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The modified Sutherland–Einstein relation for diffusive non-equilibria

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There remains a useful relation between diffusion and mobility for a Langevin particle in a periodic medium subject to non-conservative forces. The usual fluctuation–dissipation relation can be easily modified and the mobility matrix is no longer proportional to the diffusion matrix, with a correction term depending explicitly on the (non-equilibrium) forces. We discuss this correction by considering various simple examples and we visualize the various dependencies on the applied forcing and on the time by means of simulations. For example, in all cases the diffusion depends on the external forcing more strongly than does the mobility. We also give an explicit decomposition of the symmetrized mobility matrix as the difference between two positive matrices, one involving the diffusion matrix and the other involving force–force correlations.

Keywords: mobility; diffusion; non-equilibrium fluctuation–dissipation relation

1. Introduction

The relation between internal fluctuations in a system, on the one hand, and its susceptibility under an applied external field, on the other hand, is of great practical and theoretical interest. The most immediate example concerns the relation between diffusion and mobility and remains important in the development of non-equilibrium statistical mechanics. The first studies go back to the works of Sutherland (1904, 1905) and of Einstein (1905) (see also McKellar 2005). They are early examples of the fluctuation–dissipation theorem, itself a cornerstone of linear response theory for equilibrium systems (Kubo 1986; Spohn 1991).

When moving to non-equilibrium systems, the fluctuation–dissipation relation (FDR) is typically violated and there is no *a priori* reason why the system's mobility can be simply obtained from its diffusivity. All the same, mobility remains crucially important for the discussion of transport properties under non-equilibrium conditions (Spohn 1991; Ghatak *et al.* 2009). That is why we

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want to have explicit information about the corrections to the FDR, a subject that has been considered from many different aspects. We mention a few, as follows. One approach has been to associate an effective temperature with the non-equilibrium system, such as in ageing regimes (e.g. Abou & Gallet 2004; Oukris & Israeloff 2010). Another approach has been to modify the FDR by inserting the non-equilibrium stationary density, or by going to a 'moving' frame of reference using the probability current or local velocity (Blickle *et al.* 2007; Chetrite *et al.* 2008); somewhat in the spirit of the approach of Agarwal (1972); see also Hänggi & Thomas (1982), Speck & Seifert (2009) and Krüger & Fuchs (2010*a*,*b*). Specific models of interacting particles have, for example, also been treated in mathematically rigorous ways by Lebowitz & Rost (1994), Loulakis (2002), Hanney & Evans (2003) and Komorowski & Olla (2005). More recent experimental work includes Mehl *et al.* (2010), Oukris & Israeloff (2010) and Gomez-Solano *et al.* (2011).

Here, we concentrate on the non-equilibrium regime where the Sutherland–Einstein relation is modified because of non-conservative forces, starting from the inertial regime. As will become clear, not much effort is needed for finding examples where these corrections are visible and detectable. Recent work by Krüger & Fuchs (2010*a*,*b*) is similar to ours but in a different setting. The present paper gives the corrections following recent work by Baiesi *et al.* (2009, 2010), which enables us to focus on particular dependencies, such as on environment and driving parameters.

The main results of the present analysis are the explicit relations (2.7) and (2.10) between the mobility and the diffusion constant, and their numerical exploration. In particular, we typically find that for the models treated here the diffusion constant depends on the external (non-equilibrium) forcing more strongly than the mobility. The mobility is bounded from above by the diffusion, as we derive in an exact bound (5.2). When the forcing depends only on the position, then the correction to the Sutherland–Einstein relation is second order.

The plan of the paper is as follows. Section 2 contains the general relation between mobility and the diffusion matrix for Langevin dynamics in a magnetic field plus other general external forces. The correction to the Sutherland–Einstein relation is given in terms of a correlation function between the particle velocity and the applied forces. As the simplest and standard illustration, §3 reminds us of the theoretical framework of the Sutherland–Einstein relation. It is the famous proportionality of the mobility (in linear regime) with the diffusion constant (of the original system). We see from these textbook examples that our approach is suitable, and then we restart the non-equilibrium analysis. Section 4 treats non-equilibrium fluids with uniform temperature. The non-equilibrium condition is imposed by stirring the fluid (rotational or non-conservative forces). Here our motivation is primarily to illustrate the existing exact formulae and to explore more the role and the influence of the various parameters. All involved observables can be measured under the non-equilibrium averaging and, vice versa, the formulae in principle enable us to learn about unknown driving forces and parameters from the correction to the Sutherland–Einstein relation. Section 5 explores the symmetrized mobility; the diagonal elements allow some general bound. Finally, the appendices contain some more technical points dealing with analysis and numerics.

