Characterization of diffusive motion in anisotropic liquid systems

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Abstract. The translational motion of atoms in a liquid confined between two plane parallel repulsive walls is studied by computer simulation. It is shown that the motion perpendicular to the walls cannot be described in a strict sense by the conventional diffusion equation even if the diffusion constant is generalized to a space dependent diffusion tensor. Instead, for the anisotropic case, a system of linear coupled rate equations is proposed, whose time-independent rate transition matrix is shown to be necessarily spatially asymmetric, with the equilibrium mean static density as its zero eigenvalue eigenvector. This accurately describes the transverse atomic motion for times considerably larger than the velocity autocorrelation time without the need to empirically input the mean static density. This theory is tested by computer simulation and found within statistical error to be a valid quasi-microscopic description of the (slower) stochastic atomic motion. The evolution of the anisotropic self-diffusion propagators towards the quasi-periodic mean density profile is studied in detail as a function of the initial starting position.

1. Introduction and theoretical development

Macroscopic diffusive motion is well known to be irreversible and, in bulk isotropic fluids, is well described over macroscopically long time scales by the usual diffusion equation

$$\dot{\rho} = \mathrm{div}(D\nabla\rho) \tag{1.1}$$

where D is the diffusion constant which, in the bulk, is indeed a constant. For shorter time scales on the other hand the above equation clearly cannot be satisfactory since, being irreversible, its solutions decay monotonically towards a static situation and it thereby fails completely to give any description of the ongoing fluctuational motion that exists in every macroscopic system, be it in equilibrium or otherwise.

For liquids in anisotropic situations e.g. near walls, surfaces or within confined geometries (i.e. inside pores) etc, it is well known that the equilibrium mean density profile within the liquid is not uniform; for example, in the cavity between two parallel walls (which will concern us later) the mean of the equilibrated density, ρ_m, sometimes referred to as the 'static' density, is known to be non-uniform and displays marked peaks and troughs, as shown by many computer simulations (see, for example, Nicholson and

Parsonage, 1982). If we suppose the x axis to be normal to the walls, then the diffusion 'constant' (tensor) and ρ_m can only depend on x, so that (1.1) for this situation becomes

$$(\partial/\partial x) \, (D_{xx}(x) \, \partial\rho_m/\partial x) = 0$$

which means that

$$\partial\rho_m/\partial x = \text{constant}/D_{xx}(x).$$

Hence the *constant* must be zero, else the normal principal component of the diffusion tensor would need to be infinitely large at each peak and trough of the mean density profile. In turn, a zero value for the constant implies the mean density must be uniform everywhere—which we know not to be the case in the anisotropic situations we are considering.

More generally, the equilibrium mean density profile would need to obey $\text{div}(D\nabla\rho_m) = 0$, implying that $D\nabla\rho_m$ must be of the form $\text{curl}(v(r))$ where, to avoid parity violation, $v(r)$ must be some definable position-dependent *axial vector* within the fluid. For normal fluids, at least, such a non-zero local vector would appear inconceivable, so forcing the conclusion that $D\nabla\rho_m = 0$ and hence $\nabla\rho_m = 0$, which is inconsistent with the observation that ρ_m is non-constant. We thus conclude that the normal diffusion equation is inadequate to describe the mean density or the diffusive motion in any situation where the mean density is non-uniform, even with a space-dependent tensor diffusion constant, $D(r)$.

A common procedure adopted to treat diffusion in anisotropic systems is to apply the diffusion equation (usually with a tensor point function diffusion constant e.g. Groot *et al*, 1987) to the *deviation* of the density from the mean static density i.e. $\delta\rho(r, t) = \rho(r, t) - \bar{\rho}(r)$. In our opinion this is a 'patch' on the (symmetric) diffusion equation that forces $\rho(r, \infty)$ to be the static mean density, $\bar{\rho}(r)$, which (as we show later) is fundamentally erroneous in anisotropic systems as it violates classical time reversal symmetry. Further it requires the 'empirical' input of (the measured) $\bar{\rho}(r)$ which, in our opinion, should be a by product of a more complete approach. Here our philosophy is to avoid this step. As argued above, this forces us to abandon the diffusion equation too and consider instead its generalization—namely a rate equation. (In the isotropic case there is no difference as it is well known that a rate equation applied to isotropic systems in the quasistatic limit gives the diffusion equation.)

The fact that the diffusion equation is not valid for transverse atomic motion when the density is not uniform is probably not widely realized—literature on these topics abounds with references, directly or implicitly, to transverse and parallel diffusion constants, $D_\perp$ and $D_\parallel$ etc. One can also find statements such as '$D_\perp$ is zero' in these contexts. Of course, such statements are meaningful in that these 'diffusion constants' are to be interpreted in an operational sense in terms of the mean square displacement in particular directions divided by the elapsed time. These can have well-defined values even in anisotropic media defining in some sense 'effective' diffusion constants in particular directions—even when a diffusion equation with an associated diffusion 'constant' tensor point function is, strictly, invalid. In this operational sense, '$D_\perp = 0$' simply implies that the transverse motion (and hence the mean square transverse displacement) is 'bounded' e.g. by walls—as in the system we will consider in section 3. Nevertheless, here we venture the opinion that authors should, in the interest of minimizing ambiguity, avoid the use of these kinds of statements whenever a diffusion equation is not a valid description of the motion (i.e. in anisotropic systems). Rather, to state operationally what is meant is simpler, less ambiguous and more correct.

