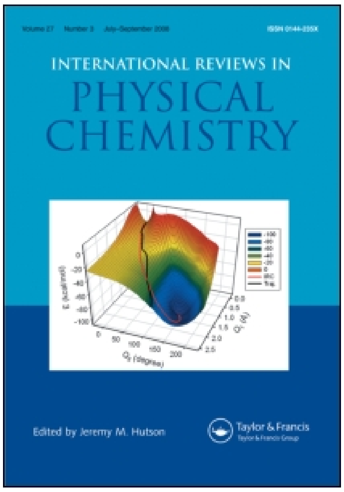

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Marginal dimensionalities for long-range energy transfer

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The averaging-out of off-diagonal disorder effects in long-range, incoherent electronic energy transfer (EET) results in marginal dimensionalities for which, and beyond which, short-time transport ceases to be dispersive. For EET induced by multipolar interactions of the order s, the marginal dimensionalities are $d_D^*=s-2$ and $d_P^*=s$ for the mean-square displacement and for the initial site survival probability, respectively, manifesting the interrogation of distinct aspects of spatial fluctuations.

1. Introduction

Incoherent, strong-scattering, electronic energy transfer (EET) in an impurity band of substitutionally disordered materials (Sakun 1972, Haan and Zwanzig 1978, Klafter and Silbey 1980, Blumen *et al.* 1980, Godzik and Jortner 1980, Gochanour *et al.* 1979, Loring *et al.* 1984) falls into a broad class of phenomena in the areas of chemical physics and of ill-condensed matter physics, e.g., particle transfer with random rates, spin waves in random systems and tight-binding disordered fermion systems (Alexander *et al.* 1981). The effects of the off-diagonal randomness on EET are manifested by the occurrence of a dispersive diffusion process (Haan and Zwanzig 1978, Klafter and Silbey 1980, Blumen *et al.* 1980, Godzik and Jortner 1980, Gochanour *et al.* 1979, Loring *et al.* 1984) in a close analogy to dispersive electron mobility in amorphous semiconductors. EET induced by isotropic multipolar interactions, which is characterized by the transition probability

$$W(r)=\tau^{-1}(R_0/r)^s \tag{1}$$

where r is the inter-impurity distance, τ is the excited lifetime (being subsequently taken as unity) and R_0 is the characteristic transfer radius, and is expected to interrogate off-diagonal disorder by long-range transfer. In the context of the manifestation of disorder effects on electronic structure and transport, it is interesting to inquire under what circumstances are disorder effects eroded by long-range interactions. As far as diagonal disorder effects are concerned, it is well known that the Anderson localization does not occur for interactions falling off as r^{-n} ($n\leqslant 3$) (Anderson 1958). We have approached the problem of the erosion of off-diagonal disorder effects by long-range interactions in EET by establishing the existence of marginal dimensionalities for EET for which and beyond which the transport ceases to be dispersive, becoming purely diffusive at short times. Our approach bears an analogy to the existence of marginal dimensionalities, d^*, for the critical threshold exponents in magnetism (Ma 1976) and in percolation (Kirkpatrick 1979), such as that for a dimensionality, d, exceeding d^*, the critical exponents assume their mean-field values. The marginal dimensionalities determined here for the observables characterizing EET provide the signature of the averaging-out of all spatial fluctuations for long-range transport.

The existence of marginal dimensionalities for EET induced by multipolar interactions is required to amend some apparent non-physical characteristics of the observables exhibited at high dimensionalities for a fixed value of s. Haan and Zwanzig (1978) have demonstrated, using an elegant scaling argument, that for transport induced by dipole–dipole interactions ($s=6$) and $d=3$, the mean square displacement (MSD) $\langle r^2(t)\rangle$ at short times behaves as $\rho t^{5/6}$, where ρ is the impurity concentration. This scaling argument has been extended (Blumen *et al.* 1980) for the case of general values of d and s, resulting in

$$\langle r^2(t)\rangle = \rho t^{(d+2)/s} \sum_{n=0}^{\infty} A_n t^{nd/s} \rho^n \tag{2}$$

A cursory examination of equation (2) reveals that for $d>(s-2)$ the motion becomes partially coherent, as is evident from the power of the first term in t which exceeds unity; for $d=(2s-2)$ the motion is coherent, i.e., $\langle r^2(t)\rangle \propto t^2$; and for $d>(2s-2)$ it is even accelerated. These conclusions are unacceptable as the starting point for the derivation of equation (2) is the Pauli master equation, where all coherent effects are eroded. One is therefore led to the inevitable conclusion that equation (2) is inapplicable for $d>s-2$. Similar difficulties are encountered in the critical scrutiny of the initial site survival probability (ISSP), $P(t)$. Using the Haan–Zwanzig argument (Haan and Zwanzig 1978, Blumen *et al.* 1980), one gets

$$P(t) = 1 - \sum_{n=1}^{\infty} C_n \rho^n t^{nd/s} \tag{3}$$

For small values of ρ and t this function is often approximated (Blumen *et al.* 1980) by the single exponential

$$P(t) = \exp\{-\alpha \rho t^{d/s}\} \tag{4}$$

For $d>s$ the ISSP, equation (4), exhibits a super-exponential decay, a behaviour which is acceptable in the case of a physical catastrophe but it is by no means applicable for the case of conventional transport considered herein.