2. A general mobility–diffusion relation

Consider a particle of mass m, which diffuses in a heat bath (e.g. some fluid) in $\mathbb{R}^3$ according to the Langevin dynamics

$$\left.\begin{aligned} \dot{\boldsymbol{r}}_t &= \frac{\boldsymbol{r}_{t+\mathrm{d}t}-\boldsymbol{r}_t}{\mathrm{d}t} = \boldsymbol{v}_t \\ \text{and} \qquad m\dot{\boldsymbol{v}}_t &= m\frac{\boldsymbol{v}_{t+\mathrm{d}t}-\boldsymbol{v}_t}{\mathrm{d}t} = \boldsymbol{F}(\boldsymbol{r}_t,\boldsymbol{v}_t) - \gamma m \boldsymbol{v}_t + \sqrt{2m\gamma T}\,\boldsymbol{\xi}_t. \end{aligned}\right\} \tag{2.1}$$

Here, $\boldsymbol{r}_t$ is the position of the particle at time t, and $\boldsymbol{v}_t$ is its velocity. The particle is passive and undergoes the influence of a heat bath in thermal equilibrium at temperature T. In the usual weak coupling regime, the particle suffers friction with coefficient γ and random collisions, here represented by the vector $\boldsymbol{\xi}_t$ of standard Gaussian white noises. This means that each of the components has a Gaussian distribution, with mean zero $\langle \xi_{t,i}\rangle = 0$ and covariance $\langle \xi_{t,i}\xi_{s,j}\rangle = \delta_{i,j}\delta(t-s)$. Throughout this text, we set Boltzmann's constant to 1. Furthermore, there is an external force $\boldsymbol{F}$ working on the particle. Throughout this text, we restrict ourselves to forces that depend periodically on the position $\boldsymbol{r}$. We make this restriction have a form of translation invariance in the system. In other words, we consider time scales over which there is no confining potential. The force $\boldsymbol{F}$ can depend on the velocity as for a magnetic field when the particle is charged.

When given an initial (probability) density $\mu(\boldsymbol{r},\boldsymbol{v})$ of such independent particles at time zero, it changes with time according to the Fokker–Planck equation

$$\frac{\partial \mu_t}{\partial t} = -\boldsymbol{v}\cdot\boldsymbol{\nabla}_r\mu_t - \boldsymbol{\nabla}_v\cdot\left[\left(\frac{\boldsymbol{F}-m\gamma\boldsymbol{v}}{m}\right)\mu_t - \frac{\gamma T}{m}\boldsymbol{\nabla}_v\mu_t\right]. \tag{2.2}$$

There are two important quantities that characterize the transport behaviour of such a system. The first quantity is the diffusion (matrix) function $D(t)$, which is defined as

$$D_{ij}(t) = \frac{1}{2t}\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;(\boldsymbol{r}_t-\boldsymbol{r}_0)_j\rangle.$$

The subscripts denote the components of the corresponding vectors, and the right-hand side is a truncated correlation function: for observables A and B

$$\langle A;B\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle. \tag{2.3}$$

For diffusive systems, i.e. for the systems described above, this diffusion function is expected to have a large time limit, called the diffusion matrix

$$D_{ij} = \lim_{t\to\infty} D_{ij}(t).$$

In other words, the (co)variance of the displacement of the particle is linear with time (for large times $t \gg 1/\gamma$), with the slope given by the diffusion constant. Some analysis is found in appendix A. Secondly, there is the mobility (matrix) function $M(t)$, defined as follows: we add to the dynamics in equation (2.1) a constant (but small) force $\boldsymbol{f}$, replacing $\boldsymbol{F}(\boldsymbol{r},\boldsymbol{v}) \to \boldsymbol{F}(\boldsymbol{r},\boldsymbol{v}) + \boldsymbol{f}$. The mobility then measures the change in the expected displacement of the particle,

$$M_{ij}(t) = \frac{1}{t}\,\frac{\partial}{\partial f_j}\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i\rangle^f\Big|_{\boldsymbol{f}=0},$$

where the superscript f is the average of the dynamics with the extra force $\boldsymbol{f}$. Again, this function is supposed to have a large time limit, which is called the mobility,

$$M_{ij} = \lim_{t\to\infty} M_{ij}(t),$$

i.e. the mobility is the linear change in the stationary velocity caused by the addition of a small constant force.

In the special case of detailed balance dynamics, these two quantities are related by the Sutherland–Einstein relation,

$$M_{ij} = \frac{1}{T} D_{ij}, \tag{2.4}$$

which is an instance of the more general fluctuation–dissipation theorem.

When the system is not in equilibrium, mobility and diffusion constants are no longer proportional. Additional terms appear for the dynamics defined in equations (2.1) we get

$$M_{ij}(t) = \frac{1}{T} D_{ij}(t) + \frac{1}{2\gamma m T t}\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; \boldsymbol{\Psi}_j\rangle, \tag{2.5}$$

where the vector $\boldsymbol{\Psi}$ is explicitly given by

$$\boldsymbol{\Psi} = m(\boldsymbol{v}_t - \boldsymbol{v}_0) - \int_0^t \mathrm{d}s \boldsymbol{F}(\boldsymbol{r}_s, \boldsymbol{v}_s). \tag{2.6}$$

The relation between the mobility and the diffusion functions is thus modified with respect to the large time limits in equilibrium systems by the addition of an extra term. This term is the (truncated) correlation function between the displacement and the functional $\boldsymbol{\Psi}$. This functional is explicitly expressed in terms of the velocity of the particle of interest and the forces that act on it. In the limit of large times, the relation (2.5) simplifies somewhat; in this limit, we get

$$M_{ij} = \frac{1}{T} D_{ij} + \lim_{t\to\infty}\frac{1}{2\gamma m T t}\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; \boldsymbol{\Phi}_j\rangle, \tag{2.7}$$

where the vector $\boldsymbol{\Phi}$ is explicitly given by

$$\boldsymbol{\Phi} = -\int_0^t \mathrm{d}s\, \boldsymbol{F}(\boldsymbol{r}_s, \boldsymbol{v}_s). \tag{2.8}$$

