Two-state random walk model of diffusion. 2. Oscillatory diffusion

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Abstract. Continuing our study of interrupted diffusion, we consider the problem of a particle executing a random walk interspersed with localized oscillations during its halts (*e.g.*, at lattice sites). Earlier approaches proceed *via* approximation schemes for the solution of the Fokker-Planck equation for diffusion in a periodic potential. In contrast, we visualize a two-state random walk in velocity space with the particle alternating between a state of flight and one of localized oscillation. Using simple, physically plausible inputs for the primary quantities characterising the random walk, we employ the powerful continuous-time random walk formalism to derive convenient and tractable closed-form expressions for all the objects of interest: the velocity auto-correlation, generalized diffusion constant, dynamic mobility, mean square displace-ment, dynamic structure factor (in the Gaussian approximation), etc. The interplay of the three characteristic times in the problem (the mean residence and flight times, and the period of the 'local mode') is elucidated. The emergence of a number of striking features of oscillatory diffusion (*e.g.*, the local mode peak in the dynamic mobility and structure factor, and the transition between the oscillatory and diffusive regimes) is demonstrated.

Keywords. Diffusion; continuous-time random walk; dynamic mobility; velocity autocorrelation; dynamic structure factor.

1. Introduction

In paper I of this series (Balakrishnan and Venkataraman 1981), we have developed in detail a two-state random walk model for the diffusion of a particle on a lattice. The formalism is based on continuous-time random walk (CTRW) theory, incorporating arbitrary holding-time distributions for the state of localized residence at the lattice sites and for that of flight between sites. The physical motivation for considering this problem, its ramifications, and the approaches used in certain studies have already been explained at length in I, and will not be repeated here.

The emphasis in I was on the positional probability or the self-correlation function, and on the roles played by the two time scales w_0 (the mean residence time at a site) and w_1 (the mean inter-site flight time) in the diffusion process. In the present paper, the focus is on " oscillatory diffusion ": the diffusing particle executes localized oscillations whenever it is in residence at a site. The ' local mode ' frequency thus introduces a third characteristic time scale into the problem. Our objective is to find the dynamic mobility (and from it the diffusion constant and the structure factor), by analysing the random process representing the *velocity* of the diffusing particle. Our model is a simple one, based on straightforward physical assumptions. It is not restricted to one-dimension, unlike more formal treatments of diffusion in a

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periodic potential that are based either on the Langevin equation (Fulde *et al* 1975) or on the Fokker-Planck equation for the conditional density $P(x, v, t \mid x_0, v_0)$ (Dieterich *et al* 1977; Risken and Vollmer 1978; see also Das 1979; Hammerberg 1980). For clarity and ease of comparison, however, we shall also restrict ourselves to the one-dimensional case in this paper. Our results will exhibit clearly the effects of the oscillatory interruptions upon the diffusive motion and vice versa, and will serve as an illustration of the power as well as the easy generalizability of the CTRW analysis, given the simplicity of the premises upon which the model rests.

The organization of the paper is as follows. While only the autocorrelation $\langle v(0)v(t) \rangle$ is required to determine the dynamic mobility, it turns out that we can quite conveniently compute the statistical average

$$\Phi (\xi, t) = \langle \exp i\xi \, [v(t) - v(0)] \rangle \tag{1}$$

itself, which of course provides additional information. This is the central calculation. The average concerned is, by definition, given by

$$\Phi(\xi, t) = \int dv_0 \int dv \, f(v_0) \, P (v, t \mid v_0) \exp [i\xi \, (v - v_0)] \tag{2}$$

where $f(v)$ is the equilibrium distribution of the velocity, and $P(v, t \mid v_0)$ is the conditional probability density of this (stationary) random variable. In §2, we indicate how $P(v, t \mid v_0)$ is constructed in the framework of the basic two-state random walk theory, now formulated in velocity space. The physical models for the functions characterizing the CTRW are laid down and explained. The analytical expressions obtained for $\Phi(\xi, t)$ and its Laplace transform $\tilde{\Phi}(\xi, s)$ are presented. Using these, we obtain in §3 answers for the frequency-dependent mobility, its real part (the dynamic mobility), and the velocity autocorrelation function. Closed-form results are presented for these, various special cases and limits are recovered from the general expressions, and graphs are plotted to illustrate the features of interest. In §4, the generalized diffusion constant and the mean square displacement are deduced and discussed. The dynamic structure factor is also considered, in the Gaussian approximation, to bring out the effects of the ' mixing ' of oscillation and diffusion upon the quasielastic and local-mode peaks. Section 5 returns to $\Phi(\xi, t)$ and the additional information that can be extracted from this quantity. We conclude with a brief summary of the main results of this paper in §6.

2. Calculation of the function $\Phi(\xi, t)$

2.1 *Construction of the conditional probability density*

The formal construction of the conditional probability density $P(v, t \mid v_0)$ in a two-state random walk model proceeds along lines that are already familiar (Singwi and Sjölander 1960; see also I). The diffusing particle alternates between a state of flight, with a holding-time distribution $q(t)$, and a state of localized residence (about lattice sites), with a holding-time distribution $p(t)$. Further, if a flight step begins with a velocity v_0 at the instant t_0, let $h(v, t \mid v_0, t_0)dv$ be the probability that the velocity

evolves to a value between v and $v + dv$ at time t, in the same state (of flight). Similarly, let $g(v, t \mid v_0, t_0)$ denote the corresponding probability density in the oscillatory state. By enumerating all possible event sequences in the interval $(0, t)$, one can now construct $P(v, t \mid v_0)$ in terms of the primary quantities p, q, g and h. We have first

$$P(v, t \mid v_0) = \sum_{n=0}^{\infty} \left[\frac{w_0}{(w_0 + w_1)} G_n(v, t \mid v_0) + \frac{w_1}{(w_0 + w_1)} H_n(v, t \mid v_0) \right], \quad (3)$$

where G_n $[H_n]$ denotes the conditional probability density for the velocity to evolve from the value v_0 at $t = 0$ in the state of residence [flight] to the value v at time t, *via* n intermediate transitions of the state of the particle. Multiple integrals (over the epochs and velocities of the intermediate states) can be written down for G_n and H_n. For example, we have (for $n \geqslant 1$)

$$G_{2n}(v, t \mid v_0) = \int_0^t dt_{2n} \dots \int_0^{t_2} dt_1 \int dv_{2n} \dots \int dv_1 \, p\,(t - t_{2n}) \, g\,(v, t \mid v_{2n}, t_{2n})$$

$$\cdot (-q'\,(t_{2n} - t_{2n-1})) \, h\,(v_{2n}, t_{2n} \mid v_{2n-1}, t_{2n-1}) \, (-p'\,(t_{2n-1} - t_{2n-2}))$$

$$\dots (-p_0'\,(t_1)) \, g\,(v_1, t_1 \mid v_0, 0), \quad (4)$$

where a prime denotes differentiation, and $p_0(t)$ is the first-waiting-time distribution associated with the distribution $p(t)$. We shall not write down here the expressions for G_{2n+1}, H_{2n}, H_{2n+1}, G_0 and H_0 in order to save space.