We will not be particularly concerned with the diffusion parallel to the walls in this paper since this raises no conceptual difficulty.

The question of how to characterize irreversibility in confined geometries remains, and this paper is mainly concerned with how to characterize diffusive behaviour in these situations. We propose a generalized description of diffusive motion in terms of a rate equation—which is more fundamental than the diffusion equation (1.1): as the latter may be derived from the former in the quasistatic limit and when the system is isotropic. Then, by comparison with data obtained from the computer simulation of diffusive motion in fluids, we proceed to investigate precisely under what conditions such rate equations apply. To do this we analyse the behaviour of the self-diffusion propagator i.e. the Green's function of molecular motion, $g_s(r_i, r_j, \tau)$, which describes the equilibrium probability (density) that a molecule (or atom) in position r_j at time t be found in position r_i at time $t + \tau$ i.e. τ later. For a given τ this, in general, is a real, non-symmetric matrix. In isotropic systems, this function is translationally invariant and reduces to the well-known 'self' part of the Van Hove (1954) space–time correlation function, $G_s(|r_i - r_j|, \tau)$ (or $G_s(r_{ij}, \tau)$) (see, for example, Egelstaff, 1967). Hence the matrix $g_s(r_i, r_j, \tau)$ is simply a generalization of $G_s(r_{ij}, \tau)$ to confined geometries or to translationally non-invariant systems in general. Classically $g_s(r_i, r_j, \tau)$ may be defined as

$$g_s(r_i, r_j, \tau) = \langle \delta(r_i - r_s(\tau))\delta(r_j - r_s(0))\rangle/\langle \delta(r_j - r_s(0))\rangle \tag{1.2}$$

where $\delta(r - r_s(t))$ represents the density of a *particular* (the sth) particle at point r and at time t. Classically, time reversal invariance (see, for example, Hansen and McDonald, chapter 7) requires

$$\langle \delta(r_i - r_s(\tau))\delta(r_j - r_s(0))\rangle = \langle \delta(r_j - r_s(\tau))\delta(r_i - r_s(0))\rangle$$

which, in turn, implies the 'detailed balance' condition

$$g_s(r_i, r_j, \tau)\langle \delta(r_j - r_s(0))\rangle = g_s(r_j, r_i, \tau)\langle \delta(r_i - r_s(0))\rangle \tag{1.3a}$$

or as

$$\langle \delta(r_i - r_s(0))\rangle = \bar{\rho}(r_i)/\bar{N} \qquad g_s(r_i, r_j, \tau)\bar{\rho}(r_i) = g_s(r_j, r_i, \tau)\bar{\rho}(r_i). \tag{1.3b}$$

Thus, in an anisotropic system, as a consequence of time-reversal symmetry, the self-diffusion propagator must be asymmetric. The probability density, $g_s(r_i, r_j, \tau)$ obeys

$$\int dr_i \, g_s(r_i, r_j, \tau) = 1 \tag{1.4}$$

which follows from (1.2) and simply expresses conservation of probability and implies that the matrix, $g_s(r_i, r_j, \tau)$, has a unity eigenvalue for any τ value. Further, by integrating (1.3b) over r_i and utilizing (1.4), it follows that

$$\int dr_i \, g_s(r_i, r_j, \tau)\bar{\rho}(r_j) = \bar{\rho}(r_j) = \int dr_i \, g_s(r_j, r_i, \tau)\bar{\rho}(r_i) \tag{1.5}$$

i.e. $\bar{\rho}(r)$ is the eigenvector belonging to this unity eigenvalue (as was expected intuitively) and is now seen to be a direct consequence of time reversal invariance. This Green's function describes how any initial density distribution of particles, $\rho(r_j, t)$, in the equilibrium system evolves according to

$$\rho(r_i, t + \tau) = \int dr_j \, g_s(r_i, r_j, \tau)\rho(r_j, t). \tag{1.6}$$

Here we investigate whether the evolution is describable by a rate equation propagator form. Imagining space to be subdivided into an infinite number of volume domains, $d\mathcal{V}_i$ centred on r_i, then, if a rate equation applies, we have

$$\frac{\partial}{\partial t}[\rho(r_i, t)\, d\mathcal{V}_i] = \sum_{j(\neq i)} d\mathcal{V}_i R(r_i, r_j)\, d\mathcal{V}_j \rho(r_j, t) - d\mathcal{V}_i \rho(r_i, t) \sum_{j(\neq i)} R(r_j, r_i)\, d\mathcal{V}_j \qquad (1.7)$$

where $R(r_i, r_j)\, d\mathcal{V}_i$ represents a time-independent transition probability that a particle in domain $d\mathcal{V}_j$ will diffuse to domain $d\mathcal{V}_i$ in unit time. It is convenient to define the diagonal element, $R(r_i, r_i)$, by

$$R(r_i, r_i)\, d\mathcal{V}_i = - \sum_{j(\neq i)} R(r_j, r_i)\, d\mathcal{V}_j$$