Indeed, the term with the correlation between the displacement and the change of velocity does not contribute to the large time limit,

$$\lim_{t\to\infty}\frac{1}{t}\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; (\boldsymbol{v}_t - \boldsymbol{v}_0)_j\rangle = 0. \tag{2.9}$$

See appendix A for the argument. In §5, we further rewrite equation (2.7) to obtain

$$\frac{M_{ij}+M_{ji}}{2}=\frac{D_{ij}}{2T}+\frac{\delta_{i,j}}{2\gamma m}-\lim_{t\to\infty}\frac{1}{4\gamma^2 m^2 Tt}\langle \boldsymbol{\Phi}_i;\boldsymbol{\Phi}_j\rangle, \tag{2.10}$$

where each term represents a symmetric matrix. Under conservative forces the second and the third term sum to give the first term on the right-hand side. Otherwise, in diffusive non-equilibrium the correction term to the Sutherland–Einstein relation is non-zero with the symmetrized mobility matrix as the explicit difference between a diffusion-related matrix and the force–force covariance matrix, as claimed in the last line of the abstract. A further bound on the symmetrized mobility is added in §5.

Our modified Sutherland–Einstein relation has the advantage of being explicit in the dynamical variables. The formula is still sufficiently complicated and some aspects of it require careful examination. We can rewrite formula (2.7) as

$$M_{ij}=\frac{1}{T}D_{ij}-\lim_{t\to\infty}\frac{1}{2\gamma mT}\int_0^t \mathrm{d}s\left\langle\frac{(\boldsymbol{r}_t-\boldsymbol{r}_0)_i}{t};F_j(\boldsymbol{r}_s,\boldsymbol{v}_s)\right\rangle. \tag{2.11}$$

It can be seen that the correction to the equilibrium mobility–diffusion relation is measured by a space–time correlation between applied forcing and displacement. One simplification is to look close to equilibrium. There, we see, by time-reversal symmetry applied to the reference equilibrium, that the correction is only quadratic in the applied forcing when $\boldsymbol{F}$ only depends on $\boldsymbol{r}$. In other words, the deviations with respect to the Sutherland–Einstein relation are then second order. Going further from equilibrium, the inverse question also becomes interesting—to characterize the non-equilibrium forcing that produces a given experimentally determined mobility–diffusion relation. We hope to see in future work that formulae such as (2.11) are also useful for learning about the driving conditions from measurements of both mobility and diffusion. Numerically, of course, the right-hand side of formula (2.11) is easier to determine than the left-hand side.

Usually, and in what follows, one considers the diffusion and the mobility of a single particle. It is however relevant and also possible to include interactions with other particles. The equations (2.1) must be changed for the force to include this dependence on the state of the other particles, but the main results remain unaffected. After all, one can simply redo all calculations in larger dimensions ($3N$ for N particles) and consider independent white noises acting on all $3N$-components. Furthermore, the force F can be time dependent and formulae (2.7)–(2.10) remain the same except where F has further time dependencies, whether they are explicit or whether they are due to the time-dependent state of other particles.

The explicit relations above have been derived in Baiesi *et al.* (2010) following a path-integral formalism. In the present paper, we provide a number of examples to discuss this relation between mobility and diffusion out of equilibrium. For each of these examples, simulations have been done to aid understanding, and to inform us about the relative importance of the various parameters and terms in formulae (2.7). On the other hand, the simulations raise new questions, not all of which we are able to answer. The appendices add more theoretical considerations to the large time limits mentioned above, and give information about the simulation method.

3. Classical equilibrium theory

(*a*) *Pure diffusion*

The simplest form of the Langevin equation is the case where all the external forces are set to zero

$$m\dot{\boldsymbol{v}}_t = -\gamma m \boldsymbol{v}_t + \sqrt{2m\gamma T}\,\boldsymbol{\xi}_t. \tag{3.1}$$

The mobility and diffusion can be computed explicitly, by first integrating the Langevin equation (adding a force $\boldsymbol{f}$),

$$\boldsymbol{v}_t = \boldsymbol{v}_0 \mathrm{e}^{-\gamma t} + \frac{\boldsymbol{f}}{\gamma m}[1-\mathrm{e}^{-\gamma t}] + \int_0^t \mathrm{d}s \mathrm{e}^{-\gamma(t-s)}\boldsymbol{\xi}_s,$$

and then using the properties of the Gaussian white noise. Because $\langle \boldsymbol{\xi}_t \rangle = 0$, we immediately obtain the mobility by again integrating over time,

$$M_{ij}(t) = \delta_{ij}\left[\frac{1}{\gamma m} - \frac{1-\mathrm{e}^{-\gamma t}}{\gamma^2 m t}\right].$$

As $\langle \xi_{i,t}\xi_{j,s}\rangle = \delta_{i,j}\delta(t-s)$ the velocity–velocity correlations equal (for $\boldsymbol{f}=0$)

$$\langle v_{i,t} v_{j,s}\rangle = \left[\langle v_{0,i} v_{0,j}\rangle - \frac{\delta_{i,j}T}{m}\right]\mathrm{e}^{-\gamma(t+s)} + \frac{\delta_{i,j}T}{m}\mathrm{e}^{-\gamma|t-s|}.$$