2.2 *Physical inputs for the functions p, q, g, h*

The simple picture of oscillatory diffusion that we adopt provides tractable inputs into the foregoing machinery for the functions p, q, g and h characterizing the CTRW, based on physical grounds. First, if the successive transitions of state are uncorrelated (see I), p and q are single exponentials, *i.e.*,

$$p\,(t) = \exp\,(-t/\tau_0), \quad q\,(t) = \exp\,(-t/\tau_1), \quad (5)$$

so that $w_0 = \tau_0$, $w_1 = \tau_1$. Further, $p_0(t) = p(t)$ and $q_0(t) = q(t)$ in this case. For ease of writing, we shall sometimes use the notation γ_0, γ_1 for $(1/\tau_0)$ and $(1/\tau_1)$ respectively. Next, we assume that the particle behaves like a classical simple harmonic oscillator whenever it falls into a residence state: *i.e.*, its velocity then evolves deterministically according to

$$v\,(t) = A \, \omega_0 \sin\,(\omega_0 t + \varphi_0), \quad (6)$$

A being the amplitude of the motion. Here ϕ_0 is the *random* initial phase into which the particle falls at the commencement of the state concerned. Thus our model for g is simply

$$g\,(v, t \mid v_0, t_0) = \delta\,(v - A \, \omega_0 \sin\,[\omega_0\,(t - t_0) + \varphi_0]), \quad (7)$$

where $A \omega_0 \sin \varphi_0 \equiv v_0$. The occurrence of the δ-functions simplifies the theory considerably, by decoupling the multiple integrals over the intermediate velocities in sequences such as (4). Further, the integration over each initial velocity v_0 with which every oscillatory state commences can be converted into one over the corresponding phase φ_0, with a *constant* weight factor (or *a priori* occupation probability) equal to $(1/2\pi)$, and over the range 0 to 2π. With the above as inputs, the summation in (3) can be carried out after a Laplace transform with respect to t. After a great deal of algebra, one obtains a closed expression for the transform $\tilde{\Phi}(\xi, s)$ of the object required, *i.e.*, $\Phi(\xi, t)$. This expression is still a functional of h and of the equilibrium velocity distribution f. The dependence on h is actually quite marginal: by virtue of the conservation of probability, this function gets integrated out to unity (regardless of its actual form) in all the intermediate states in which it occurs, because of the decoupling mentioned earlier. It survives explicitly only in places where it represents the terminal diffusive state in G_{2n+1} and H_{2n}. This circumstance* drastically reduces the 'error' introduced by any approximate form assumed for the function h, provided the latter satisfies certain basic physical requirements. *Given this, and the physical fact that h describes flight over a single lattice distance at most*, it is not unreasonable to take the velocity to be a constant over the step (*i.e.* to assume free flight); in other words, to set

$$h(v, t \mid v_0, t_0) = \delta(v - v_0). \tag{8}$$

Indeed, it is this approximation, together with the simple exponential form for $q(t)$, that specializes an otherwise general theory to the case of diffusion in a *lattice*. With more general forms for q and h, the theory could easily be formulated to describe oscillatory diffusion in a liquid or a disordered solid. (In the latter case, a distribution in ω_0 could for example be incorporated in the function g). In a liquid, for instance, the individual flight steps are over variable distances. In a sufficiently long flight step, frictional effects (thermalization) must also be taken into account. It is therefore appropriate in this case to specify h *itself* as the solution of a ' diffusion ' equation (Singwi and Sjölander 1960)—in the case of the velocity variable, we should choose the solution of the (potential-free) Fokker-Planck equation. Thus $h(v, t \mid v_0, t_0)$ would be a Gaussian distribution in the variable $[v - v_0 \exp(-\gamma(t - t_0))]$, γ being the friction constant or the reciprocal of the correlation time of the velocity. When $t \ll \gamma^{-1}$, this solution tends to the δ-function of (8). The latter is therefore a plausible choice for the single-lattice-distance jumps (with a mean flight time $\tau_1 \sim 10^{-12}$ sec, say) occurring in the current problem.

2.3 *The equilibrium velocity distribution*

Finally, we turn to the specification of the equilibrium distribution $f(v)$. Since the flight steps are assumed to leave the velocity unaltered (see (8)), $f(v)$ is essentially determined by the motion in the oscillatory state. Here the velocity has the functional form $v = A \omega_0 \sin \phi$, and the occupation probability density in the space of the phase

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*For, of the $(N + 1)(N + 2)/2$ individual states taken into account in $\Sigma_0^N G_n$, any approximation for h affects only $[(N + 1)/2]$ states. One therefore expects the relative error to become negligible when a complete summation is done, *i.e.*, when $N \to \infty$. A similar statement holds good for ΣH_n.

variable ϕ is a constant, namely, $1/(2\pi)$. Hence the relation $f(v)\,dv = d\phi/(2\pi)$ trivially yields (with θ denoting the step function)

$$f(v) = \pi^{-1}\,(A^2\,\omega_0^2 - v^2)^{-1/2}\,\theta\,(A\,\omega_0 - |\,v\,|). \qquad (9)$$

It remains to specify the amplitude A of the oscillatory motion. Equating the mean square velocity in equilibrium to $k_B T/m$ (where m is the mass of the diffusing particle), *i.e.*, using the equipartition theorem, we get

$$A = (2\,k_B\,T/m\omega_0^2)^{1/2}. \qquad (10)$$

The normalized equilibrium distribution $f(v)$ that we use then reads

$$f(v) = \pi^{-1}\,(\sigma^2 - v^2)^{-1/2}\,\theta(\sigma - |\,v\,|) \qquad (11)$$

where $\qquad \sigma\,(= A\omega_0) = (2k_B\,T/m)^{1/2}. \qquad (12)$

Incidentally, it is clear that (10)–(12) also ensure that there is no preferred ' condensation' of the diffusing particles into one or the other of the two states (flight and residence).

Before the results of the calculations are presented, a few further remarks on the distribution (11) are in order. These are best made in the form of a comparison with the conventional Maxwellian distribution of velocities,

$$f_M(v) = (\pi\sigma^2)^{-1/2}\,\exp\,(-v^2/\sigma^2). \qquad (13)$$

Both f and f_M are symmetric, and their second moments are of course equal. For the Maxwellian, $\langle v^{2n}\rangle = (\sigma^2/4)^n\,(2n)!/n!$. The corresponding moment for $f(v)$ is smaller by a factor $(1/n!)$. Being of compact support, $f(v)$ must clearly have a negative excess of kurtosis; the actual value turns out to be $-3/2$. And lastly, while the characteristic function corresponding to (13) is

$$\int_{-\infty}^{\infty} dv\,f_M(v)\,\exp\,(i\xi v) = \exp\,(-\xi^2\sigma^2/4), \qquad (14)$$

which is again a Gaussian, that for the distribution at hand is

$$\langle \exp\,(i\xi v)\rangle_{equil} = \int_{-\infty}^{\infty} dv\,f(v)\,\exp\,(i\xi v)$$

$$= (2\pi)^{-1}\int_0^{2\pi} d\phi\,\exp\,(i\xi\sigma\,\sin\,\phi) = J_0(\sigma\xi), \qquad (15)$$

where σ is given by (12). It is worth noting, too, that

$$(2\pi)^{-1}\int_0^{2\pi} d\phi\,\exp\,[i\xi\sigma\,\sin\,(\omega_0 t + \phi)] = J_0(\sigma\xi), \qquad (16)$$

and $\qquad (2\pi)^{-1} \int\limits_{0}^{2\pi} d\phi \, \exp \left[i\xi\sigma \left\{\sin \left(\omega_0 t + \phi\right) - \sin \phi\right\}\right] = J_0(2\sigma\xi \sin \tfrac{1}{2} \omega_0 t).$ (17)

These integrals occur in the calculations.

2.4 *Result for* $\Phi(\xi, t)$

Using the foregoing as input, we may calculate the statistical average $\Phi(\xi, t)$ defined in (1) and (2). Suppressing the (lengthy) algebra entirely, we present the final result for the Laplace transform $\tilde{\Phi}(\xi, s)$:

$$\tilde{\Phi}(\xi, s) = \int\limits_{0}^{\infty} dt \, \left\langle \exp i\xi \, [v(t) - v(0)] \right\rangle \exp\left(-st\right)$$

$$= \left[\tau_1^2 + \frac{(\tau_0 + \tau_1 + s\tau_0\tau_1)}{s(1 + s\tau_0)} J_0^2 (\sigma\xi) + (\tau_0 + \tau_1 + s\tau_0\tau_1) \int\limits_{0}^{\infty} dt'\right.$$

$$\left.\times J_0(2\sigma\xi \sin \tfrac{1}{2}\omega_0 t') \exp\left\{- t' \left(s + \tau_0^{-1}\right)\right\}\right] \Big/ \, [(\tau_0 + \tau_1) (1 + s\tau_1)],$$

$$\tag{18}$$

where (to recall the notation) τ_0 is the mean residence time at a site, τ_1 is the mean flight time between steps, ω_0 is the 'local mode' frequency, and $\sigma = (2k_B T/m)^{1/2}$. The Bessel functions appear as a consequence of the oscillatory motion. In the next section, we shall determine the dynamic mobility with the help of (18).