so that we may write compactly

$$\frac{\partial}{\partial t}\rho(r_i, t) = \sum_j R(r_i, r_j)\rho(r_j, t)\, d\mathcal{V}_j = \int dr_j\, R(r_i, r_j)\rho(r_j, t) \qquad (1.8)$$

where the transition matrix, $R(r_i, r_j)$ is such that $\int dr_i\, R(r_i, r_j) = 0$, i.e. the sum of all elements in each of its columns vanishes, implying that $R(r_i, r_j)$ possesses a zero eigenvalue. Furthermore, all off-diagonal elements represent transition probabilities and hence are positive and real. The formal solution of (1.8) is

$$\rho(r_i, t + \tau) = \int dr_j\, \exp(R\tau)(r_i, r_j)\rho(r_j, t) \qquad (1.9)$$

where $\exp[R\tau](r_i, r_j)$ stands for the (i, j)th element of the exponentiated matrix, $R\tau$. On comparison with (1.6), we see that, if a rate equation applies, the propagator, $g_s(r_i, r_j, \tau)$, has the representation

$$g_s(r_i, r_j, \tau) = \exp[R\tau](r_i, r_j). \qquad (1.10)$$

We pause to remark here that the aforementioned approach to anisotropic diffusion, namely to apply the diffusion equation (usually with a tensor point function diffusion constant) to the *deviation* of the density from the static mean density i.e. $\delta\rho(r, t) = \rho(r, t) - \bar{\rho}(r)$, is not consistent with (1.10). For, if a stochastic rate equation for the evolution of the probability density of a single particle is meaningful under some conditions, (e.g. in the quasistatic limit) then a rate matrix, R is meaningful under the same conditions—whence it is essentially related to $g_s(r_i, r_j, \tau)$ by (1.10). In anisotropic systems, we have seen that classical time reversal invariance (or the 'detailed balance' equation (1.3)) *requires* $g_s(r_i, r_j, \tau)$ to be asymmetric—in which case it follows directly from (1.10) that R must be asymmetric too. This is an alternative (and equivalent) argument to the one given earlier for the need for an asymmetric rate matrix in systems with non-uniform mean static density. The rate equation (1.8) is, however, linear in $\rho(r, t)$ and the static density, $\bar{\rho}(r)$, being the zero eigenvalue eigenvector of R, evidently obeys

$$\frac{\partial}{\partial t}\bar{\rho}(r_i) = \int dr_j\, R(r_i, r_j)\bar{\rho}(r_j) = 0.$$

Subtracting this from (1.8) implies that $\delta\rho(r, t)$ must obey (1.8) too. As alluded to earlier, this is at variance with the approach in which a symmetric rate equation (which, in the long-wavelength limit, amounts to a diffusion equation with a space-dependent diffusion constant, $D_{\mu\nu}(r)$) is applied to $\delta\rho(r, t)(=\rho(r, t) - \bar{\rho}(r))$. Thus it appears irrefutable that, in the limit of a rate equation applying exactly, an exact description of the evolution of $\delta\rho(r, t)$ also requires the same anisotropic rate matrix. Additionally, the approach utilizing an anisotropic rate equation obviates the need to empirically input $\bar{\rho}(r)$, as the latter is implied by the form of the rate matrix.

Thus, considerable insight into the precise conditions under which a rate equation is applicable would result from checking to what extent the matrix **R** turns out to be independent of τ. **R** can be deduced, via (1.10), from the self-diffusion propagator, $g_s(r_i, r_j, \tau)$, which may be obtained by a molecular dynamics simulation of a system within confined geometry. As we have already remarked, we cannot expect a rate equation to apply over short time intervals due to the ongoing thermal fluctuations. Thus the analysis must proceed with caution and, as one of its conclusions, should indicate the time scale over which a rate equation applies reasonably accurately. The results reported here tackle this problem essentially by diagonalizing the matrix $g_s(r_i, r_j, \tau)$ for several values of τ. In the general case this matrix, though real, is not symmetric so that its eigenvalues must in general be expected to be either real or in complex conjugate pairs, though they must all be of modulus ≤ 1, as the 1-norm of the matrix is unity (see Wilkinson, 1965). This follows when we bear in mind that all elements of $g_s(r_i, r_j, \tau)$, being probabilities, are positive semidefinite, so implying that the sum of the moduli of all elements in any column is the same as the sum of all elements in that column—which we know, from (1.4), to be unity for all columns. To find these eigenvalues and their associated eigenvectors we have employed the QR-algorithm for non-symmetric matrices (see Wilkinson 1965 or Wilkinson and Reinsch 1971). For translationally invariant or isotropic systems $g_s(r_i, r_j, \tau)$ is symmetric, which leads to a considerable simplification as discussed in section 2 below. Our more general results for non-isotropic systems will be discussed in section 3.