Simply integrating over time then gives the diffusion,

$$D_{ij}(t) = \frac{1}{2\gamma^2 t}\left[\langle v_{0,i}; v_{0,j}\rangle - \frac{T\delta_{ij}}{m}\right][1-\mathrm{e}^{-\gamma t}]^2 + \delta_{ij}T\left[\frac{1}{\gamma m} - \frac{1-\mathrm{e}^{-\gamma t}}{\gamma^2 m t}\right].$$

Taking the limit of large times, we see that

$$M_{ij} = \lim_{t\to\infty} M_{ij}(t) = \frac{\delta_{ij}}{\gamma m} = \lim_{t\to\infty}\frac{D_{ij}(t)}{T} = \frac{D_{ij}}{T}.$$

(*b*) *A periodic potential*

When a force is added that derives from a periodic potential U,

$$\left.\begin{aligned} &\dot{\boldsymbol{r}}_t = \boldsymbol{v}_t \\ \text{and}\quad &m\dot{\boldsymbol{v}}_t = -\nabla_r U(\boldsymbol{r}_t) - \gamma m \boldsymbol{v}_t + \sqrt{2m\gamma T}\,\boldsymbol{\xi}_t;\end{aligned}\right\} \tag{3.2}$$

then, the general expression (2.5) gives

$$\begin{aligned} M_{ij}(t) = \frac{1}{T}D_{ij}(t) &+ \frac{1}{2\gamma T t}\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; (\boldsymbol{v}_t - \boldsymbol{v}_0)_j\rangle \\ &- \frac{1}{2\gamma m T t}\int_0^t \mathrm{d}s\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; \nabla_{r_j} U(\boldsymbol{r})\rangle. \end{aligned} \tag{3.3}$$

The second term on the right-hand side tends to zero for large times, as mentioned above, as does the third term,

$$\lim_{t\to\infty}\frac{1}{t}\int_0^t \mathrm{d}s\langle(\boldsymbol{r}_t - \boldsymbol{r}_0)_i; \nabla_{r_j} U(\boldsymbol{r})\rangle = 0, \tag{3.4}$$

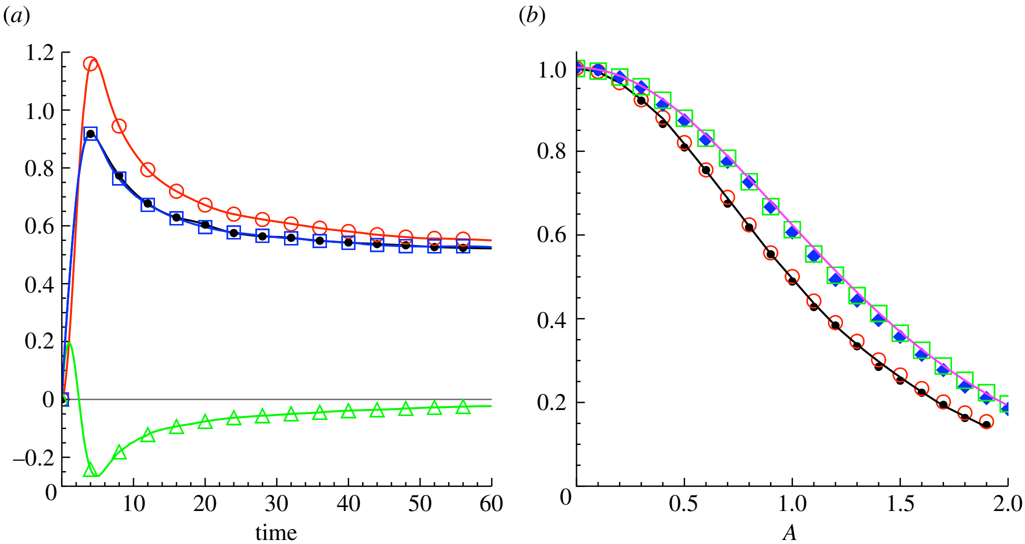

Figure 1. Diffusion in potential $U(x) = A\cos x$. (*a*) $A = 1$ and the evolution through time is shown. Here, $T = \gamma = m = 1$. $C(t)$ here represents the last two terms on the right-hand side of equation (3.3) (filled circles, $M(t)$; open circles, $D(t)/T$; open triangles, $C(t)$; open squares, $D(t)/T + C(t)$). (*b*) The long time limits of the mobility and diffusion are shown for values of A ranging from 0 to 2. $M1$ and $D1$ are the mobility and diffusion for the case $T = \gamma = m = 1$, while $M2$ and $D2$ correspond to $T = 1$, $\gamma = 10$, $m = 0.1$ (filled circles, $M1(A)$; open circles, $D1(A)/T$; filled diamonds, $M2(A)$; open squares, $D2(A)/T$; solid line, $D3(A)/T$). Finally, $D3$ is the diffusion that is explicitly calculated by equation (3.5). (Online version in colour.)

yielding the standard $M_{ij} = D_{ij}/T$ (see also appendix A). Of course, the mobility and diffusion are no longer equal to $\delta_{ij}/(\gamma m)$. A summary is shown in figure 1. Observe, for example, that the mobility decreases with the amplitude of the conservative force, which is logical, since the particle needs to escape potential wells to have a non-zero velocity.