Inversion of the Laplace transform (18) yields after simplification the following expression for $\Phi(\xi, t)$:

$$\Phi(\xi, t) = \left\langle \exp i\xi[v(t) - v(0)] \right\rangle$$

$$= \frac{1}{(\tau_0 + \tau_1)} \left[\tau_1 \exp\left(- t/\tau_1\right) + \tau_0 J_0(2\sigma\xi \sin \tfrac{1}{2}\omega_0 t) \exp\left(- t/\tau_0\right)\right.$$

$$+ \frac{J_0^2 (\sigma\xi)}{(\tau_0 - \tau_1)} \cdot \left\{\tau_0^2(1 - \exp\left(- t/\tau_0\right)) - \tau_1^2(1 - \exp\left(- t/\tau_1\right)\right\}$$

$$\left.+ \exp\left(- t/\tau_1\right) \int\limits_{0}^{\infty} dt' \cdot J_0\left(2\sigma\xi \sin \tfrac{1}{2}\omega_0 t'\right) \exp\left(- t' \left(\tfrac{1}{\tau_0} - \tfrac{1}{\tau_1}\right)\right)\right].$$

$$\tag{19}$$

Before proceeding further, we must check the conservation of probability. It is evident that $\Phi(0, t)$ must be equal to unity by definition, as must $\Phi(\xi, 0)$. It is easily verified that the final expression in (19) meets these requirements. This is tantamount to a confirmation that all possible event sequences have been properly included in the determination of the conditional probability $P(v, t \mid v_0)$.

The second important check is the $t \to \infty$ limit. Under equilibrium conditions, one must have $P(v, t \to \infty \mid v_0) \to f(v)$ (fluctuation dissipation). Hence, from (2) and (15),

$$\lim_{t \to \infty} \Phi(\xi, t) = \langle \exp (i\xi v) \rangle_{\text{equil}} \langle \exp (i\xi v_0) \rangle_{\text{equil}} = J_0^2(\sigma \xi). \tag{20}$$

Once again, an inspection of (19) affirms that this limiting value is recovered.

3. The velocity autocorrelation function and the dynamic mobility.

3.1 *The frequency-dependent mobility*

The velocity response is described by a generalized susceptibility, namely, the frequency-dependent mobility $\hat{\mu}(\omega)$. As is well-known from linear response theory, this is given by

$$\hat{\mu}(\omega) = \beta \int_0^\infty dt \, \langle v(t) \, v(0) \rangle \exp (i\omega t), \tag{21}$$

i.e., by the Fourier-Laplace transform of the velocity autocorrelation. This is found easily by expanding $\widetilde{\Phi}(\xi, s)$ as given by (18) in powers of ξ, and isolating the term proportional to ξ^2. Analytic continuation of the result to $s = -i\omega$ is trivial. We obtain, after using the fact that $\langle v^2 \rangle = (k_B T/m)$, the compact expression

$$\hat{\mu}(\omega) = \frac{1}{m(\tau_0 + \tau_1)(1 - i\omega\tau_1)} \left[\tau_1^2 + \frac{\tau_0(1 - i\omega\tau_0)(\tau_0 + \tau_1 - i\omega\tau_0\tau_1)}{(1 - i\omega\tau_0)^2 + \omega_0^2 \tau_0^2} \right]. \tag{22}$$

The effect of the ' local mode ' is contained in the second term in the square brackets. The solution in the absence of oscillatory behaviour can be obtained by letting $\omega_0 \to \infty$ (and simultaneously $A \to 0$: recall that $A^2 \omega_0^2/2$ has been set equal to $k_B T/m$) so that the particle is static in the state of residence. The result is

$$\hat{\mu}(\omega) \to \tau_1^2 / [m (\tau_0 + \tau_1)(1 - i\omega\tau_1)]. \tag{23}$$

This differs from the standard ' free diffusion ' expression

$$\hat{\mu}_0(\omega) = 1/m (\gamma_1 - i\omega), \tag{24}$$

(where $\gamma_1 = 1/\tau_1$ is the friction constant) only by the factor $\tau_1/(\tau_0 + \tau_1)$. The latter is easily understood as the fraction of time the particle spends in the ' diffusive ' state. Other limits and special cases are discussed in what follows.

The structure of the exact result for $\hat{\mu}(\omega)$ for diffusion in a periodic potential is a complicated one. The analysis is complicated, and various systematic approximation schemes have been developed (Fulde *et al* 1975; Dieterich *et al* 1977; Risken and Vollmer 1978). The frequency-dependent mobility can be obtained as an infinite

continued fraction, for instance.   While the concise expression (22) clearly does not possess this structure, owing to our adoption of a simple model of oscillatory diffusion, it does provide a reasonable facsimile of the actual physical situation in that it demonstrates most of the non-trivial features one may expect the susceptibility concerned to possess.   It is also sufficiently general to encompass several known results as special cases, as will be seen shortly.

3.2   *The velocity autocorrelation function*

The autocorrelation function $\langle v(t) v(0) \rangle$ conveys much information about the random process representing the velocity of the diffusing particle, in a physically perspicuous manner.   Using (22) for $\hat{\mu}(\omega)$ and inverting the transform in (21), we obtain

$$\langle v(t) v(0) \rangle = \left(\frac{k_B T}{m}\right) \frac{1}{(\gamma_0 + \gamma_1) \, [(\gamma_0 - \gamma_1)^2 + \omega_0^2]} [\gamma_0 (\gamma_0^2 - \gamma_0 \gamma_1 + \omega_0^2)$$

$$\exp(-\gamma_1 t) + \gamma_1 (\gamma_1^2 - \gamma_0 \gamma_1 + \omega_0^2) \cos(\omega_0 t) \exp(-\gamma_0 t)$$

$$+ \gamma_0 \gamma_1 \omega_0 \sin(\omega_0 t) \exp(-\gamma_0 t)], \tag{25}$$

where $\gamma_0 = 1/\tau_0$, $\gamma_1 = 1/\tau_1$ as defined earlier. It is trivially verified, on setting $t = 0$, that $\langle v^2 \rangle = (k_B T/m)$.   For ready comparison, it may be recalled that the Langevin equation for the Brownian motion of a simple harmonic *oscillator* (which is of course distinct from that for Brownian motion in a periodic potential) yields the result (Uhlenbeck and Ornstein 1930, Chandrasekhar 1943)

$$\langle v(t) v(0) \rangle = (k_B T/m) (\cos \tilde{\omega} t - (\gamma/2\tilde{\omega}) \sin \tilde{\omega} t) \exp(-\gamma t/2), \tag{26}$$

where γ is the friction coefficient and $\tilde{\omega}^2 = (\omega_0^2 - \gamma^2/4)$. Note that there is no diffusion in this instance, as the integral of (26) over t from 0 to ∞ vanishes. Indeed, the displacement $x(t)$ is itself a stationary random variable in this case, with an exponentially decaying autocorrelation function.