2. The isotropic case

By the term 'the isotropic case' we mean the conventional bulk liquid and the absence of external body forces. In this case, the general equations derived above simplify considerably. As a consequence of translational invariance,

$$g_s(r_i, r_j, \tau) = G_s(|r_i - r_j|, \tau) = G_s(r_{ij}, \tau). \tag{2.1}$$

The matrix, $g_s(r_i, r_j, \tau)$, is now trivially symmetric as well as real, and accordingly possesses real eigenvalues and must be diagonalizable by an orthogonal transformation. The eigenequation of $G_s(r_{ij}, \tau)$, that is,

$$\int dr_j \, G_s(r_{ij}, \tau)v^{(n)}(r_j) = \lambda^{(n)}v^{(n)}(r_i) \tag{2.2}$$

is trivial, for by Fourier transformation (which is a unitary transformation), (2.2) becomes

$$\bar{G}_s(k, \tau)v_k^{(n)} = \lambda^{(n)}v_k^{(n)} \tag{2.3}$$

thus showing that the eigenvalues are $\bar{G}_s(k, \tau) = \int \mathrm{d}r\, G_s(r, \tau)\, \mathrm{e}^{\mathrm{i}k \cdot r}$, for *any* value of (an even distribution of) k. Note here, that $G_s(r, \tau)$ is *not* a periodic function of $r\ (= |r|)$ even though we may be carrying out a simulation in a periodic box with the usual Born–Von Karman boundary conditions. This is because we follow each particle as it diffuses from one periodic box to the next and r is the total distance travelled. The eigenvectors (in k space) are, trivially, $v_k^{(n)} = \delta_{k,k_n}$, k_n being any member of a uniform distribution of k vectors that one might think of as 'allowed' by the boundary conditions pertaining to a box of side length L_x that may be as large as one likes. Thus the 'distribution' of eigenvalue magnitudes will be given by the Fourier transform, $\bar{G}_s(k, \tau)$, weighted with a uniform 'density of k levels', $(L_x/2\pi)^3$, which is virtually infinite as L_x may be considered as large as one chooses—the diffusive motion not being spatially restricted. This merely reflects the unbounded number of domains accessible to the isotropic motion, so implying the self-diffusion propagator is an infinite-dimensional matrix. For the normal diffusion equation (1.1) it is easy to show, from the well known Gaussian form of the Green's function of the diffusion equation, that the eigenvalues are distributed according to $\lambda^{(n)} = \exp(-\tau D k_n^2)$. Clearly, in this case, the eigenvalues of **R**, $\lambda_R^{(n)}$, would be $-D k_n^2$ and are τ independent and negative semidefinite.

To test the actual situation, we have simulated a conventional Lennard-Jones 12–6 liquid with cyclic boundary conditions in a cubic box of periodic length, $L = 11.28\sigma$ containing 1020 particles corresponding to a density of $0.71\sigma^{-3}$. The temperature was $1.40\varepsilon/k_B$ and the total run time was in excess of 2000 'Verlet' units of $(m\sigma^2/48\varepsilon)^{1/2}$. Note the '48' in this definition of the time unit—some readers may be used to time units where this factor is omitted. Of course, ε and σ are the familiar energy and length constants that appear in the 12–6 Lennard-Jones potential. It is sufficient to evaluate the propagator, $G_s(x, \tau)$, for motion in the x direction only. We have evaluated the eigenvalue distribution, $\lambda_R^{(n)}$, of **R** viz.

$$\lambda_R^{(n)} = \tau^{-1} \ln(\bar{G}_s(k_n, \tau)) = \tau^{-1} \ln\left(\int \mathrm{d}x\, G_s(x, \tau)\, \mathrm{e}^{\mathrm{i}k_n x}\right). \tag{2.4}$$

The results for various τ values are summarized in the curves shown in figure 1, which comprise nine plots of $-\lambda_R^{(n)}$ corresponding to reduced values of τ of 8, 16, 24, 32, 40, 48, 56, 72 and 80, respectively. The Fourier transforms were performed by non-linear least squares fitting of the $G_s(x, \tau)$ data to a fit function of a Gaussian $\times$ polynomial form (which has an analytic Fourier transform) and subject to one (holonomic) constraint: that the fit function must always integrate to unity.

Note that all eigenvalues (apart from the zero eigenvalue) are negative and, of course, real. The key feature to note is that those that decay most slowly, i.e. those $\lambda_R^{(n)}$ corresponding to k_n values of modulus less than about $2.2\,\sigma^{-1}$, are to a good approximation, independent of τ, whereas those of larger modulus do appear to depend on τ. This is, of course, sufficient to justify the validity of a rate equation, but only over time scales considerably longer than that corresponding to the largest eigenvalue magnitude that appears to be τ independent. As may be deduced from figure 1 this is about 0.09 units which implies times greater than about $0.09^{-1} \sim 10$ 'Verlet' time units. For shorter times the τ dependence of the eigenvalues reflects the thermal fluctuations. We suggest that if the construction of an effective **R** matrix that omits the effects of fluctuations for the purposes of deducing a rate equation is desired, then one can simply keep only the contributions due to the small negative eigenvalues in the range $-0.09 \rightarrow 0$ that are virtually τ independent as discussed above in reconstructing the self-diffusion propagator according to the inverse of (2.4). Of course, having done this, the inverse
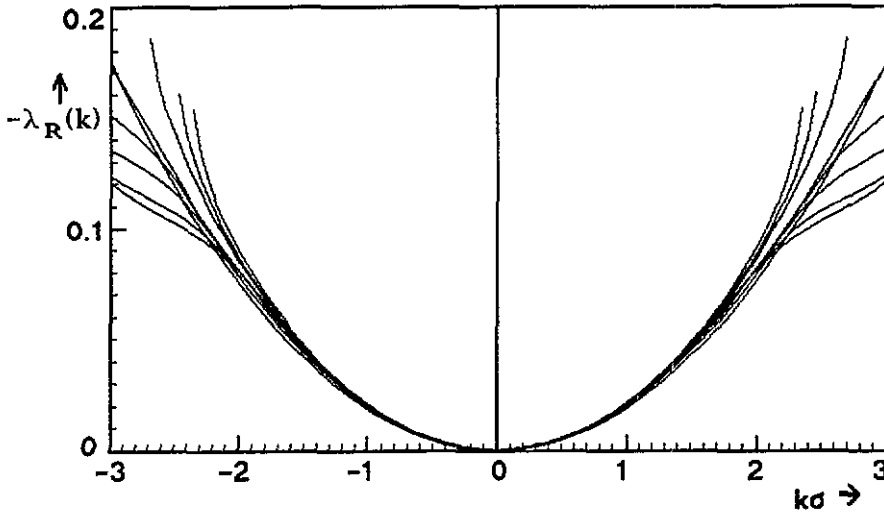
Figure 1. Plots of $\ln[\bar{G}_s(k, \tau)]/\tau$ for nine different τ values.