In fact, Festa & Galleani d'Agliano (1978) derived an explicit expression for the diffusion for overdamped Langevin equations with periodic potentials. The overdamped Langevin equation is what one gets when the friction is high and the mass of the particle is small, so that inertial effects can be ignored. Formally, one lets $\gamma \to \infty$ and $m \to 0$, while keeping $\chi = 1/m\gamma$ constant and finite. The result is that one can make $m\dot{\boldsymbol{v}}_t$ zero in equation (3.2). The resulting Langevin equation can then be written solely in terms of the position,

$$\dot{\boldsymbol{r}}_t = -\chi \nabla_r U(\boldsymbol{r}_t) + \sqrt{2\chi T}\,\xi_t.$$

The formula of Festa & Galleani d'Agliano (1978) for one-dimensional diffusion is given by

$$D = \frac{\chi T R^2}{\int \mathrm{d}x\, \mathrm{e}^{U(x)/T} \int \mathrm{d}x\, \mathrm{e}^{-U(x)/T}}, \tag{3.5}$$

where R is the period of the potential, and the integrals in the denominator are over one period. We give a new and short proof of equation (3.5) in appendix B.

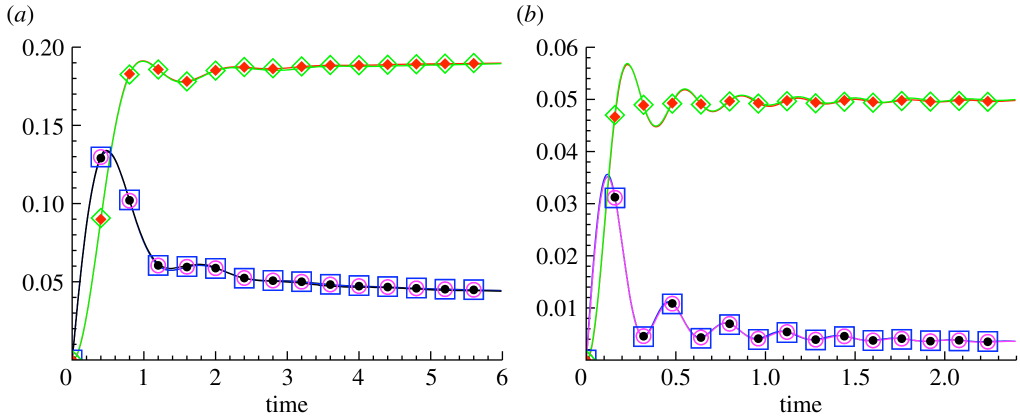

Figure 2. Diffusion with a magnetic field in the z-direction. Here, $T=\gamma=m=1$, while (a) $B=5$ and (b) $B=20$. Filled circles, $M_{xx}(t)$; filled diamond, $M_{xy}(t)$; open circles, $D_{xx}(t)/T$; open squares, $K_{xx}(t)/T$; open diamonds, $K_{xy}(t)/T$. (Online version in colour.)

In figure 1, we plotted this explicit expression, for a potential $U=A\cos(x)$ for various values of A. This curve corresponds nicely with the mobility and diffusion we got from simulations, where we took $\gamma=10$ and $m=0.1$.

(c) *A magnetic field*

The first choice of a velocity-dependent force $\boldsymbol{F}$ in equation (2.1) could be a magnetic field. If we add to equation (3.1) a magnetic field, say a homogeneous magnetic field in the z-direction, $\boldsymbol{r}_t=(x_t,y_t,z_t)$, $\boldsymbol{B}=(0,0,B)$, with unit electric charge,

$$\left.\begin{aligned} m\dot{v}_{x,t}&=Bv_{y,t}-\gamma m v_{x,t}+\sqrt{2m\gamma T}\,\xi_{x,t}\\ \text{and}\qquad m\dot{v}_{y,t}&=-Bv_{x,t}-\gamma m v_{y,t}+\sqrt{2m\gamma T}\,\xi_{y,t};\end{aligned}\right\}\tag{3.6}$$

then, equation (2.7) immediately gives

$$M_{xx}=\frac{D_{xx}}{T}-\frac{BD_{xy}}{\gamma m T},\quad M_{xy}=\frac{D_{xy}}{T}+\frac{BD_{xx}}{\gamma m T},$$
$$M_{yx}=\frac{D_{yx}}{T}-\frac{BD_{yy}}{\gamma m T}\quad\text{and}\quad M_{yy}=\frac{D_{yy}}{T}+\frac{BD_{yx}}{\gamma m T}.$$

Further explicit calculations show that

$$D_{xx}=D_{yy}=\frac{\gamma m T}{\gamma^2 m^2+B^2}\quad\text{and}\quad D_{xy}=D_{yx}=0.$$

The diagonal elements of M and D are proportional, but this is not the case for the off-diagonal elements. Therefore, adding a magnetic field to an otherwise equilibrium dynamics breaks the equilibrium Einstein relation. This may be counterintuitive, because adding a magnetic field leaves the equilibrium Boltzmann distribution intact. In figure 2, the results of simulations are shown.

We took the initial position as being equal to zero, and the velocity is Maxwellian $\rho(v) \propto \exp(-mv^2/2T)$, which is the stationary velocity distribution. The $K(t)$ show the right-hand side of equation (2.5). As one can see, they coincide nicely with the mobility (left-hand side of equation (2.5)). Note that the oscillations of the mobility and diffusion have a period $2\pi m/(BT)$.