Consider now the special cases deducible from (25). First, if there is free diffusion with no halts at sites, $\tau_0 \to 0$,   *i.e.*, $\gamma_0 \to \infty$. Then

$$\langle v(t) v(0) \rangle \to (k_B T/m) \exp(-\gamma_1 t). \tag{27}$$

This is just the answer obtained from the ordinary Langevin equation, and quite evidently is equivalent to (24) for $\hat{\mu}_0(\omega)$. On the other hand, instantaneous jump diffusion implies that $\tau_1 = 0$, so that

$$\langle v(t) v(0) \rangle \to (k_B T/m) \exp(-\gamma_0 t) \cos \omega_0 t, \tag{28}$$

which is again readily understood—the correlation function for an oscillator, modulated by the holding-time distribution $\exp(-\gamma_0 t)$.

3.3 The dynamic mobility

The quantity of direct experimental interest is the dynamic mobility*

$$\mu\,(\omega) \equiv \mathrm{Re}\,\hat{\mu}\,(\omega) = \beta \int_0^\infty dt\, \langle v\,(t)\, v\,(0)\rangle \cos \omega t. \tag{29}$$

(The integral on the right is just $1/4$ times the power spectral density of the velocity variable.) We find, from (22),

$$\mu\,(\omega) = \frac{\gamma_0\,\gamma_1}{m\,(\gamma_0+\gamma_1)\,[(\gamma_0-\gamma_1)^2 + \omega_0^2]} \left[\frac{(\gamma_0^2-\gamma_0\,\gamma_1+\omega_0^2)}{(\gamma_1^2+\omega^2)} \right.$$
$$\left. + \frac{1}{2} \frac{(\gamma_1^2-\gamma_0\,\gamma_1+2\omega_0^2+\omega\,\omega_0)}{\gamma_0^2+(\omega+\omega_0)^2} + \frac{1}{2} \frac{(\gamma_1^2-\gamma_0\,\gamma_1+2\omega_0^2-\omega\,\omega_0)}{\gamma_0^2+(\omega-\omega_0)^2} \right]. \tag{30}$$

The simultaneous occurrence of diffusive and oscillatory characteristics, and the build-up of the 'local mode' peak in $\mu\,(\omega)$, are illustrated in figure 1.
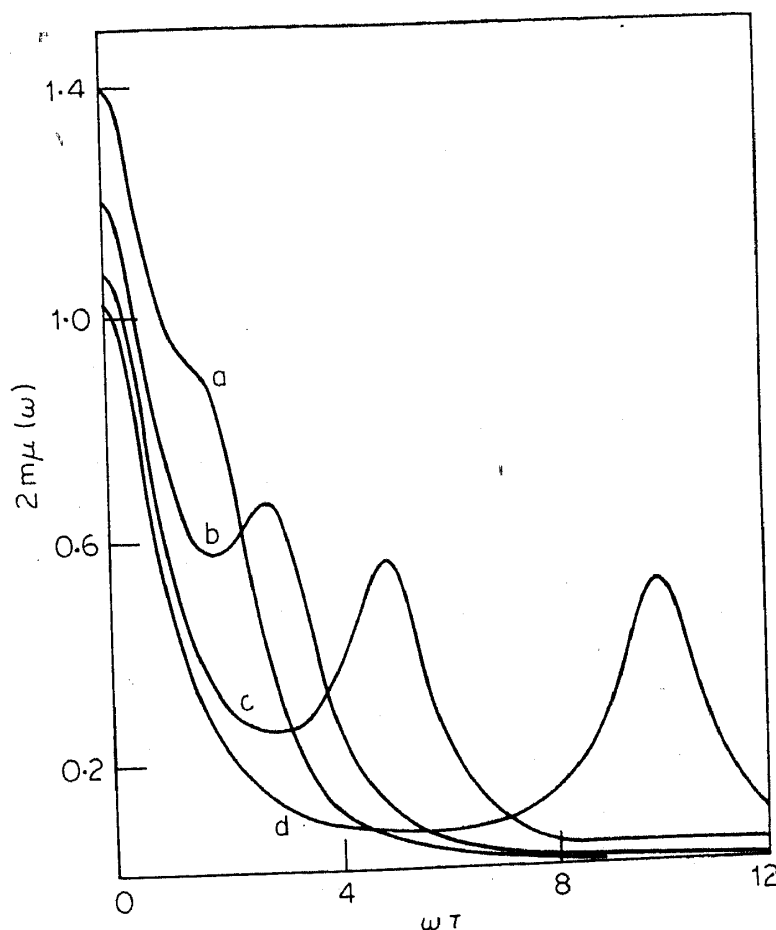

Figure 1. Variation of the dynamic mobility $\mu(\omega)$ with frequency (equation (30)), illustrating the occurrence of both 'diffusive' and 'oscillatory' peaks, in the case $\gamma_0 = \gamma_1\,(\equiv 1/\tau)$. Curves (a) through (d) refer respectively to $\omega_0\tau = 2, 3, 5$ and 10.

*For instance, in the modelling of superionic conductance via diffusion in a periodic potential $\mu\,(\omega)$ is directly related to the conductivity.

As in earlier works (*e.g.*, Dieterich *et al* 1977), it is convenient to normalize $\mu(\omega)$ by dividing it by the static mobility $\mu_0 = \hat{\mu}_0(0) = 1/(m\,\gamma_1)$ corresponding to free diffusion. Figure 2 shows the enhancement of the local mode peak at the expense of the diffusive peak in the quantity $\mu(\omega)/\mu_0$, as τ_1 decreases relative to τ_0. These plots are complemented by those in figure 3, in which the family of curves corresponds to a fixed value of τ_1 and varying values of τ_0. (It is of course evident on physical grounds that the ' local mode ' peak will disappear whenever $\omega_0\,\tau_0 \leqslant 1$.) Comparing the total picture gathered from figures 1–3 with that deduced by other approaches (Fulde *et al* 1975, Dieterich *et al* 1977, Risken and Vollmer 1978), we conclude that the results of our simple model display all the essential features expected of the exact velocity response in oscillatory diffusion*, without necessitating any *involved* analysis or approximation scheme. Note, for instance, the minimum in $\mu(\omega)$ at a finite value of ω in curves (b) and (c) of figure 2; as pointed out in Dieterich *et al* (1977), this feature is peculiar to oscillatory diffusion (or diffusion in a periodic potential). It *cannot* be reproduced by simpler approaches (such as a generalized Langevin equation with an exponential memory kernel) that lead to a two-pole approximation to the continued
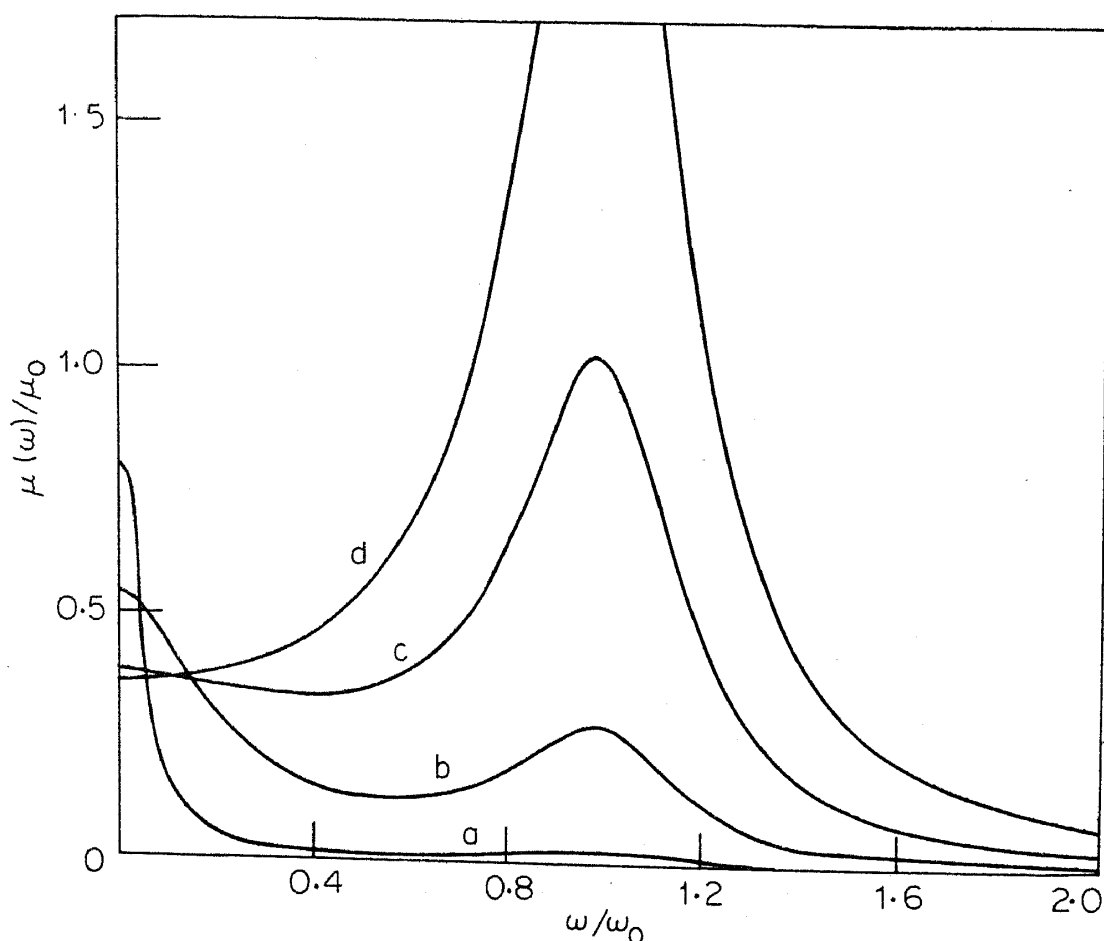