transform reconstructs $\mathbf{R}(x)$. Note that the ensuing rate equation should be far more effective (i.e. work over much shorter time intervals) than the normal diffusion equation (1.1) whose 'proof' is only valid asymptotically in the quasistatic limit. The long time behaviour is unaltered by this procedure, being affected only by the eigenvalues of the smallest modulus i.e. those close to $k = 0$. It is straightforward to show, for example, that $\langle x^2 \rangle / \tau = - (R''(k))_{k=0}$ in the long time $(\tau \to \infty)$ limit, which, for the normal diffusion equation, would have the value 2D.

3. The anisotropic case: confined geometries

We now generalize the treatment described in section 2 to the anisotropic case. Still of paramount interest is to test the range of validity of equation (1.8) but, of course, we must not now expect $g_s(r_i, r_j, \tau)$ or, equivalently, $R(r_i, r_j)$ to be symmetric matrices. This asymmetry arises because it may be easier for a particle to diffuse from r_i to r_j in time τ than vice-versa. This can be attributed to various effects: a primary effect such as 'wall forces' if one of these domains is close to a boundary, and also secondary effects like a prevailing density gradient. Of course, we have termed the latter secondary since they would not exist in the bulk i.e. far from walls. It is perhaps worth emphasizing that an anisotropic density can persist much further into the fluid from the wall than the wall forces themselves—an extreme case being 'hard' repulsive wall potentials. Accordingly, as the R matrix should describe diffusive motion in the 'equilibrated' system, we must expect the latter to be asymmetric over similar distances to those for which the mean density is anisotropic.

As a preliminary investigation we have simulated a Lennard-Jones fluid in equilibrium within a slab confined between two repulsive soft walls (we used a repulsive wall potential that varied inversely as the ninth power of the perpendicular distance from the wall) i.e. $V_{\text{wall}}(x_i - x_{\text{wall}}) = \frac{4}{5}\varepsilon\sigma^9/|x_i - x_{\text{wall}}|^9$. For the y and z directions we employed periodic boundary conditions as in normal (bulk) simulations. We had two parallel walls at $x = 0$ and $x = 15\sigma$ and there were 1020 particles in the simulation. The periodicity
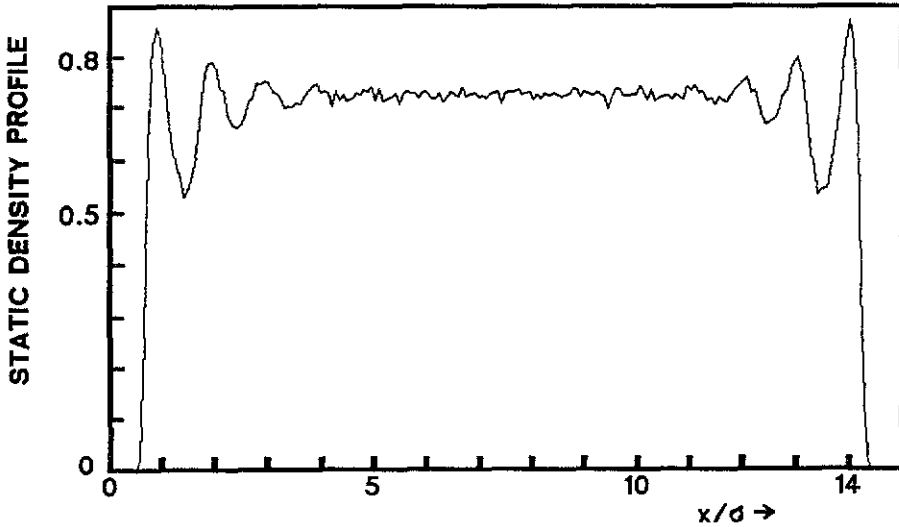
Figure 2. The anisotropic density profile.

distances in the y and z directions were equal at about 10.27σ. After the system had equilibriated, it displayed the density profile shown in figure 2 between the walls and a temperature of $1.30\varepsilon/k_B$. The total simulation time was in excess of 15 000 Verlet units of $(48\varepsilon/m\sigma^2)^{-1/2}$. We see that the mean density has fluctuations close to the walls and tails off to a fairly constant (bulk) value of about $0.72\sigma^{-3}$ in the middle region.