4. Non-conservative forces

Recall that we work in unbounded spaces with periodic forces. In that sense, we consider diffusion on the torus. A conservative force is then a force for which every contour integral that starts and ends in equivalent points equals zero. Equivalent points have the same coordinates modulo as the period of the force. If not, we call the force non-conservative. Practically, we distinguish two kinds of non-conservative forces. First of all there are forces that cannot be derived from a potential (or, equivalently, which have a non-zero curl) in the full space. Secondly, there are forces that can be derived from a potential in the full space but not from a potential on the torus. We give examples of both cases in this section.

(*a*) *Non-periodic potential*

Consider again a particle diffusing on an infinite line, with potential $U(x) = \cos x$. To this, we add a constant force F

$$\dot{x}_t = v_t$$

and

$$m\dot{v}_t = F + \sin x_t - \gamma m v_t + \sqrt{2m\gamma T}\,\xi_t.$$

The force $F + \sin x$ can be derived from the potential $-Fx + \cos x$, but this potential is not periodic. The relation (2.5) becomes here

$$M(t) = \frac{D(t)}{T} + \underbrace{\frac{1}{2\gamma Tt}\langle (v_t - v_0); (x_t - x_0)\rangle}_{C1(t)} + \underbrace{\frac{1}{2\gamma mTt}\int_0^t \mathrm{d}s \left\langle \frac{\mathrm{d}U}{\mathrm{d}x}(x_s); (x_t - x_0)\right\rangle}_{C2(t)}.$$

Note that $\langle F; (x_t - x_0)\rangle = 0$ because F is a constant. We have simulated this system for various values of the force F. In figure 3, the mobility, the diffusion, the correlation of the displacement with the change in velocity ($C1$) and the correlation of the displacement with the integrated force ($C2$) are shown for $F = 1.5$ (figure 3*a*) and $F = 2.5$ (figure 3*b*). In both cases, the initial conditions are $x_0 = v_0 = 0$. Note that all quantities converge to a constant value. This is because the diffusion and other correlations are defined as truncated correlation functions (equation (2.3)), so that the diverging parts of the correlations are subtracted.

It is clear that the Sutherland–Einstein relation $M = D/T$ is violated. Even though the correction term $C1$ tends to zero for large times, the correction term $C2$ does not. However, the correction to the Sutherland–Einstein relation is not always equally big. For example, for small forces the correction is small. For large driving, as in figure 3*b*, the correction is also small. The force is then so big that the potential U does not play an important role. Without the potential U the

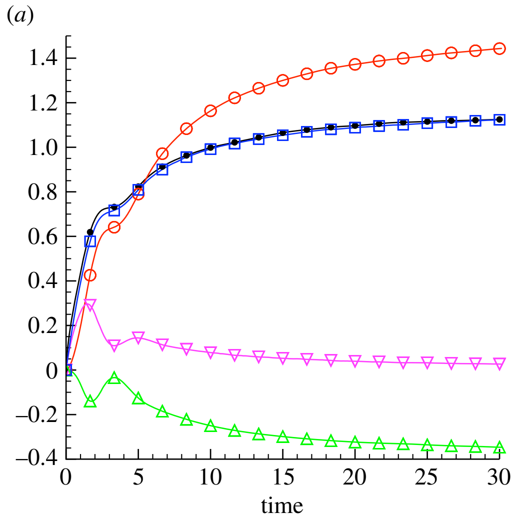

Figure 3. Simulations of a diffusion with a potential $-Fx + \cos x$. Here, $T = \gamma = m = 1$. (*a*) $F = 1.5$ and (*b*) $F = 2.5$. Filled circles, $M(t)$; open circles, $D(t)/T$; open triangles, $C1(t)$; open inverted triangles, $C2(t)$; open squares, $D(t)/T + C1(t) + C2(t)$. (Online version in colour.)

