

Comments on the Effect of Disorder on Transport with Intermediate Degree of Coherence: Calculation of the Mean Square Displacement*

Y.M. Wong

Department of Physics, Catholic University of America, Washington, USA

V.M. Kenkre

Department of Physics and Astronomy, University of Rochester,
Rochester, New York, USA

Received December 16, 1981

We use the generalized master equation with a simple exponential memory but with disorder in its spatial dependence to analyze the combined effect of coherence and randomness on the transport of quasiparticles. We calculate the mean-square-displacement and find that it retains well-known properties in the presence of randomness.

I. Introduction

The study of Förster migration [1] of electronic excitation among randomly distributed molecules in solution was greatly revived as a result of an important contribution of Haan and Zwanzig [2]. The analysis of these authors was extended to high density and/or large times by Gochanour et al. [3]. The continuous-time random walk approach of Montroll and Weiss [4], developed and applied to related problems with great success [5] by Scher and Lax, and by Scher and Montroll, has been recently given further support by the formal analysis of Klafter and Silbey [6]. Multipolar and exchange transfer rates have been studied by Godzik and Jortner [7] and by Blumen et al. [8]. Many years ago, Miller and Abraham [9] derived a possible incoherent hopping rate for the case of impurity conduction at low concentration in an *n*-type semiconductor. Recently McInnes et al. [10] have made a comparison study of the a.c. conductivity which is closely related to the mean square displacement of the species undergoing transport.

In all the above works, one studies the effect of disorder on *incoherent* (or hopping) motion, i.e. one that is described by an irreversible rate equation. The intrinsic coupled coherent-incoherent motion, if it exists in a random medium [3], is not treated. Recently, motion of an arbitrary degree of transport coherence but in ordered systems has been studied extensively by various authors [11-14]. In a disor-

dered system the only treatment of coherence is that by Huber and collaborators [15] in the extreme limit of complete coherence. It is clearly necessary therefore to study the combined effect of randomness and of an arbitrary degree of coherence on the transport properties. We begin such an analysis by using the generalised-master-equation approach [14] and calculating the mean-square-displacement in several situations.

In Sect. II, we briefly mention the relevant features of the generalized-master-equation. In Sect. III, we exhibit the modification of the time-dependence of the mean-square-displacement brought about by randomness for the case of Förster [1], Dexter [16] and Miller-Abraham [9] transfer rates. In Sect. IV, closely following Gochanour et al. [3], we argue that the essential time-dependence of the mean-square-displacement is not affected by increasing the density. A discussion forms the concluding Sect. V.

II. Generalized-Master Equation with a Phenomenological Memory

The extensive work that has been recently done on the simultaneous description of coherent and incoherent motion of quasiparticles may be classified into two categories: that which uses the stochastic Liouville equation (SLE) [11, 12] and that which uses the generalized master equation (GME) [13, 14]. In view of the relations and equivalences shown [14] to exist between the two approaches it suffices

* Supported by NSF grant no. DMR-7919539

for our present purposes to choose either the SLE or the GME. The mean-square-displacement is a quantity which requires only the diagonal elements of the density matrix in a site-representation and the GME is therefore the more appropriate starting point. It has the form

$$\frac{dP_m}{dt} = \int_0^t dt' \sum_n [W_{mn}(t-t') P_n(t') - W_{nm}(t-t') P_m(t')] \quad (2.1)$$

It describes the evolution of the probabilities of occupation $P_m(t)$, m denoting the sites, and the key quantities are the memory functions $W_{mn}(t)$. The extreme limit

$$W_{mn}(t) = w_{mn} \delta(t) \quad (2.2)$$

describes complete incoherence and corresponds to previous analyses [2, 3]. We shall allow disorder in w_{mn} as in [2, 3] but replace $\delta(t)$ by a time-dependence that is less drastic so that the coupled coherent and incoherent-behaviour may be analysed. We shall use the simple choice of an exponential and write

$$W_{mn}(t) = w_{mn} \alpha e^{-\alpha t}. \quad (2.3)$$

The limit $\alpha \rightarrow \infty$ reduces (2.3) to (2.2). It is true that choices such as (2.3) must be used with caution because they are oversimplistic in their separation of the time and space parts. But it is known that even when such an oversimplification gives unacceptable P_m 's from (2.1) it often gives the accurate mean-square displacement [12, 14]. We shall assume here that the choice does not introduce undesirable features. The exponential approximation to (2.3) has been used earlier [13, 14] to demonstrate the essential features of the coupled coherent and incoherent motion. Its consequences in presence of disorder are explored below.