2. Marginal dimensionalities for $\langle r^2(t)\rangle$ and $P(t)$

The way out of these difficulties rests on the definition of marginal dimensionalities for $\langle r^2(t)\rangle$ and for $P(t)$. We shall utilize the self-consistent diagrammatic method (SCDM) of Gochanour *et al.* (1979) with the two-body approximation for the self-energy. The SCDM rests on the diagrammatic expansion of the Fourier–Laplace transform of the configurationally averaged Green's function (GF)

$$\tilde{G}(\mathbf{k};\varepsilon) = \int_0^t dt \exp(-\varepsilon t) \sum_{\mathbf{r}} \exp(i\mathbf{kr}) G(\mathbf{r};t) \tag{5}$$

where $G(\mathbf{r};t)$ is the GF determining the configurationally averaged probability $P(\mathbf{r},t)$ obtained from the solution of the master equation, i.e.,

$$P(\mathbf{r},t) = \int G(\mathbf{r},t) P(\mathbf{r},0) d\mathbf{r}.$$

The topological reduction of the diagrammatic expansion results in the following Dyson-type equation for the GF (Gochanour *et al.* 1979)

$$\tilde{G}(\mathbf{k};\, \varepsilon) = G^d(\varepsilon)/\{1 - \rho G^d(\varepsilon) \tilde{\sum}(\mathbf{k};\, G^d(\varepsilon))\} \tag{6}$$

where $G^d(\varepsilon)$ is the Laplace transform of the ISSP and $\tilde{\Sigma}(\mathbf{k};\, G^d(\varepsilon))$ is the self-energy. $G^d(\varepsilon)$ is determined from the self-consistency equation (Gochanour *et al.* 1979)

$$G^d(\varepsilon) = 1/\{\varepsilon + \tilde{\sum}(0;\, G^d(\varepsilon))\} \tag{7}$$

which ensures probability conservation. Systematic approximations maintaining unitarity can now be introduced. In the simplest two-body approximation we shall adopt (Gochanour *et al.* 1979)

$$\tilde{\sum}{}^{(2)}(\mathbf{k};\, G^d(\varepsilon)) = \int d\mathbf{r} \exp(i\mathbf{kr}) \frac{W(\mathbf{r})}{1 + 2G^d(\varepsilon)W(\mathbf{r})} \tag{8}$$

The probability conservation constraint for the problem at hand bears an analogy to the unitarity of the S-matrix and the introduction of unitarity relations for the decay of elementary particles (Lipkin 1973). It is important to emphasize that the SCDM results, which rest on equation (8), are exact for the term linear in the concentration and in this context they are not associated with the two-body approximation. To demonstrate this cardinal point, we note that the Laplace transform of the MSD can be expressed in the form (Gochanour *et al.* 1979)

$$\langle \tilde{r}^2(\varepsilon) \rangle = -\frac{1}{\varepsilon^2} \nabla_k^2 \tilde{\sum}(\mathbf{k};\, G^d(\varepsilon))|_{k=0} \tag{9}$$

The n-body approximation to the self-energy is exact up to (and including) the terms of the order ρ^{n-1}. Accordingly,

$$\tilde{\sum}(\mathbf{k};\, G^d(\varepsilon)) = \rho \tilde{\sum}{}^{(2)}(\mathbf{k};\, G^d(\varepsilon)) + O(\rho^2) \tag{10}$$

From equations (9) and (10) it is apparent that the MSD is exact in the first order in ρ. The Laplace transform of $P(t)$ can be analysed in terms of the density expansion of the SCDM (Knoester and Van Himbergen 1984). The $G^d(\varepsilon)$ is determined self-consistently within the n-body approximation, which was shown to be exact up to the order $(n-1)$ in the concentration. Therefore, in our case

$$G^d(\varepsilon) = \frac{1}{\varepsilon} + a(\varepsilon)\rho + O(\rho^2) \tag{11}$$

We conclude that the results of the two-body version of the SCDM are exact to the first order in concentration both for the MSD and for the ISSP. This is sufficient for our purpose.

The self-consisting equation, equation (7), can now be expressed in the form

$$G^d(\varepsilon) = \frac{1}{\varepsilon + I(d;\, s)} \tag{12}$$

where

$$I(d;\, s) = \rho S_d \int_a^{R_c} \frac{dr\, r^{d-1}(R_0/r)^s}{1 + 2G^d(\varepsilon)(R_0/r)^s} \tag{13}$$

S_d is the surface of the d-dimensional hypersphere, a is the lower cut-off distance, which is of the order of lattice constant, and R_0 is the upper cut-off distance, which is of the order of the crystal size.