Figure 2. Normalized dynamic mobility $\mu(\omega)/\mu_0$ as a function of ω/ω_0, for varying values of the mean flight time τ_1. All the curves correspond to $\omega_0\tau_0 = 5$, with (a) $\omega_0\tau_1 = 20$, (b) $\omega_0\tau_1 = 5$, (c) $\omega_0\tau_1 = 2$, (d) $\omega_0\tau_1 = 1$.

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*Compare, for instance, curve (*b*) of figure 3 with the experimental curve of the conductivity $\sigma(\omega)$ for the superionic conductor AgI, reported in Brüesch *et al* (1975).
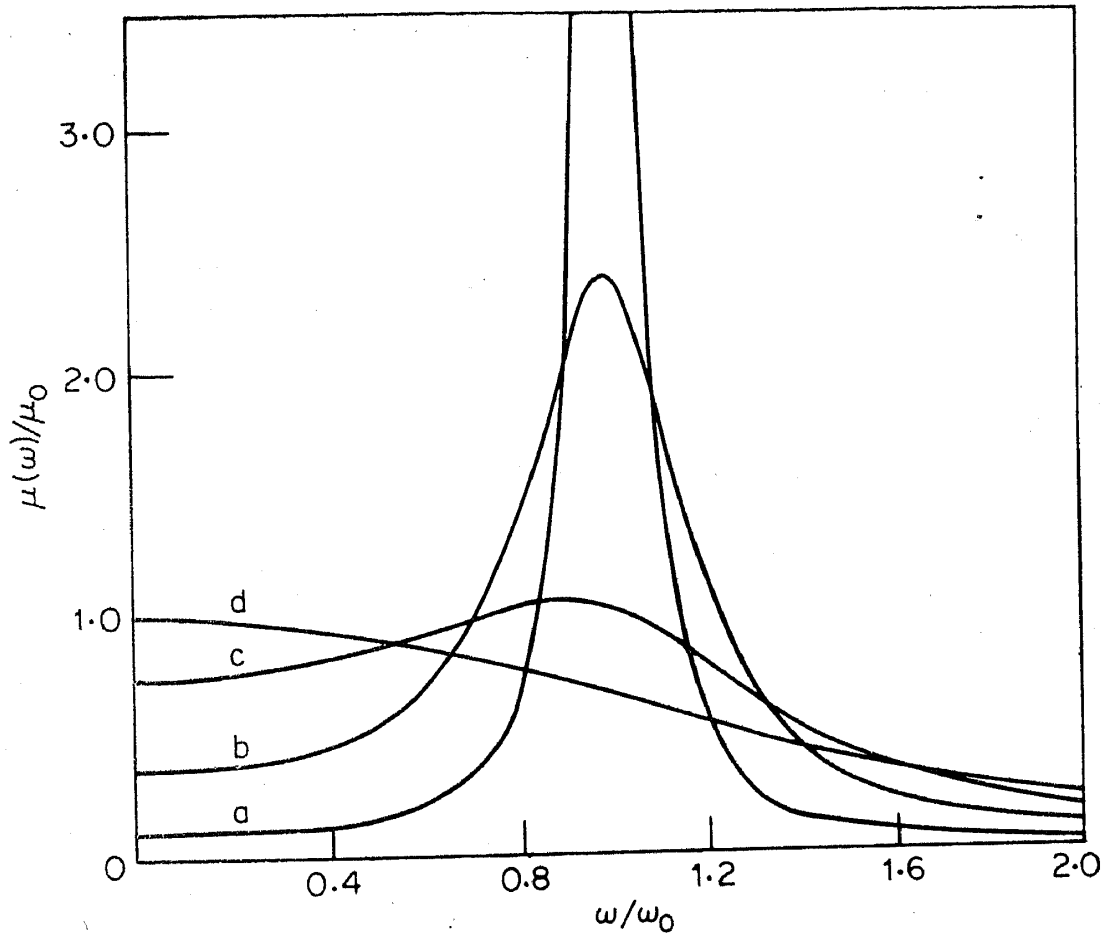
Figure 3. Normalized dynamic mobility $\mu(\omega)/\mu_0$ as a function of ω/ω_0, for varying values of the mean residence time τ_0. All the curves correspond to $\omega_0\tau_1 = 1$, with (a) $\omega_0\tau_0 = 20$, (b) $\omega_0\tau_0 = 5$, (c) $\omega_0\tau_0 = 2$, (d) $\omega_0\tau_0 = 1$.

fraction representation for $\hat{\mu}(\omega)$. We emphasize, therefore, that (30) is more than a mere ' two-pole approximation ' of this sort.

4. The static mobility and the structure factor

4.1 *The generalized diffusion constant*

The static mobility is measured by the diffusion constant D, according to

$$D = k_B T \hat{\mu}(0) = k_B T \mu(0). \tag{31}$$

Our theory yields the expression

$$D = \left(\frac{k_B T}{m}\right)\left[\frac{\tau_0}{(1 + \omega_0^2 \tau_0^2)} + \frac{\tau_1^2}{(\tau_0 + \tau_1)}\right], \tag{32}$$

which, *albeit* simple in appearance, has a non-trivial structure built into it. Note in particular that D is *not* simply given by $(a^2 + \langle x_{osc}^2 \rangle)/2 \, (\tau_0 + \tau_1)$ (where a is

the lattice constant and $\langle x^2_{osc} \rangle$ is the mean square displacement in the oscillatory state), as one may expect at first sight and as is sometimes written down in the literature. However, the two terms in the square brackets in (32) do represent respectively ' oscillatory ' and ' diffusive ' contributions to D.

When $\tau_0 = 0$, the well-known free diffusion result $D_0 = (k_B T/m \gamma_1)$ is retrieved from (32). Further, if the ' local mode ' is absent, *i.e.*, if during residence at a site the particle is static, then (32) yields (on letting $\omega_0 \to \infty$) the physically understandable result

$$D = D_0 \tau_1 / (\tau_0 + \tau_1). \tag{33}$$

This is precisely the effective diffusion constant used, for instance, in the description of diffusion in the presence of traps (Schroeder 1976).