We looked, in particular, at the one-dimensional motion along the x direction i.e. perpendicular to the walls. The x domain ranged up to 15σ and we divided this into sixty subdomains, each of equal width 0.25σ. During the simulation we kept a record of the x positions of all particles, and so we could evaluate the matrix of probabilities, $P_{i \leftarrow j}(\tau)$, that a particle in the equilibrated system, which is initially in domain j shall be in domain i at a later time, τ. In the limit, when the domain size is so small that it can be labelled by its x position co-ordinate, it is clear that $P_{i \leftarrow j}(\tau)$ (after division by the destination domain volume width, dx_i) asymptotes to the self-diffusion Green's function, $g_s(x_i, x_j, \tau)$. In figure 3, $g_s(x_i, x_j, \tau)$ is plotted for five values of starting position x_j: 1.125σ, 3.625σ, 7.625σ, 11.375σ and 13.875σ, and, for each of these, $g_s(x_i, x_j, \tau)$ is plotted for four values of τ: 8, 32, 56 and 80 i.e. 20 curves in all. Of course, at $\tau = 0$, $g_s(x, x_j, 0) = \delta(x - x_j)$, and the plots broaden monotonically with increasing τ so that the curves in figure 3 are easily identified. Note that, by symmetry, the two outer sets of curves should be mirror images of each other, and the fact that we find this to be *accurately* so testifies to the very small statistical errors in our results. Note also how, for the larger τ values, the broadened $g_s(x, x_j, \tau)$'s develop auxiliary peaks at positions corresponding to peaks in the mean density as shown in figure 2. For $\tau \rightarrow \infty$, $g_s(x, x_j, \tau)$ must tend to $\rho_m(x)$, the particles by then having lost all recollection of their initial starting position, x_j.

To test the validity of the rate equation, (1.8), we investigate whether **R**, as derived from **P** by solving (1.10), does turn out to have time-independent real and positive off-diagonal elements representing transition probabilities with corresponding time-independent eigenvalues with negative real parts. If a rate equation was an *exact* description of the motion, this would imply that any initial density distribution would evolve monotonically to a 'static' mean profile, $\rho_m(x)$, predicted by the zero eigenvalue eigenvector of **R** (which of course is the same as the unity eigenvalue eigenvector of **P**).
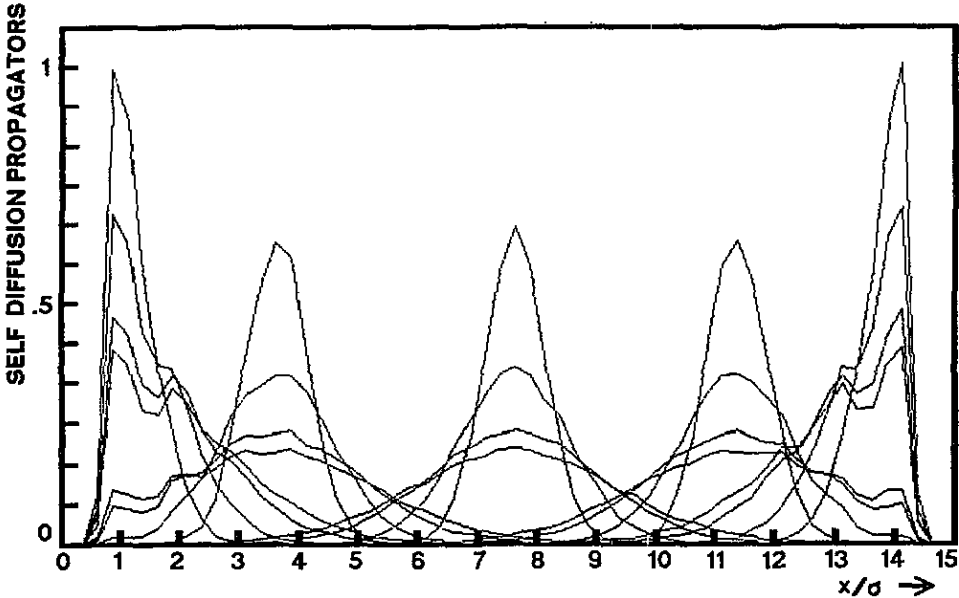
Figure 3. 20 plots of the self-diffusion propagator, $g_s(x, x_j, \tau)$ for each of five values of x_j/σ: 1.125, 3.625, 7.625, 11.375 and 13.875. Four curves are plotted for τ values of 8, 24, 56 and 80