III. Low-Density Limit

A primary result of Haan and Zwanzig [2] is the following: in Laplace ε space

$$\langle \widetilde{r^2}(\varepsilon) \rangle \equiv \mathcal{L} \langle r^2(t) \rangle = \frac{\rho}{2} \int d^3 \mathbf{r} r^2 \left[\frac{1}{\varepsilon} - \frac{1}{\varepsilon + 2w(r)} \right]. \quad (3.1)$$

Here $\langle r^2(t) \rangle$ is the mean-square-displacement. ρ is the density of transferring sites, which is assumed [2] to be small. We now introduce into (3.1) the memory factor discussed above and write

$$\langle \widetilde{r^2}(\varepsilon) \rangle = \frac{\rho}{2} \int d^3 \mathbf{r} r^2 \left[\frac{1}{\varepsilon} - \frac{1}{\varepsilon + \frac{2\alpha}{\varepsilon + \alpha} w(r)} \right]. \quad (3.2)$$

The factor $\alpha/(\varepsilon + \alpha)$ signals the presence of possible coherence in the transport. Substituting the Förster rate i.e.

$$w(r) = \frac{1}{\tau} \left(\frac{R_0}{r} \right)^6 \quad (3.3)$$

in (3.2), one obtains after an integration [2]

$$\langle \widetilde{r^2}(\varepsilon) \rangle = \frac{C}{2^{1/6}} \pi R_0^2 \left(\frac{\alpha}{\tau} \right)^{5/6} \frac{1}{\varepsilon^{1/6} (\varepsilon + \alpha)^{5/6}} \quad (3.4)$$

where $C \equiv (4\rho\pi R_0^3)/3$ is a dimensionless density. A short-time analysis gives

$$\langle r^2(t) \rangle \sim \frac{C}{2^{1/6}} \pi R_0^2 \left(\frac{\alpha}{\tau} \right)^{5/6} \frac{1}{(\frac{5}{3}!)} t^{5/3}. \quad (3.5)$$

In (3.5) we have an interesting result. It should be compared with the previously derived incoherent expression [2] in which $\langle r^2(t) \rangle$ is proportional to $t^{5/6}$.

It is well known that in the *periodic lattice*, for purely diffusive motion, $\langle r^2(t) \rangle \sim t$ whereas the coherent limit, or equivalently the unified approach at short times, gives a t^2 -dependence. Thus we conclude that at short times, when coupled coherent-incoherent transport is suspected to exist, the tendency for the motion to be faster in terms of the mean-square-displacement is retained even in the presence of slight disorder in the system. Indeed, the fact that the t -dependence in the coherent limit is the square of the t -dependence in the incoherent limit holds both in the presence and absence of disorder. Furthermore, since there is no way to scale an exponential function in contrast to a power law dependence, the scaling law proposed by Haan and Zwanzig does not hold here. Equation (3.4) will be true for all time. But this will not interest us here since an asymptotic analysis will recover the master equation result.