The extraction of D in the jump diffusion limit ($\tau_1 \to 0$) from (32) requires a bit of care. In the first term, one may replace $k_B T/m$ by $\omega_0^2 \langle x^2_{osc} \rangle$. In the second term, since $k_B T/m = \langle v^2 \rangle$, and τ_1 is the mean flight time between neighbouring sites, we may write $2 k_B T/m = a^2/\tau_1^2$ Hence (32) may be re-written as

$$D = \frac{\langle x^2_{osc} \rangle}{\tau_0} \left\{ \frac{(\omega_0 \tau_0)^2}{1 + (\omega_0 \tau_0)^2} \right\} + \frac{a^2}{2(\tau_0 + \tau_1)}. \tag{34}$$

Letting $\tau_1 \to 0$ in *this* representation yields D for jump diffusion. When there is no oscillatory motion, the first term on the right in (34) disappears. The familiar formula $D = a^2/2 \tau_0$ is recovered. Note also that when $\omega_0 \tau_0 = 1$, and only then, is the diffusion constant for jump diffusion given by $(a^2 + \langle x^2_{osc} \rangle)/2 \tau_0$.

Given the fact that (32) encompasses all the special cases above, it is of interest to see how the static mobility varies with the ' friction ' γ_1 ($= 1/\tau_1$). This is shown in figure 4, in which we plot $m\omega_0 \mu(0)$ (or $m\omega_0 D/k_B T$) against γ_1/ω_0 for various fixed values of $\omega_0 \tau_0$. A similar plot is depicted in figure 2 of Dieterich *et al* (1977). However, the latter is restricted to the rather narrow range $0 \cdot 3 \lesssim \gamma_1/\omega_0 \lesssim 1 \cdot 6$, and moreover there is no explicit parameter corresponding to τ_0 in the work referred to[*]. Within the above range of γ_1/ω_0, there is broad agreement with the results of the present work, specifically with the curve corresponding to $\omega_0 \tau_0 \simeq 20$. Finally, it is easy to show from (32) that $\mu(0) \gtrless \mu_0$ according as $\omega_0^2 \lessgtr \gamma_0 \gamma_1$, *i.e.*, $\omega_0 \lessgtr (\tau_0 \tau_1)^{-1/2}$.

4.2 *The mean square displacement*

Making use of the stationary of the velocity, the mean square displacement in a time interval t is given by

$$\langle (x(t) - x(0))^2 \rangle = 2 \int_0^\infty dt' (t - t') \langle v(t') v(0) \rangle. \tag{35}$$

[*]There is of course the parameter $V_0/k_B T$, where V_0 is the depth of the well in the periodic potential; if interpreted as the rate of escape over the barrier represented by a maximum of the potential, $\gamma_0 = 1/\tau_0$ can be related to this parameter.
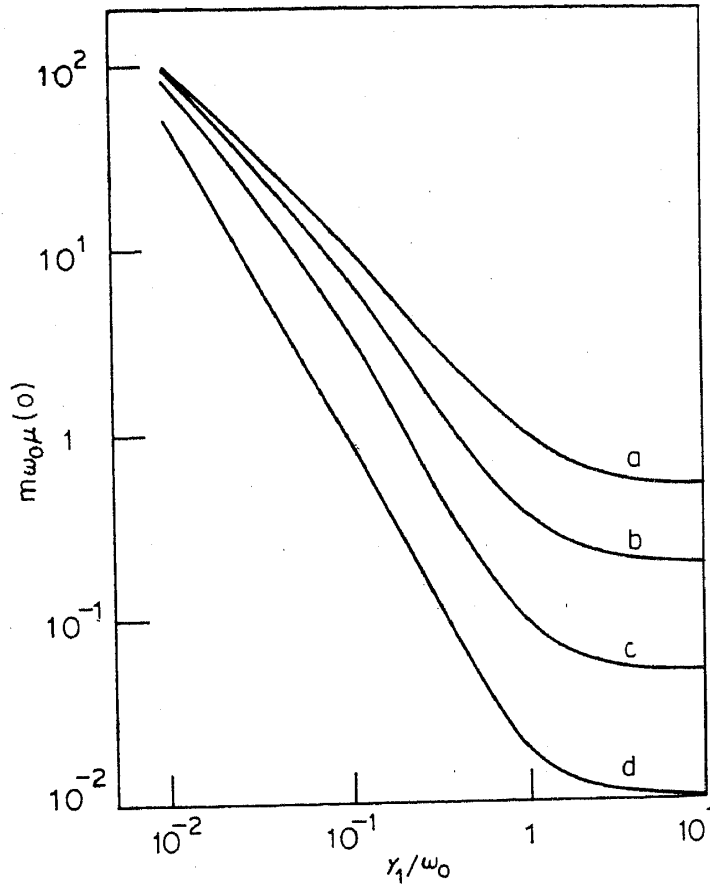
Figure 4. Variation of the static mobility $\mu(0)$ with friction. Curves (a) through (d) refer respectively to $\omega_0\tau_0 = 1, 5, 20$ and 100.

Substituting (25) for the autocorrelation function and integrating, we find

$$\langle (x(t) - x(0))^2 \rangle = 2\,Dt - \left(\frac{2k_B T}{m}\right) \frac{1}{(\gamma_0 + \gamma_1)\,[(\gamma_0 - \gamma_1)^2 + \omega_0^2]}$$

$$\times \left\{ c_1\,[1 - \exp(-\gamma_1 t)] + c_2\,[1 - \exp(-\gamma_0 t)\cos \omega_0 t] \right.$$

$$\left. + c_3 \exp(-\gamma_0 t)\sin \omega_0 t \right\}, \tag{36}$$

where D is the diffusion constant (as required), and the constants c_i are defined by

$$\left. \begin{aligned} c_1 &= \gamma_0\,(\gamma_0^2 - \gamma_0\,\gamma_1 + \omega_0^2)/\gamma_1^2, \\ c_2 &= \gamma_1\,\{2\,\gamma_0^2\,\omega_0^2 + (\gamma_1^2 - \gamma_0\,\gamma_1 + \omega_0^2)\,(\gamma_0^2 - \omega_0^2)\}/(\gamma_0^2 + \omega_0^2)^2; \\ c_3 &= \gamma_0\,\gamma_1\,\omega_0\,(2\,\gamma_1^2 - 2\,\gamma_0\,\gamma_1 - \gamma_0^2 + 3\,\omega_0^2)/(\gamma_0^2 + \omega_0^2)^2. \end{aligned} \right\} \tag{37}$$

Once again, on letting $\gamma_0 \to \infty$, we recover the free diffusion result

$$\langle (x(t) - x(0))^2 \rangle = (2\,D_0/\gamma_1)\,(\gamma_1 t - 1 + \exp(-\gamma_1 t)) \tag{38}$$

where $D_0 = (k_B T/m \gamma_1)$ as already defined. Similarly, if there is no local mode but only static residence (*i.e.*, $\omega_0 \to \infty$ but $\gamma_0 < \infty$), we find for the mean square displacement exactly the same functional form as in (38), with however D_0 replaced by the effective diffusion constant $D_0 \tau_1/(\tau_0 + \tau_1)$. These results tally with those derived in I by a totally different route, namely, from a consideration of the random walk problem on the lattice in real space. Finally, in the case of jump diffusion and in the absence of the oscillatory motion, all that survives on the right-hand side in (36) is the term $2Dt$ where D now stands for $a^2/2\tau_0$. This too is as it should be, for the self-correlation function in this special case obeys (the discrete or lattice analogue of) the simple diffusion equation, and the solution is a Gaussian, with a variance proportional to t.

