Aspects of Dynamic Disorder in Charge Transport in Polymers

V. M. Kenkre

Center for Advanced Studies and Department of Physics
University of New Mexico, Albuquerque, NM 87131

ABSTRACT

Aspects of dynamic disorder in charge transport in polymers are investigated. Basic issues such as polaron formation, the validity of semiclassical arguments and the memory function method of mobility calculation are studied.

keywords: polarons, selftrapping, dynamic disorder, semiclassical

Charge transport in polymers is characterised by disorder. Of the two primary kinds of disorder, static disorder is of special importance to polymers because the environment is not translationally invariant, the site energies being inequivalent and the transfer interactions being dependent on the site locations. Dynamic disorder, on the other hand, by which is meant the destruction of translational invariance that the charge carrier feels as a result of strong interactions with the vibrations of the solid, is present in all solids including polymers. Its understanding provides the theoretical underpinning for all considerations of transport in these systems. This talk is aimed at issues of dynamic disorder which have come to the fore as a result of very recent work.

The most productive manner of envisaging carrier motion is in terms of relative values of the various energies involved. The carrier bandwidth V describes the speed of the bare carrier motion in the absence of other effects. In systems such as electrons moving in metals or inorganic semiconductors, V is of the order of an eV and thus overwhelms all other energies. Bloch states provide a good description of transport and other interactions are simply weak perturbations on V. In polymers this intellectually dull state of affairs does not exist. The bandwidth is hundreds of times smaller than in metals and all energies compete with one another: the bandwidth V, the phonon energy $\hbar\omega$, the polaron binding energy $\hbar g^2\omega$, various dispersion quantities, and even the thermal broadening k_BT and the static broadening α. As a result of this fierce competition, perturbation methods fail and entirely new theoretical concepts have to be developed. It is the difficulty, and therefore the interest, of the problem that makes recent re-investigations into dynamic disorder, specifically polaron concepts, important.

Preceding the most recent work on these issues, three periods can be identified in the development of polaron concepts. The first spans the 50's and 60's and is represented by the original ideas of Landau,[1] Pekar,[2] Holstein,[3] and Toyosawa.[4] In that period the basic concept was developed that a charge carrier in strong interaction with vibrations surrounds itself with a lattice distortion, and thus makes itself heavier, impairing mobility and sometimes causing selftrapping. The second period spanned the 70's: dressing transformations[5–9] and field theoretic techniques[1,10–12] were developed, often in the context of excitonic polarons. One of the outcomes of this period was the memory function approach (based on generalised master equations) which was successful in providing a satisfactory explanation of carrier transport in aromatic hydrocarbons. The third period spans

0-8194-1885-4/95/$6.00

the 80's and proceeded in large part without interaction with existing polaron studies, attention being focused on the so-called Davydov solitons. Semiclassical equations of motion and the discrete nonlinear Schrödinger equation[13–21] were used to explore a number of phenomena in biological systems.

The work that is being reported in this talk consists of the examination of the validity of previous polaron and soliton ideas through an inspection of *exact* solutions of a highly *simplified* system. The advantage of this work lies in the fact that the solutions are free of the uncertainties of the validity of any approximation methods. The disadvantage is that there is concern that the simplification that one needs to invoke to make possible exact solutions might eliminate some of the essential features of the underlying physics. However, this is the normal state of affairs in physics for any nontrivial problem, and progress is only possible by combining this kind of analysis with approximation-based investigations. The work we report[22,23] has been strongly motivated by the analysis of Grigolini et al.[24–28]

The basic Hamiltonian in standard notation is

$$\hat{H} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{mn} a_m^\dagger a_n + \sum_q \hbar\omega_q (b_q^\dagger b_q + \frac{1}{2}) + N^{-1/2} \sum_{m,q} \hbar\omega_q g_q \exp(iq \cdot R_m)(b_q + b_{-q}^\dagger) a_m^\dagger a_m. \quad (1)$$

Solutions to this problem have never been found except in extremes of $V = 0$ and $g = 0$. We simplify the problem into that of a degenerate dimer interacting with one vibrational mode, and solve the problem to *any* desired accuracy via well-defined numerical methods. The quantum mechanical solutions are then compared with various approximations and conclusions drawn unambiguously about the validity of the latter.

Of the approximations we investigate, two are particularly important: the semiclassical approximation, and the memory function approach. We begin with the former. The semiclassical approximation is the basis of an enormous amount of soliton literature and is also representative of a great deal of 'intuitive' thinking in polaron physics. Thus, the idea of selftrapping can be attained perfectly easily through semiclassical arguments and a key ratio that is ubiquitous is $\hbar g^2\omega/V$. If this ratio is large, the intuitive expectation is that polarons are the carriers in question and selftrapping occurs. If it is small, free motion is supposed to occur.

Our exact calculations show that these expectations are not universally correct. It is easy to show that, when the ratio $\hbar g^2\omega/V$ is large w.r.t. 1, the semiclassical arguments clearly predict selftrapping whereas the exact evolution is quite free if the phonon energy is larger than, or even of the order of, the carrier bandwidth. The discrepancy is dramatic and shows without doubt the dangers of semiclassical arguments. This part of our analysis agrees with and supports the conclusions drawn by Grigolini et al.[24–28] and early remarks of Brown et al.[29,30] Highly useful are several additional findings of our studies. We find the exact solutions characterised by a time scale hierarchy. Features of the exact evolution include rapid oscillations and envelope decay followed by 'silent runs' in which carrier transport stops in a much more drastic manner than as represented by semiclassical evolution, and repeated recurrences and eventual tunneling. The silent runs, the recurrences and the tunneling are completely beyond the reach of the semiclassical analysis. We also find not only that the semiclassical approximation improves steadily as the vibrational frequency decreases but that an unambiguous limit exists in which the semiclassical argument is exact. This limit corresponds to an infinitely massive oscillator and represents $\omega \to 0, g \to \infty, g^2\omega = const.$ Of the various time scales in the hierarchy only one, viz. the reciprocal of $g^2\omega$ survives in this limit and thus all the other features of the exact evolution are eliminated.