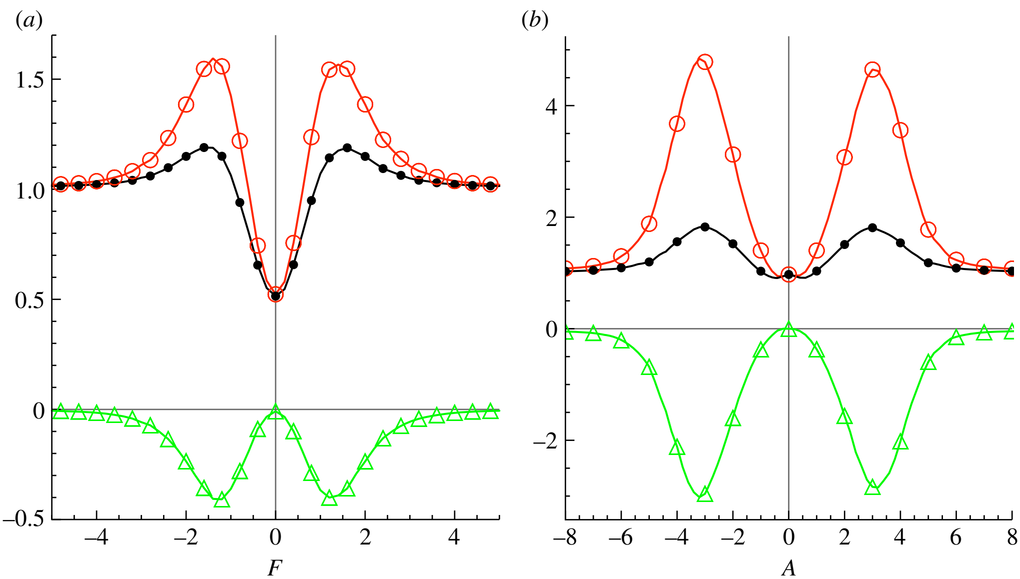

Figure 4. The long time limits of the mobility and diffusion are shown. (*a*) Simulations of a diffusion with a potential $-Fx + \cos x$, where F ranges from -5 to 5. (*b*) The potential is $-A(x - \cos x)$ with A ranging from -8 to 8. In both cases, $T = \gamma = m = 1$. Filled circles, M; open circles, D; open triangles, C. (Online version in colour.)

dynamics of the system is completely translation invariant, and with a simple change of coordinates one can prove that the Sutherland–Einstein relation holds. Therefore one expects that in the limit $F \to \infty$ the mobility and diffusion are proportional, and have the same values as those for pure diffusion. This can

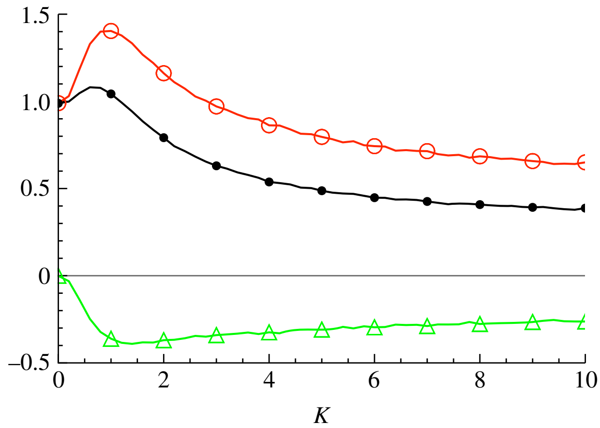

Figure 5. The long time limits of the mobility and diffusion are shown for a potential given by $-Fx + \cos Kx$, with K ranging from 0 to 10. Again, we took $T = \gamma = m = 1$. Filled circles, M; open circles, D; open triangles, C. (Online version in colour.)

indeed be seen in figure 4*a* for the mobility and diffusion in a range of forces going from -5 to 5. For a force that is five times the amplitude of the potential, the mobility and diffusion are very close to 1, the expected value for a pure diffusion. Finally, as is also shown in figure 4, both $M(t)$ and $D(t)$ are symmetric under the force flip $F \to -F$. The resulting curves for mobility and diffusion are very similar to the overdamped case, as, for example, in fig. 3 of Speck & Seifert (2006), where the stationary probability density is exactly known.

Figure 4*b* shows the mobility and diffusion (long time limits) for a force $A(1 + \sin x)$, with A between -8 and 8. Again, for large amplitude A, the relation approaches that of pure diffusion just as for $F \to \infty$ in figure 4. The reason for that is unclear; the forcing is large but also the potential is large now. At any rate, the diffusion is clearly much more sensitive to the strength of the force than is the mobility.

Finally, figure 5 shows the mobility and diffusion (long time limits) for a potential $-Fx + \cos Kx$, with K between 0 and 10. For K between 1 and 10 the difference between mobility and diffusion is almost constant.

(*b*) *Rotational force*

Apart from forces coming from non-periodic potentials, non-equilibrium can also be installed from forces with a non-zero curl on the full space. They induce vortices and let the particles undertake rotational motion, but with more drastic departures from the Sutherland–Einstein relation than in the case (3.6) of a magnetic field.

As an example, we simulated the two-dimensional dynamics

$$\left.\begin{aligned} m\dot{v}_{x,t} &= F_x(x_t, y_t) - \gamma v_{x,t} + \sqrt{2m\gamma T}\,\xi_{x,t} \\ \text{and} \qquad m\dot{v}_{y,t} &= F_y(x_t, y_t) - \gamma v_{y,t} + \sqrt{2m\gamma T}\,\xi_{y,t}. \end{aligned}\right\} \tag{4.1}$$

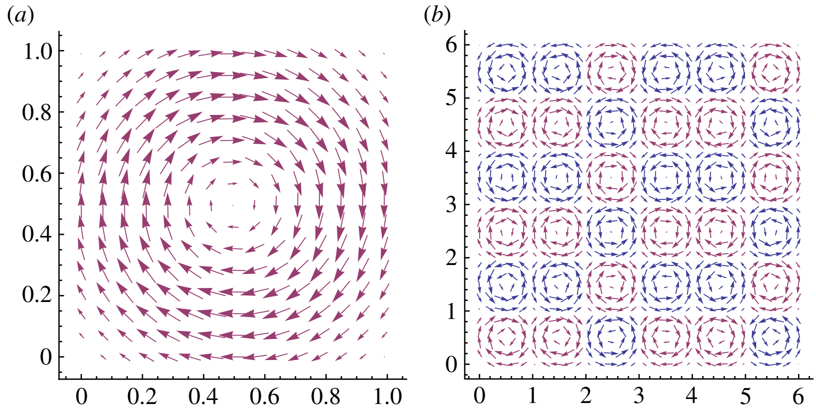

Figure 6. Vector plot of the force F in equation (4.1). (Online version in colour.)