4.3 *The dynamic structure factor*

We now consider in brief the dynamic structure factor $S(k, \omega)$, as this aspect of diffusion is among those closest to experiment. Our purpose is to comment on the manner in which the mutual interference of oscillation and free diffusion is manifested in the shape of $S(k, \omega)$. For sufficiently small values of k, a satisfactory approximation to $S(k, \omega)$ is

$$S(k, \omega) \simeq (1/\pi) \int_0^\infty dt \cos \omega t \exp \left\{ -\tfrac{1}{2}k^2 \langle (x(t) - x(0))^2 \rangle \right\}. \tag{39}$$

The mean square displacement has the form displayed in (36). Using this in (39), we may draw the following conclusions. The quasi-elastic peak in $S(k, \omega)$ has an FWHM that is approximately equal to $2Dk^2$, where D is the generalized diffusion constant found earlier. The interplay of oscillatory and diffusive characteristics in D is already explicit in (34). For sufficiently large values of $\omega_0 \tau_0$, there is a secondary 'local mode' peak in $S(k, \omega)$ near $\omega = \omega_0$. This peak has an FWHM approximately equal to $2(Dk^2 + \gamma_0)$, and is therefore considerably broadened, relative to the quasi-elastic peak.

Figure 5 illustrates the sort of result obtained by numerical integration of (39) after (36) is inserted for the mean square displacement. The values chosen for the various parameters are approximately the same as those employed in Dieterich *et al* (1977) (see § 6 and figure 5 of their paper), for the sake of comparison. Thus we set $2\pi\gamma_1/\omega_0$ (denoted by Γ in the latter paper) equal to unity, and

$$(k^2/\omega_0^2) (k_B T/m) \equiv 2(k^2/k_0^2) (k_B T/V_0) = 2 \times (0 \cdot 2)^2 \times (0 \cdot 3) = 0 \cdot 024, \tag{40}$$

and finally $\gamma_0/\omega_0 = 20$. Then

$$\pi\omega_0 S(k, \omega) = \int_0^\infty dz \cos (z\omega/\omega_0) \exp \left\{ - F(z) \right\},$$

where $F(z) = 0 \cdot 0369z - 0 \cdot 2193 (1 - \exp(-0 \cdot 16z)) + 0 \cdot 0182$

$$(1 - \exp(-0 \cdot 05z) \cos z) - 0 \cdot 0027 \exp(-0 \cdot 05z) \sin z. \tag{41}$$
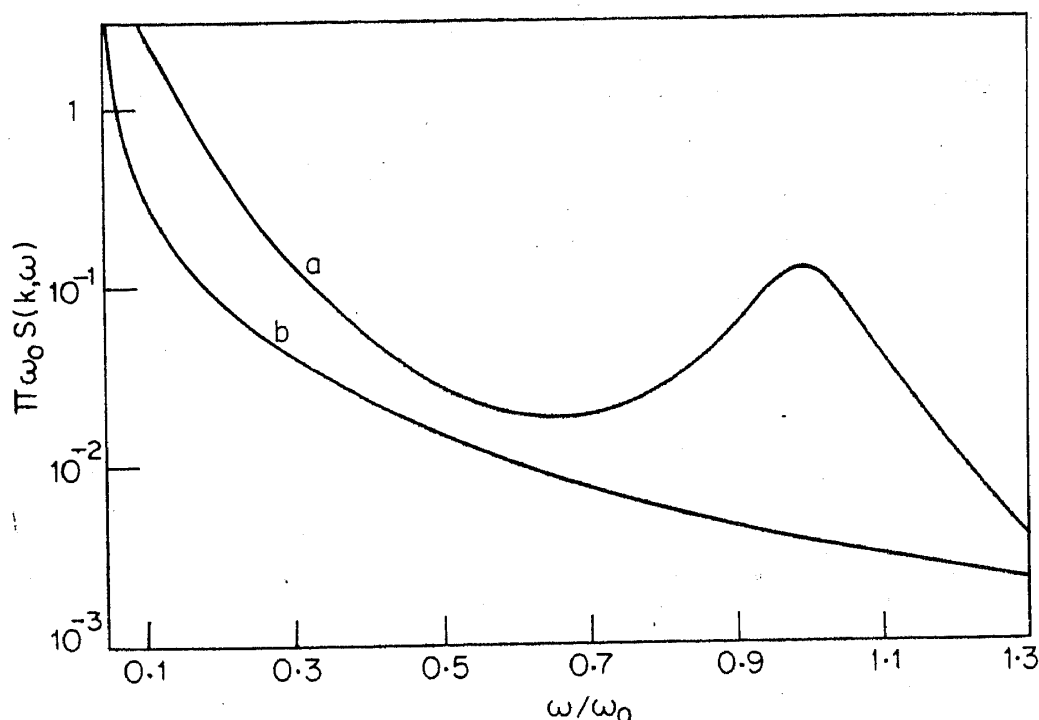
Figure 5. Dynamic structure factor as a function of ω/ω_0, in the Gaussian approximation (the ordinate is on a logarithmic scale). The numerical values of the parameters are specified in (40) *ff*. Curve (a) corresponds to the full integrand in (41). For comparison, curve (b) is the Lorentzian obtained by retaining only the first term ($0\cdot0369z$) in the expression (41) for $F(z)$.

Curve (a) in figure 5 is a plot of the structure factor given by (41) as a function of the frequency, exhibiting the additional local mode peak at $\omega \approx \omega_0$. If we use merely the term $0\cdot0369z$ for $F(z)$ the outcome is the Lorentzian plotted in curve (b). This amounts to approximating the mean square displacement in (39) by its asymptotic value $2Dt$, and helps give an idea of what the quasielastic peak would look like if the other contributions to the mean square displacement were absent.

5. The velocity increment distribution; connection with ' interpolation ' models

We have computed, in the foregoing, the autocorrelation $\langle v(t)v(0)\rangle$ (and all the other quantities related to it such as $\hat{\mu}(\omega)$, D, etc.) without explicitly obtaining first the joint probability density $P(v, t; v_0, 0) \equiv f(v_0) P(v, t \mid v_0)$. This is because the convolution-structured CTRW formalism makes it natural and convenient to work in terms of an appropriate Fourier transform with respect to the velocity variable*. It is evident from the definition (1·2) that $\Phi(\xi, t)$ is the transform of $P(v, t; v_0, 0)$ with respect to the difference variable $(v - v_0)$. Clearly, $\Phi(\xi, t)$ does not contain as much information as, say, the characteristic function $X(\xi_1, \xi_2; t)$ of the distribution $P(v, t; v_0, 0)$, being a special case: $\Phi(\xi, t) = X(\xi, -\xi; t)$. It does, however, carry more information on the velocity variable than is incumbent in the autocorrelation $\langle v(t) v(0)\rangle$, and it is this aspect to which we now turn, for the sake of completeness.

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*And, of course, a Laplace transform with respect to the time.

5.1 *The probability density of the velocity increment*

The explicit form of $\Phi(\xi, t)$ has already been written down in (19), and the limiting values for $t \to 0$, $t \to \infty$ (representing respectively the conservation of probability and the fluctuation-dissipation theorem) have been checked. One may first ask what the inversion of the Fourier transform with respect to the variable ξ yields. The answer, which we denote by $P(u, t)$, is easily seen to be

$$P(u, t) \equiv (1/2\pi) \int_{-\infty}^{\infty} d\xi \, \Phi(\xi, t) \exp(-iu\xi)$$

$$= \int dv_0 \, f(v_0) \, P(v_0 + u, t \,|\, v_0). \tag{42}$$

The physical meaning of $P(u, t)$ is quite evident: it is the net probability density associated with a velocity *increment* u in the time interval t. Performing the Fourier inversion of the function $\Phi(\xi, t)$ given by (19), we find

$$\pi(\tau_0 + \tau_1) \, P(u, t)$$

$$= \pi\tau_1 \, \delta(u) \exp(-t/\tau_1) + \tau_0 \exp(-t/\tau_0) \, (4\sigma^2 \sin^2 \tfrac{1}{2} \omega_0 t - u^2)^{-1/2}$$