The memory function approach[7–9] consists of the use of a dressing transformation and a perturbation resulting in evolution in terms of a memory function. The approach has been successful in the past[7] in explaining the mobility of charge carriers in naphthalene. Its validity can be studied clearly in the context of the simplified model explained above. It is found that the approach is surprisingly accurate in a wide variety of parameter ranges. It is almost always preferable to the semiclassical approximation, it is valid both for large $g^2\omega$ and for small g, and it represents several realistic systems excellently. They include thermal polarons, charge carriers,

and vibrational excitations. Highly important is the fact that the memory approach correctly addresses all the features of the exact evolution including the silent runs, recurrences, and tunneling. Furthermore, the time scale hierarchy in the exact evolution can be understood easily in terms of the memory both from a mathematical and a physical point of view. The range of situations in which the memory approach breaks down (certain initial conditions and an intermediate $\hbar g^2\omega/V$) is also made clear by our analysis. We also find that a semiclassical symmetrisation procedure suggested by Brown et al.[31] as a better alternative to our original memory function[8] is actually always worse and sometimes severely so. Extension of our study to finite temperature and bath effects and to realistically extended systems and many modes is under way. It is a pleasure to thank my collaborators in this work: A. Bishop, S. Raghavan and M. Salkola.

1 REFERENCES

[1] L. D. Landau and S. Pekar, Zh. Eksp. i. Teor. Fis. 16, 341 (1942).

[2] S. Pekar, *Untersuchungen über die Electrontheorie der Kristalle* (Akadamie-Verlag, Berlin, 1954).

[3] T. D. Holstein, Ann. Phys. 8, 325, 343 (1959).

[4] Y. Toyosowa, Progr. Theor. Phys. (Kyoto) 12, 421 (1954).

[5] R. Silbey, Ann. Rev. Phys. Chem. 27, 203 (1976).

[6] R. Silbey and R. W. Munn, J. Chem. Phys. 72, 2763 (1980).

[7] V. M. Kenkre, J. D. Andersen, D. H. Dunlap, and C. B. Duke, Phys. Rev. Lett. 62, 1165 (1989).

[8] V. M. Kenkre and T. Rahman, Phys. Lett. A50, 170 (1974).

[9] V. M. Kenkre, Phys. Rev. B 12, 2150 (1975).

[10] T. D. Lee, F. E. Low and D. Pines, Phys. Rev. 90, 297 (1953);

[11] I. G. Lang and Y. A. Firsov, Zh. Eksp. Teor. Fis. 43, 1843 (1962) [Sov. Phys. JETP 16, 1301 (1963)].

[12] H. Haken, *Quantum Field Theory of Solids: An Introduction* (North-Holland, Amsterdam, 1976).

[13] A. C. Scott, Phys. Rep. 217, 1 (1992).

[14] *Davydov's Soliton Revisited: Self-Trapping of Vibrational Energy in Protein*, eds. P. L. Christiansen and A. C. Scott (Plenum, New York, 1990).

[15] J. C. Eilbeck, A. C. Scott, and P. S. Lomdahl, Chem. Phys. Lett. 113, 29 (1985); Physica 16D, 318 (1985).

[16] V. M. Kenkre and D. Campbell, Phys. Rev. B34, 4959 (1986).

[17] V. M. Kenkre in *Singular Behaviour and Nonlinear Dynamics*, eds. St. Pnevmatikos, T. Bountis, and Sp. Pnevmatikos (World Scientific, Singapore, 1989).

[18] V. M. Kenkre, Physica D 68, 153 (1993).

[19] V. M. Kenkre and L. Cruzeiro-Hansson, Z. Physik B 95, 379 (1994).

[20] V. M. Kenkre, S. Raghavan, and L. Cruzeiro-Hansson, Phys. Rev. B 49, 9511 (1994).

[21] L. Cruzeiro-Hansson and V. M. Kenkre, Phys. Lett. A 190, 59 (1994).

[22] M. Salkola, A. R. Bishop, V. M. Kenkre, and S. Raghavan, Phys. Rev. B, 52, ... (1995), scheduled for publication.

[23] V. M. Kenkre, S. Raghavan, A. R. Bishop, and M. Salkola, Phys. Rev. B, submitted for publication.

[24] D. Vitali, P. Allegrini, and P. Grigolini, Chem. Phys. 180, 297 (1994).

[25] L. Bonci, P. Grigolini, D. Vitali, Phys. Rev. A 42, 4452 (1990).

[26] L. Bonci, P. Grigolini, R. Roncaglia, and D. Vitali, Phys.Rev. A 47, 3538 (1993).

[27] L. Bonci, R. Roncaglia, B. J. West, and P. Grigolini, Phys. Rev. A 45, 8490 (1992).

[28] D. Vitali and P. Grigolini, Phys. Rev. A 42, 7091 (1990).

[29] D. Brown, B. West, and K. Lindenberg, Phys. Rev. A 33, 4110 (1986).

[30] D. Brown, K. Lindenberg, and B. West, Phys. Rev. B 35, 6169 (1987); see also W. C. Kerr and P. S. Lomdahl, Phys. Rev. B 35, 3629 (1987).

[31] D. Brown, K. Lindenberg, and B. West, Phys. Rev. A 37, 2946 (1988); see in particular the appendix.