We now turn to the Dexter exchange rate [16], given by

$$w(r) = A e^{-Br}. \quad (3.6)$$

When substituted into (3.2), equation (3.5) gives, after some simple manipulations,

$$\begin{aligned} \langle \widetilde{r^2}(\varepsilon) \rangle &= \frac{4\pi\rho}{B^5 \varepsilon^2} \frac{\alpha A}{\varepsilon + \alpha} \int_0^\infty dx x^4 \frac{1}{e^x + \frac{2\alpha A}{\varepsilon(\varepsilon + \alpha)}} \\ &\sim \frac{4\pi\rho}{B^5 \varepsilon^2} \frac{\alpha A}{\varepsilon + \alpha} \sum_{n=0}^\infty \frac{(-1)^n}{n!} \left[\frac{2\alpha A}{\varepsilon(\varepsilon + \alpha)} \right]^n \frac{4}{(n+1)^5}. \end{aligned} \quad (3.7)$$

The last expression follows by identifying $x=4$, $y=2\alpha A/\varepsilon(\varepsilon+x)<1$ and $\beta=0$ in (A.1) in the Appendix. A short-time analysis gives

$$\langle r^2(t) \rangle \sim t^2. \quad (3.8)$$

For a Miller-Abraham type of exchange [9] i.e.

$$w(r) = a r^{3/2} e^{-br} \quad (3.9)$$

a similar procedure gives

$$\langle r^2(\varepsilon) \rangle = \frac{4\pi\rho a}{V b \varepsilon^2} \left(\frac{x}{\varepsilon+x} \right) \int_0^\infty dx \frac{x^{11/2}}{e^x + \frac{2\alpha a x^{3/2}}{\varepsilon(\varepsilon+x) b^{11/2}}} \quad (3.10)$$

which again can be expressed in powers of $[\varepsilon(\varepsilon+x)]^{-1}$, when one identifies $x=11/2$, $y=(2\alpha a)/[\varepsilon(\varepsilon+x)b^{11/2}]$ and $\beta=3/2$ in (A.1). Again, a short-time analysis gives $\langle r^2(t) \rangle \sim t^2$ as found in the Dexter exchange rate case.

It is not surprising to find that in the low transfer site limit the mean-square-displacement at short time has the same time dependence in both ordered and slightly disordered medium for an exponentially dominated spatial transfer rate. This should be clear from the physical argument that the particle cannot travel very far to sample enough sites to distinguish whether it is in a periodic or random medium. Mathematically it is the presence of an exponential factor that allows one to express the integral in an inverse power series of $\varepsilon(\varepsilon+x)$ and thus, for short times, it is the factor outside the integral that determines the time-dependence of $\langle r^2(t) \rangle$. For a transfer rate of the form $r^n e^{-\alpha r}$, where n is a large power, one may expect a different time-dependence of $\langle r^2(t) \rangle$ since the integral has to be treated differently.

IV. Extension to High Densities

The propagator $\hat{G}^s(\varepsilon)$ relevant to the high-density situation has been given by Gochanour et al. [3] in their (86):

$$\hat{G}^s(\varepsilon) = \left[\varepsilon + \rho \int_0^\infty d^3 r \frac{r^2 w(r)}{1 + 2 \hat{G}^s(\varepsilon) w(r)} \right]^{-1} \quad (4.1)$$

which determines the mean square displacement in Laplace variable ε through the following two expressions

$$\langle \tilde{r}^2(\varepsilon) \rangle = \frac{6}{\varepsilon^2} \hat{D}(0, \varepsilon) \quad (4.2)$$

and

$$\hat{D}(0, \varepsilon) = \frac{\rho}{6} \int d^3 r \frac{r^2 w(r)}{1 + 2 \hat{G}^s(\varepsilon) w(r)}. \quad (4.3)$$

Here $\hat{D}(0, \varepsilon)$ is the long-wavelength limit of the generalised diffusion coefficient $\hat{D}(k, \varepsilon)$ [2]. With the replacement of $w(r)$ by $[x/(\varepsilon+x)] w(r)$ in (4.1) and solving for $\hat{G}^s(\varepsilon)$, one obtains

$$\hat{G}^s(\varepsilon) = \frac{1}{4\tau \varepsilon^2} \cdot \left\{ \frac{\pi^2 C \alpha}{4(\varepsilon+x)} \left[1 - \sqrt{1 + \frac{32\varepsilon\tau(\varepsilon+x)}{\pi^2 c^2 x}} \right] + 4\varepsilon\tau \right\}. \quad (4.4)$$

Equations (4.2) to (4.4), after a short-time analysis give

$$\langle r^2(t) \rangle \sim t^{5/3} \quad (4.5)$$

for the Förster transfer rate. Thus we see that the inclusion of the two-body self-energy diagram [3] does not change the effect of transport coherence on the mean-square-displacement at short times.