$$\times \, \theta(|\, 2\sigma \sin \tfrac{1}{2}\omega_0 t \,| - |\, u \,|) + \frac{1}{2\sigma} P_{-1/2}\left(\frac{u^2}{2\sigma^2} - 1\right)$$

$$\times \, \left\{\frac{\tau_0^2 \, [1 - \exp(-t/\tau_0)] - \tau_1^2 \, [1 - \exp(-t/\tau_1)]}{\tau_0 - \tau_1}\right\} \, \theta(2\sigma - |\, u \,|)$$

$$+ \exp(-t/\tau_1) \int_0^t dt' \exp\left[-t'\left(\frac{1}{\tau_0} - \frac{1}{\tau_1}\right)\right]$$

$$\times \, (4\sigma^2 \sin^2 \tfrac{1}{2} \omega_0 t' - u^2)^{-1/2} \, \theta(|\, 2\sigma \sin \tfrac{1}{2} \omega_0 t' \,| - |\, u \,|), \tag{43}$$

where, to recall (12), $\sigma = (2k_B T/m)^{1/2}$, and $P_{-1/2}$ stands for the Legendre function of order $-\tfrac{1}{2}$. The restriction of $|\, u \,|$ to values $\leqslant 2\sigma$ is easily understood, for the velocity itself is restricted to the range $-\sigma \leqslant v \leqslant \sigma$.

5.2 *Conditional density for free diffusion*

It is essentially the interleaving of two random processes, with correlation times τ_0 and τ_1 respectively, that has necessitated the use of the powerful CTRW formalism in the present work. At various stages, we have paused to consider the limiting cases of free diffusion ($\tau_0 = 0$) and jump diffusion ($\tau_1 = 0$). We shall now show that $P(v, t \,|\, v_0)$ can itself be obtained explicitly in these special cases, from an inspection of the structure of $\Phi(\xi, t)$. This exercise is instructive, as it provides some insight into the make-up of the CTRW approach to the general problem. We consider first the case of free diffusion, *i.e.* $\tau_0 = 0$.

In the above limit, (19) reduces to

$$\Phi\,(\xi,t) = \exp\,(-\gamma_1\,t) + J_0^2\,(\sigma\,\xi)\,[1-\exp\,(-\gamma_1\,t)]. \qquad (44)$$

The autocorrelation function corresponding to (44) is of course the simple exponential already given in (27), which matches the standard Langevin equation result. We have also compared the equilibrium distribution $f(v)$ (see (9)), the characteristic function of which is $J_0\,(\sigma\,\xi)$, with the Maxwellian $f_M(v)$ (see (13)). Continuing the comparison, in the conventional picture the velocity is a Gaussian random variable, so that

$$\Phi\,(\xi,t) = \exp\left\{-\frac{k_B\,T\,\xi^2}{m}\,[1-\exp\,(-\gamma_1\,t)]\right\}. \qquad (45)$$

Further, $P\,(v,\,t\,|\,v_0)$ satisfies the Fokker-Planck equation, and the solution is the Ornstein-Uhlenbeck distribution (Uhlenbeck and Ornstein 1930). What is $P\,(v,\,t\,|\,v_0)$ (for free diffusion) in the present case?

The answer is quite simple, and may indeed be guessed at from (44) itself. It is

$$P\,(v,\,t\,|\,v_0) = \delta\,(v-v_0)\,\exp\,(-\gamma_1\,t) + f(v)\,[1-\exp\,(-\gamma_1\,t)]. \qquad (46)$$

In other words, when one of two correlation times (here, τ_0) vanishes, the CTRW result simplifies to an *interpolation model* for the conditional density: the expression in (46) interpolates between the initial distribution $\delta(v-v_0)$ and the equilibrium distribution $f(v)$. The Chapman-Kolmogorov equation is also obeyed by (46), so that the Markovian nature of the velocity process is retained. The structure of interpolation models for a Markov process, comparison with the solution of the Fokker-Planck equation, and generalization to the non-Markovian case have already been presented elsewhere (Balakrishnan 1979).

5.3 *Conditional density for jump diffusion*

When $\tau_1 = 0$, so that the inter-site flights are instantaneous jumps, (19) becomes

$$\Phi\,(\xi,t) = J_0\,(2\,\sigma\,\xi\,\sin\tfrac{1}{2}\,\omega_0\,t)\,\exp\,(-\gamma_0\,t) + J_0^2\,(\sigma\,\xi)\,[1-\exp\,(-\gamma_0\,t)]. \qquad (47)$$

The autocorrelation function is the exponential-modulated cosine already written down in (28). The non-trivial deterministic evolution of the velocity in the resident state (see (6)) precludes the process from being Markovian. However, $P\,(v,\,t\,|\,v_0)$ can again be shown to fall within the purview of interpolation models of a somewhat more generalized nature (Balakrishnan 1979). It can be verified that the solution that leads to (47) is

$$P\,(v,\,t\,|\,v_0) = \delta\,[v-\sigma\,\sin\,(\omega_0\,t+\phi_0)]\,\exp\,(-\gamma_0\,t) + f(v)$$
$$\times\,[1-\exp\,(-\gamma_0\,t)], \qquad (48)$$

where $\sigma \equiv A\,\omega_0 = (2k_B\,T/m)^{1/2}$ (equation (12)), $f(v)$ is given by (9) as always, and ϕ_0 is defined by $\sigma\,\sin\phi_0 = v_0$.

P.—2

As already stated, when both τ_0 and τ_1 are non-zero, the structure of the theory becomes non-trivial.

6. Concluding remarks

The significance of the general problem of interrupted diffusion has already been expounded in paper I. Physical applications of current interest include superionic conductance, diffusion in the presence of traps, and the diffusion of hydrogen in metals—specifically, in the transition regime between jump diffusion in a lattice and fluid-like diffusion, when the mean residence time at a site and the mean inter-site flight times are comparable. Oscillatory diffusion, as occurs for instance in the presence of a local mode, complicates the problem further; a third characteristic time is introduced. Earlier approaches address themselves to the problem of diffusion in a periodic potential (in one dimension), and treat it in terms of a Fokker-Planck equation for the conditional probability density. Rather complicated systematic approximation schemes are then developed to evaluate the relevant response functions (such as the frequency-dependent mobility, etc.), and to demonstrate the simultaneous occurrence of oscillatory and diffusive effects in these. In contrast, we have visualized a two-state generalized random walk model of the diffusion process, in which the particle alternates between a state of flight between lattice sites and one of localized oscillation about a site. With the help of simple physical inputs for the primary quantities characterizing this random walk, we have, in this paper, used the very effective CTRW technique in velocity space to derive convenient and physically sensible closed-form expressions for all the quantities of interest in oscillatory diffusion. The structure of these expressions is quite non-trivial, while remaining eminently tractable, and a number of known results are recovered as special cases on passing to the appropriate limits. The result for the generalized diffusion constant D that is displayed in (32), and the subsequent discussion, should serve as a convincing illustration of these statements.

The scope of this paper has throughout been restricted to the following broad objective: the derivation of a theoretical description encompassing certain *qualitative* features expected of oscillatory diffusion on the basis of a variety of experimental observations (*e.g.*, the frequency-dependent conductivity of certain superionic conductors, the structure factor probed by neutron scattering studies of hydrogen in metals, etc.) The features referred to include the transition region from jump diffusion to fluid-like diffusion, the peak at a non-zero value of the frequency in the dynamic mobility, the secondary peak in the dynamic structure factor, and so on. The attainment of such an objective is clearly an essential prelude to the detailed analysis of specific experimental findings. The latter would in any case involve a tailoring of the general theory in its details, depending upon the particular case under study. Not the least of the advantages in favour of the approach adopted here is its ready amenability to the generalizations or modifications that may be required in this regard: for example, the important one of extension to three dimensions; the incorporation of more involved holding-time distributions controlling the diffusion process; and the use of different functional forms for the basic probability distributions g and h to take into account the distinct physical circumstances encountered in different problems.

Acknowledgements

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