We know from (1.5) that the mean density, $\bar{\rho}(x)$, must indeed be the eigenvector pertaining to the unity eigenvalue of **P**. After the system has relaxed to this mean density we know the situation will hardly be 'static' for, even in equilibrium, there are ongoing fluctuations in the density and virtually all other properties, so the evolution cannot be monotonic towards any 'fixed' static state. This being so, it follows directly, as is well realised, that no stochastic equation can be *exact*. These considerations effectively suggest a minimum limit on the time period over which a rate equation may be expected to be valid. At shorter times we expect fluctuations to invalidate (1.1) and we expect this to manifest itself in terms of the larger eigenvalues of $\mathbf{R}(\tau)$ (corresponding to quickly changing density components) to be τ-dependent and somewhat random. However the longer lived density components that correspond to the eigenvalues of **R** with small real parts should all turn out negative and τ independent if a rate equation is to be a meaningful description over longer periods. To check this, we diagonalized our 60×60 matrix, $P_{i \leftarrow j}(\tau)$, using the QR algorithm for non-symmetric matrices, for a similar range of τ values as in the above-described isotropic case. Now, of course, as our matrix is asymmetric, the eigenvalues will not, in general, be real. However, all elements of $P_{i \leftarrow j}(\tau)$ will be real and positive, being probabilities, and conservation of particles implies that $\Sigma_i P_{i \leftarrow j}(\tau)$ must be unity for all column labels, j. Thus, as argued previously for $g_s(x_i, x_j, \tau)$ in section 1, the 1-norm of this matrix, $P_{i \leftarrow j}(\tau)$, is also one, implying that all its eigenvalues must be of modulus less than or equal to unity. Furthermore, there is (at least) one eigenvalue which is unity, as, from the aforementioned points, all rows of $P_{i \leftarrow j}(\tau) - \lambda \delta_{i,j}$ add to zero if $\lambda = 1$, and so are then linearly dependent, thus indicating the unity eigenvalue. Translated to the rate matrix, **R**, defined in terms of $P_{i \leftarrow j}(\tau)$ by

$$P_{i \leftarrow j}(\tau) = [\exp(\mathbf{R}\tau)]_{ij} \tag{3.1}$$

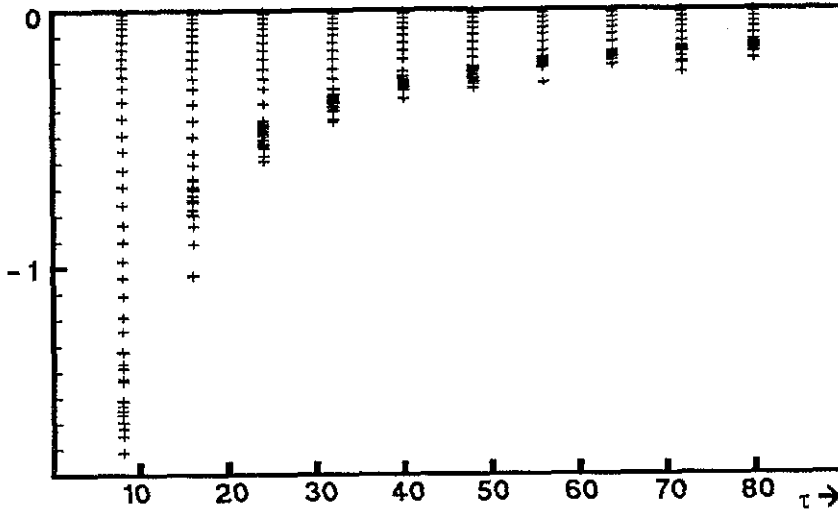implies that all eigenvalues of **R** must have a real part which is negative semidefinite,

Figure 4. Real parts of all 60 eigenvalues of **R** plotted against τ.

one eigenvalue, of course, being exactly zero. It is precisely the negative real part of these eigenvalues which determines how long it takes for their component contributions to the self-diffusion propagators to decay, the ones with smallest modulus dominating the long-term diffusion probability. Thus we appreciate the analogy with the isotropic case discussed earlier. Provided it turns out that these long-lived eigenvalues are τ independent, there will be a satisfactory description of the anisotropic diffusion in terms of a rate equation and, furthermore, we can construct the relevant rate matrix if we know the eigenvectors associated with these eigenvalues.

Figure 4 shows the results of our analysis and displays the real part of all the 60 eigenvalues of **R** for τ values of 8, 16, 24, 32, 40, 48, 56, 64, 72 and 80. Clearly the largest negative eigenvalues most definitely depend on τ, generally diminishing as τ increases. However, the τ dependence of the small (i.e. least negative) eigenvalues is different.

