local frequency,  $\omega$ . However, because of the possibility of bonds to reorganize as described above, any local strain will relax with the characteristic time,  $\tau$  (fig. 2). It is seen that even this simple model already contains typical viscoelastic features.

Denoting by  $m$  the typical segment mass, the distortion  $\Delta x$  is related to the force  $F$  by  $\Delta x = F/m\omega^2$ . The shear velocity under steady state conditions is therefore  $v = \Delta x/\tau$ . The dissipation

rate per bond is therefore  $Fv = m\omega^2v^2\tau$ . The dissipation rate per unit volume is thus

$$\frac{dE}{V dt} = \frac{m\omega^2\tau p(v)}{a} \left(\frac{v}{a}\right)^2. \quad (4)$$

On the other hand, the dissipation per unit volume is given also by  $\eta(\nabla v)^2 = \eta(v/a)^2$ . Putting also  $\omega = kc - c/a$  where  $c$  is the speed of sound, we finally obtain

$$\eta = \frac{mc^2 p}{a^3} \tau, \quad (5)$$

where we have used  $p \sim p(v)$  for the fraction of intact bonds. Note that if the condition  $v\tau/a \ll 1$  does not hold, the dissipation is no longer proportional to  $(\nabla v)^2$  (with velocity independent coefficient) and this simple picture breaks down.

Equation (5) is the desired relation between  $\eta$  and  $\tau$ . Taking  $c = 3 \times 10^4$  cm/s,  $m = 100$  hydrogen mass units,  $a = 10$  Å and  $p = 0.5$ , we obtain  $\tau(\text{sec}) \cong 10^{-8}\eta$ , where  $\eta$  is expressed in cgs units.

### 3. Discussion

The estimate (5) of the relation between the network relaxation time (or network 'renewal' time [1a-c]) is based on an extremely oversimplified model. The main drawback of this estimate lies in the obviously erroneous assumption that a single relaxation time,  $\tau$ , is associated with the mechanical relaxation (eq. (4)) and the 'bond' (pathways for ionic motion) fluctuations (eq. (2)) which dominate the ionic diffusion and conductivity. In fact there is a multiplicity of relaxation times associated with relaxation processes occurring on multiple length scales. For the same reason, the viscosity that enters into eq. (5) is not the macroscopic viscosity but a microscopic local quantity associated with the local segmental motion. The important point is that this quantity is accessible to experimental measurements, e.g. by Brillouin scattering [5] thus providing at least in principle a quantitative way to relate the ionic mobility to mechanical relaxation as obtained from light scattering studies.

A treatment of mechanical relaxation in polymer networks within the framework of dynamic

percolation theory can be given in more quantitative terms. Granek and Nitzan [6] have recently developed an effective medium theory (EMT) for the high-frequency small-amplitude motions in a random harmonic bond network, thus generalizing (within the EMT) the Alexander-Orbach theory [7] of vibrations in random spring networks (e.g. glasses) to the case which include bond dynamics described by eq. (2) (e.g. polymers above their glass transition). Work in this direction is continuing.

### 4. Conclusion

Ionic diffusion in polymer/salt complexes has been discussed in terms of a dynamic disorder hopping model in which two times enter: one is the inverse elastic frequency. The other is a renewal time, which characterizes the dynamical relaxation of the host. By constructing a simple model for shear relaxation, we have shown here that a renewal time can be associated with the microscopic, local viscosity, and that (eq. (5)) this time is in fact directly proportional to the viscosity.

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