V. Conclusion

Though a phenomenological memory has been used in the GME (2.1), we believe that the time-dependence of $\langle r^2(t) \rangle$ is correctly predicted since $\langle r^2(t) \rangle$ is intimately related to the time-derivative of the memory which has quite a universal time-dependence at short times. Technically such a choice has the advantage of mathematical tractability as shown in Sects. 3 and 4.

It is then not surprising that transport coherence has the same effect of enhancing the $\langle r^2(t) \rangle$ for both periodic and disordered systems i.e. $\langle r^2(t) \rangle \sim t^2$ goes over to $t^{2\alpha}$. This is explicitly shown for three different transfer rates: Förster, Dexter, and Miller-Abraham. Furthermore, extension to slightly higher densities i.e. to those corresponding to the inclusion of the 2-body self-energy diagram, does not alter the above conclusion at short times.

Appendix. Evaluation of a Useful Integral

The integral to be evaluated is

$$I(x, \beta, y) = \int_0^\infty dx \frac{x^\alpha}{e^x + y x^\beta} \quad (A.1)$$

where (i) $y \ll 1$ and (ii) α and β can both be multiples of half-integers. (A.1) can be written formally as

$$I(\alpha, \beta, y) = \lim_{\varepsilon \rightarrow 0} \int_0^{\infty} dt \frac{t^{\alpha}}{e^t + y t^{\beta}} e^{-\varepsilon t} \\ = \lim_{\varepsilon \rightarrow 0} \int_0^{\infty} dt \frac{t^{\alpha}}{1 + y e^{-t} t^{\beta}} e^{-(\varepsilon+1)t}. \quad (\text{A.2})$$

It is sufficient for us to consider the case when $\beta \leq e^{3/2}$, then $t^{\beta} e^{-t} < 1$ for all t and since $y \ll 1$ by definition, (A.2) becomes on expanding in power of $y t^{\beta} e^{-t}$

$$I(\alpha, \beta, y) = \lim_{\varepsilon \rightarrow 0} \int_0^{\infty} dt \sum_{n=0}^{\infty} \frac{(-y)^n}{n!} t^{\alpha+n\beta} e^{-(\varepsilon+n+1)t}. \quad (\text{A.3})$$

(I) If α and β are integers, using the fact that

$$\int_0^{\infty} dt t^m e^{-\varepsilon t} = \frac{m!}{\varepsilon^{m+1}} \quad (\text{A.4})$$

from any standard Laplace transform table, one obtains

$$I(\alpha, \beta, y) = \sum_{n=0}^{\infty} \frac{(-y)^n}{n!} \frac{(\alpha+n\beta)!}{(n+1)^{\alpha+(n\beta+1)}}. \quad (\text{A.5})$$

(II) If α and β are multiples of half-integers, to perform the sum, one has to split the summation into odd and even parts. In the former case, since $\alpha + (2n+1)\beta$ is an integer now, the odd sum of (A.3) becomes

$$I_{\text{odd}} = \sum_{n=0}^{\infty} \frac{(-y)^{2n+1}}{(2n+1)!} \frac{[\alpha+(2n+1)\beta]!}{(n+1)^{\alpha+(2n+1)\beta+1}}. \quad (\text{A.6a})$$