Figure 5 shows an enlargement of that part of figure 4 just below the real axis, i.e. depicting only those eigenvalues that lie in the range $-0.4 \rightarrow 0$. We see clearly that the longest lived (i.e. smallest) eigenvalues are independent of τ to an excellent approximation so justifying, to high accuracy, a rate equation description of our simulated system. Note that, as in the isotropic case, the most rapidly decaying eigenvalues do appear to be τ dependent, indicating that a rate equation description cannot be valid over these shortest times that are commensurate with the decay times of these τ dependent components. Note that the distribution of eigenvalues here appears in good qualitative agreement with the corresponding eigenvalue distribution for the isotropic case. Here the 'stochastic' eigenvalues (i.e. those that appear to be time independent) extend over a range of values from 0 down to magnitudes of about -0.125 reciprocal Verlet time units. The corresponding range in the isotropic simulation described in section 2 is 0 down to about -0.09. Consequently, we would expect a rate equation to be applicable for time intervals greater than about 8 Verlet units, $(m\sigma^2/48\varepsilon)^{1/2}$, or rates slower than about 0.12 reciprocal Verlet units. This result is of the same order as the corresponding time (~ 10 Verlet units) estimated for the isotropic case in section 2 and we should perhaps reiterate that in both simulations the temperatures were similar, and the density
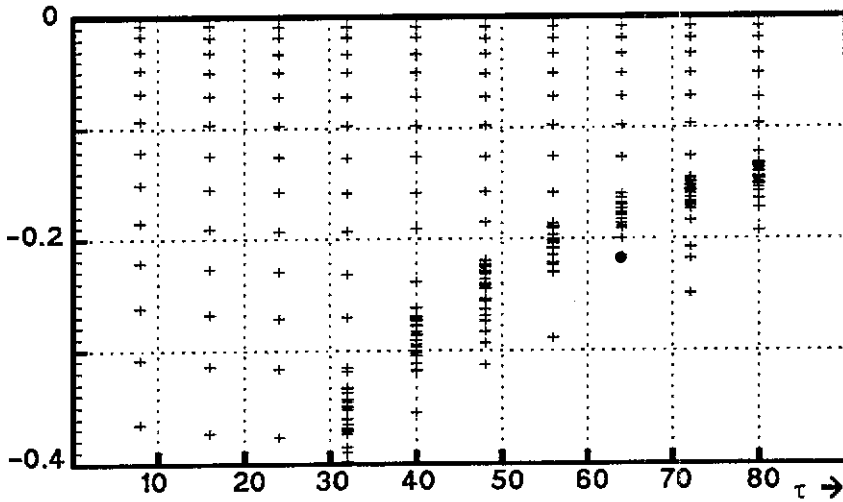
Figure 5. The τ dependence of the 'longest lived' eigenvalues of **R**.

in the isotropic simulation was virtually equal to that in the uniform region midway between the walls of our anisotropic system.

From figures 1 and 5 it appears possible to separate the 'stochastic' from the 'non-stochastic' motion according to which range of eigenvalue distribution of the **R** matrix appears to be τ independent (which we will call the 'stochastic' eigenvalues). It is clear that the 'stochastic' eigenvalues are those with the least negative real part i.e. the longest lived. This suggests a reconstruction of the **R** matrix that governs 'stochastic' motion by means of the Dirac representation (generalized to non-symmetric matrices). By matrix diagonalization, which is optimal via the QR algorithm, one deduces the similarity transformation, **S**, that diagonalizes **P** (and simultaneously **R**) according to $\mathbf{S}^{-1}\mathbf{PS} = \mathbf{P}_{\text{diag}}$. The Dirac representation

$$\mathbf{R} = \sum_n \lambda_n |v_v\rangle\langle\bar{v}_n| \tag{3.2}$$

expresses **R** in terms of the complete set of eigenvalues, λ_n, the corresponding eigenvectors, $|v_n\rangle$, and the adjoint eigenvectors, $\langle\bar{v}_n|$ (which are simply the rows of $\mathbf{S}^{-1}$). In the reconstruction, we propose to include *accurately* the 'stochastic' eigenvalues but redefine the other (non-stochastic) ones to all have a negative infinite real part. This is tantamount to ignoring the contributions due to these in the reconstruction of the self-diffusion propagator

$$\exp(\mathbf{R}t) = \sum_n \exp(\lambda_n t)|v_n\rangle\langle\bar{v}_n| \tag{3.3}$$

which might reasonably be expected to give an accurate account of motions for all rates for which the stochastic concept appears applicable. In the isotropic situation for example, this description, whilst in agreement with the relevant diffusion equation in the quasistatic (long-wavelength) limit, would be expected to be significantly better at accounting for the *faster-but-still-stochastic* motion. We intend to investigate this in future work.

For shorter intervals, the non-decaying dynamical process i.e. the thermal fluctuations, invalidate a rate equation description. If the latter was valid then every com-

ponent except the zero-eigenvalue component would decay monotonically to zero, in which case the mean observed density (shown in figure 2) would (apart from an arbitrary sign (phase factor)) correspond to the eigenvector corresponding to the zero eigenvalue. As we have seen (equation (1.5)), classical time-reversal invariance does require the unity eigenvalue eigenvector of $g_s(r_i, r_j, t)$ (equivalent to the zero-eigenvalue eigenvector of **R**) to be proportional to the mean static density, $\bar{\rho}(r)$. The current simulation results, however, did not show this definitively. Comparing the analyses of distinct but equivalent simulation runs we found that, whereas the 'stochastic' eigenvalues proved very reproducible, the corresponding eigenvectors, even allowing for their arbitrary phase factors, could not be claimed to be similarly reproducible. In particular the zero-eigenvalue eigenvector was not, in general, monotonic in sign—which, by definition, $\bar{\rho}(r)$ certainly must be. Thus it would appear that to get consistent eigenvectors from our various simulation runs requires a much higher order of statistical accuracy than for obtaining consistent eigenvalues. Furthermore, more systematic investigations of these observations would appear desirable. Though unlikely, it is also conceivable that ill-conditioning in the (NAG Library) QR algorithm for the real asymmetric matrices that we used might account for the apparent non-reproducibility of the eigenvectors.

Acknowledgments

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