Two-state random walk model of lattice diffusion.
1. Self-correlation function

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Abstract. Diffusion with interruptions (arising from localized oscillations, or traps, or mixing between jump diffusion and fluid-like diffusion, etc.) is a very general phenomenon. Its manifestations range from superionic conductance to the behaviour of hydrogen in metals. Based on a continuous-time random walk approach, we present a comprehensive two-state random walk model for the diffusion of a particle on a lattice, incorporating arbitrary holding-time distributions for both localized residence at the sites and inter-site flights, and also the correct first-waiting-time distributions. A synthesis is thus achieved of the two extremes of jump diffusion (zero flight time) and fluid-like diffusion (zero residence time). Various earlier models emerge as special cases of our theory. Among the noteworthy results obtained are: closed-form solutions (in d dimensions, and with arbitrary directional bias) for temporally uncorrelated jump diffusion and for the 'fluid diffusion' counterpart; a compact, general formula for the mean square displacement; the effects of a continuous spectrum of time scales in the holding-time distributions, etc. The dynamic mobility and the structure factor for 'oscillatory diffusion' are taken up in part 2.

Keywords. Diffusion; self-correlation function; continuous-time random walk theory; two-state random walk; renewal process.

1. Introduction

Diffusion in a periodic potential is of considerable current interest. It provides a description of the diffusion of an impurity atom in a crystal, including certain aspects of the complex phenomenon of the motion of hydrogen interstitials in metals. In addition, the general problem of Brownian motion in a periodic potential has a large number of applications, such as superionic conductance, orientational diffusion in molecular crystals, etc. A basic problem is to elucidate the consequences of the simultaneous occurrence of two features: random flights from site to site, and localized oscillations about each site. The non-trivial interference between these two aspects is manifested in physical quantities such as the frequency-dependent mobility $\mu(\omega)$ and the dynamic structure factor $S(k, \omega)$.

There are two broad approaches to the problem. The first is a 'stochastic process' approach that deals with Brownian motion in a periodic potential. For technical reasons, explicit calculations are restricted to the one-dimensional case, *i.e.*, the position and the velocity of the diffusing particle are treated as scalar random processes. One may then write down the Langevin equation for a particle in a sinusoidal potential, and use a generalization of Mori's well-known continued-fraction method to obtain a representation for $\mu(\omega)$ (Fulde et al 1975; Schneider
1976). Alternatively, one can work with the Fokker-Planck equation for the conditional probability density $P(x, v, t | x_0, v_0)$ of the position and velocity of the particle in a periodic potential. A short-time expansion coupled with a perturbative technique may be employed (Dieterich et al. 1977) to generate representations for $\mu(\omega)$ and $S(k, \omega)$. An eigenfunction expansion method (Risken and Vollmer 1978) yields similar results.

The second approach is more directly concerned with diffusion in a three-dimensional lattice. Random walk analysis is combined with assumptions regarding uncorrelated jumps to develop what are essentially variants of a certain jump diffusion model. The diffusing particle is assumed to hop instantaneously (i.e., with vanishing flight time) from site to site, while simultaneously executing localized oscillations whenever it is resident at a site. Starting with the simple model of Chudley and Elliott (1961), a considerable literature exists on various refinements of detail (Gissler and Rother 1970; Springer 1972 and references therein). Simultaneously, work has been carried out on two- and multi-state random walk models, one of the earliest being that of Singwi and Sjölander (1960) for diffusion in liquids. This permits the introduction of a finite mean flight time for the jumps. Now the mean residence and flight times can be quite comparable in many instances of diffusion in solids. It is therefore of great interest to examine such models in the framework of diffusion on a lattice (Gissler and Stump 1973; Wert 1978 and references therein; Kutner and Sosnowska 1979). Neutron scattering is the experimental probe primarily kept in mind in these analyses.

Concurrently with these developments, a picture has emerged of the relevance of continuous time random walk (CTRW) theory (Montroll and Weiss 1965; Weiss 1976) to generalized diffusion (see, in particular, Kehr and Haus 1978 and references therein). This technique offers a powerful approach to a wide variety of such problems, including that of diffusion in disordered media (Scher and Lax 1973). It is our purpose, in what follows, to present a general theory of the diffusion of a particle in a lattice based on the principles of CTRW. This will be done in two parts. In the first (the present paper), our primary objective is the evaluation of the conditional probability density for the position of the particle. In the classical limit (which is all that we consider), this quantity is equal to the van Hove self-correlation function, whose Fourier transform is measured by the differential cross-section for incoherent neutron scattering. We shall also be concerned with the mean square displacement. In paper 2 of this series, we shall consider the velocity of the diffusing particle. The velocity autocorrelation function (and thence the dynamic mobility and the effective diffusion constant) will be evaluated in a CTRW model in velocity space, allowing for localized oscillations at each lattice site as well as a distribution of flight times between sites.

To summarize: we shall calculate the self-correlation function for a particle diffusing by nearest-neighbour flights on a regular lattice. An arbitrary holding-time distribution for the state of residence at a site is allowed for; so is a distribution for the flight time between sites. Since these distributions are not restricted to exponential ones, cognizance must be taken of the first-waiting-time distribution in each case. A general, complete solution is obtained, in the sense that a closed expression is presented for the Laplace transform of the generating function of the random walk. There is no restriction to one-dimension, and the random walk may have an arbitrary directional bias.