In the even case,

$$I_{\text{even}} = \sum_{n=0}^{\infty} \frac{(-y)^{2n}}{(2n)!} \lim_{\varepsilon \rightarrow 0} \int_0^{\infty} dt t^{\alpha+2n\beta} e^{-(\varepsilon+n+1)t} \\ = \sum_{n=0}^{\infty} \frac{y^{2n}}{(2n)!} \lim_{z \rightarrow n+1} \int_0^{\infty} dt t^{1/2} t^{(z-1/2)+2n\beta} e^{-zt} \\ = \sum_{n=0}^{\infty} \frac{y^{2n}}{(2n)!} \lim_{z \rightarrow n+1} \left(-\frac{d}{dz} \right)^{z-1/2+2n\beta} \int_0^{\infty} dt t^{1/2} e^{-zt} \\ = \sum_{n=0}^{\infty} \frac{y^{2n}}{(2n)!} \lim_{z \rightarrow n+1} \left(-\frac{d}{dz} \right)^{z-1/2+2n\beta} \frac{\sqrt{\pi}}{2} \frac{1}{z^{3/2}} \\ = \sum_{n=0}^{\infty} \frac{y^{2n}}{(2n)!} \frac{(\alpha+2n\beta)!}{(n+1)^{\alpha+2n\beta+1}}. \quad (\text{A.6b})$$

Expressions (A.5–6) will allow one to calculate $\langle r^2(t) \rangle$ at short times for both the Dexter and Miller-Abraham short range exchange transfer rates.

References

1. Förster, Th.: Ann. Phys. Leipzig **2**, 55 (1948)
2. Haan, S.W., Zwanzig, R.: J. Chem. Phys. **68**, 1879 (1978)
3. Gochanour, C.R., Andersen, H.C., Fayer, M.D.: J. Chem. Phys. **70**, 4254 (1979)
4. Montroll, E.W., Weiss, G.H.: J. Math. Phys. **6**, 167 (1965)
5. Scher, H., Lax, M.: Phys. Rev. B **7**, 4502 (1973)
6. Scher, H., Montroll, E.W.: Phys. Rev. B **12**, 2455 (1975)
7. Klafter, J., Silbey, R.: Phys. Rev. Lett. **44**, 55 (1980)
8. Godzik, K., Jortner, J.: Chem. Phys. **38**, 227 (1979); Chem. Phys. Lett. **63**, 428 (1979)
9. Blumen, A., Klafter, J., Silbey, R.: J. Chem. Phys. **72**, 5320 (1980)
10. Miller, A., Abrahams, E.: Phys. Rev. **120**, 745 (1960)
11. McInnes, J.A., Butcher, P.N., Clerk, J.D.: Philos. Mag. **41**, 1 (1980)
12. Haken, H., Strobl, G.: Z. Phys. **262**, 135 (1973)
13. Reineker, P.: In: Exciton Dynamics in Molecular Crystals: The Stochastic-Liouville-Equation Approach. Höhler, G. (ed.). Berlin, Heidelberg, New York: Springer-Verlag 1982 (in press) and references therein
14. Gover, M., Silbey, R.: J. Chem. Phys. **54**, 4843 (1971)
15. Silbey, R.: Annu. Rev. Phys. Chem. **27**, 203 (1976) and references therein
16. Kenkre, V.M., Knox, R.S.: Phys. Rev. B **9**, 5279 (1974)
17. Kenkre, V.M.: In: Statistical Mechanics and Statistical Methods in Theory and Application. Landman, U. (ed.). New York: Plenum Press 1977
18. Kenkre, V.M.: In: Exciton Dynamics in Molecular Crystals: The Generalized-Master-Equation Approach. Höhler, G. (ed.). Berlin, Heidelberg, New York: Springer-Verlag 1982 (in press) and references therein
19. Kenkre, V.M.: Phys. Rev. B **11**, 1741 (1975)
20. Kenkre, V.M.: Phys. Rev. B **12**, 2150 (1975)
21. Huber, D.L.: Phys. Rev. B **20**, 2307; 5333 (1979)
22. Ghosh, K.K., Huber, D.L.: J. Lumin. **21**, 225 (1980) and references therein
23. Dexter, D.L.: J. Chem. Phys. **21**, 836 (1953)

Y.M. Wong
Department of Physics
Catholic University of America
Washington, DC 20064
USA

V.M. Kenkre
Department of Physics and Astronomy
University of Rochester
Rochester, NY 14627
USA