The MSD can be expressed from equation (9) as

$$\langle r^2(\varepsilon)\rangle = \frac{d}{(d+2)}\frac{R_0^2}{\varepsilon^2}I(d+2;\, s) \tag{14}$$

We proceed to the evaluation of the integral $I(d; s)$, equation (13), which determines the observables. For $d<s$, the lower limit can be taken to be equal to zero, while the upper limit is extended to infinity without affecting the final result (Blumen *et al.* 1980):

$$I(d;\, s) = \frac{dcK(d;\, s)}{[2G^d(\varepsilon)]^{1-d/s}} \tag{15}$$

where c is the number of molecules within the sphere of radius $R_0(c=\rho S_d R_0^d/d)$ and

$$K(d;\, s) = \frac{\pi}{s\sin(\pi d/s)} \tag{16}$$

It is easy to show that the standard scaling results (Haan and Zwanzig 1978, Blumen *et al.* 1980) are recovered by substituting equation (15) into equations (12) and (14). For $d \geqslant s$ one has to account properly for the integration limits in equation (13), which now assumes the form

$$I(d;\, s) = \begin{cases} \dfrac{cd}{(d-s)}(R_c/R_0)^{d-s}, & d>s \\ cd\ln(R_c/R_0), & d=s \end{cases} \tag{17}$$

The $I(d; s)$ $(d \geqslant s)$ integral exhibits interesting size effects for finite systems. A notable feature of equation (17) is that the final expression is independent of the function $G^d(\varepsilon)$. From equations (14) and (17), we get

$$\langle r^2(t)\rangle = \frac{dI(d;\, s)}{(d+2)}R_0^2 t + O(\rho^2), \quad d \geqslant s-2 \tag{18}$$

and the MSD exhibits a linear time dependence. Next, we utilize equations (12) and (17) to obtain

$$P(t) = 1 - I(d;\, s)t + O(\rho^2) \tag{19}$$

so that for short times

$$P(t) \simeq \exp\{-I(d;\, s)t\} \tag{20}$$

and the ISSP reveals an exponential decay.

Equations (18) and (20) establish the existence of marginal dimensionalities for the observables which characterize long-range EET. For $d \geqslant s-2$, equation (2) is no longer valid and should be replaced by the conventional diffusive behaviour $\langle r^2(t)\rangle \propto t$. Thus, $d_D^* = s-2$ is the marginal dimensionality for the MSD. Similarly, for $d \geqslant s$, the ISSP at short times is characterized by the single exponential decay, equation (20). Accordingly, $d_p^* = s$ is the marginal dimensionality for the ISSP. The existence of different marginal dimensionalities d_D^* and d_p^* for the problem of long-range EET originates from the interrogation of different aspects of local disorder by these two observables. The ISSP represents a local property, which is very sensitive to the local disorder, while the MSD constitutes a global property where some of the disorder effects are partially averaged out. Accordingly, a higher marginal dimensionality is required for the complete averaging-out of disorder effects on the ISSP than for the MSD.

From the foregoing analysis, we conclude that:

(1) Each of the observables specifying EET is characterized by a well defined time exponent for any given dimensionality.
(2) These exponents exhibit a systematic variation with changing d saturating at $d \geqslant d_D^*$ and $d \geqslant d_p^*$.
(3) For d exceeding d_D^* and d_p^*, conventional energy diffusion is exhibited.†
(4) Different observables are characterized by distinct marginal dimensionalities for EET, in contrast to the percolation problem (Kirkpatrick 1979), where $d^* = 6$ constitutes the universal marginal dimensionality.

A complementary criterion for the existence of marginal dimensionalities for EET rests on the divergence of the spatial moments of the transition rates

$$M_p = \int_0^\infty dr\, r^p W(r),$$

with p being real and positive. Provided that M_p diverge for $p \geqslant p^*$, then p^* is the marginal dimensionality for the ISSP, and $(p^* - 2)$ is the marginal dimensionality for the diffusion. On the other hand, when all the moments are finite, marginal dimensionalities do not exist. This is the case for EET induced by exchange interactions when the transition rates decay exponentially with distance. Under these circumstances, short-time dispersive diffusion will prevail for all dimensionalities.

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† A more profound analysis of long-range EET in high-dimensional ($d > 3$) spaces may require the modification of the Coulomb law. The electrostatic potential, Φ, should be taken as the solution of the Poisson equation in a d-dimensional space $\nabla^2\Phi = -(d-2)S_d\sigma$, where σ is the charge density and S_d is the surface of the d-dimensional hypersphere, assuming the form $\Phi(r) \propto r^{-(d-2)}$. Dipole–dipole transition rates in a d-dimensional space fall off with distance as r^{-2d}, so that for multipolar interactions $s \geqslant 2d$. Accordingly, in such a scheme which allows for the dimensional modification of the electrostatic interaction potential, EET induced by the multipolar coupling is always dispersive for any dimensionality. Thus, marginal dimensionalities will then exist only for interactions which are of longer range than those of the dipole–dipole type.