The force $\boldsymbol{F} = A\boldsymbol{f}$, with A some constant and with, for $0 \le x, y < 1$,

$$f_x(x, y) = \left(r - \sqrt{2}\right)\left(\frac{1}{2} - y\right)$$

and

$$f_y(x, y) = \left(r - \sqrt{2}\right)\left(x - \frac{1}{2}\right),$$

with $r = \sqrt{(x - 1/2)^2 + (y - 1/2)^2}$. This is shown in figure 6a.

This force field is repeated outside that unit square; however, sometimes it is in the reverse direction. More precisely,

$$f_x(x, y) = a\left(r - \sqrt{2}\right)\left(y - \frac{1}{2}\right),$$

$$f_y(x, y) = a\left(r - \sqrt{2}\right)\left(\frac{1}{2} - x\right)$$

and $$a = (1 - 2\delta_{2,x \bmod 3})\,(1 - 2\delta_{1,y \bmod 2}).$$

This gives the pattern shown in figure 6b. The specific choices are probably not so important. Simulation results for this system are shown in figure 7.

We show only the diagonal elements of the mobility, diffusion and the correction (C); the off-diagonal elements turn out to be zero. In both cases, the diffusion in the x-direction is greater than in the y-direction. Furthermore, when comparing $A = 20$ with $A = 40$, we see that the diffusion very much depends on the strength of the force, while the mobility is in both cases approximately the same. To see this more clearly, figure 8 shows the large time limits of mobility, diffusion and their difference, for A in the range $[-60, +60]$.

Observe that the diffusion increases rapidly with the amplitude $|A|$ of the force, while the mobility remains almost constant (it even decreases a little). In particular, large forcing $A \uparrow \infty$ does not at all lead to pure diffusion here,

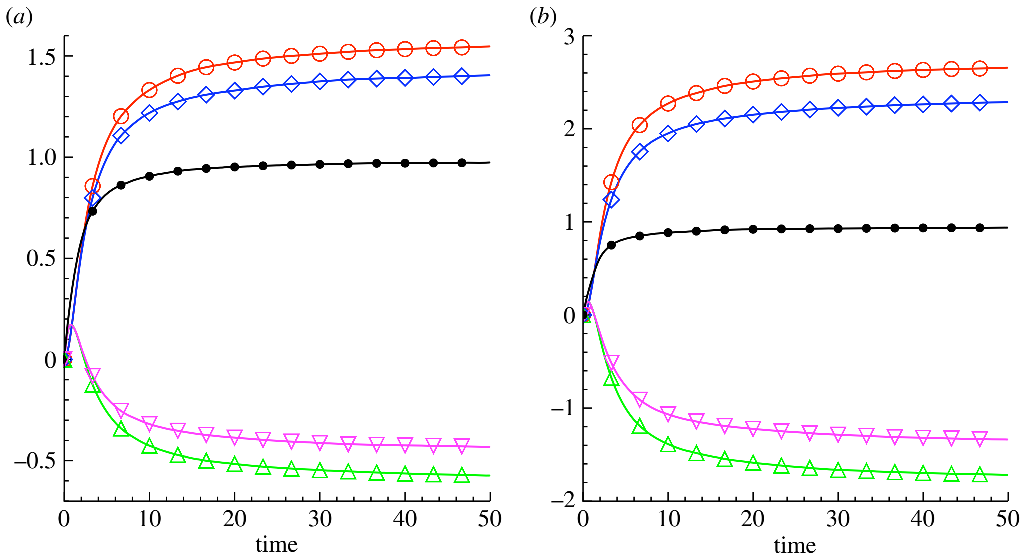

Figure 7. Values $T=\gamma=m=1$. (*a*) Constant $A=20$; (*b*) $A=40$. Initial conditions in both cases take the position and velocity equal to zero. Filled circles, $M_{xx}(t)=M_{yy}(t)$; open circles, $D_{xx}(t)$; open diamonds, $D_{yy}(t)$; open triangles, $C_{xx}(t)$; open inverted triangles, $C_{yy}(t)$. (Online version in colour.)

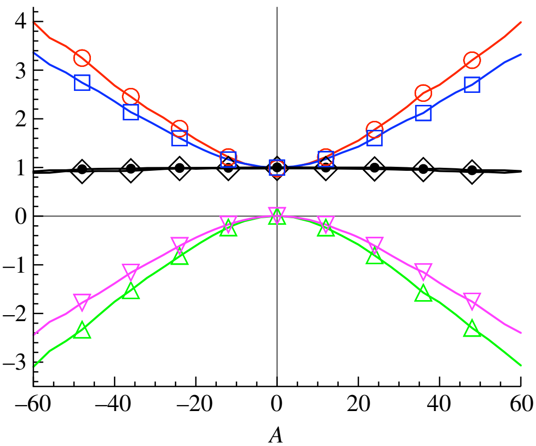

Figure 8. Again $T=\gamma=m=1$, and A ranges from -60 to $+60$. Open diamonds, M_{xx}; filled circles, M_{yy}; open circles, D_{xx}; open squares, D_{yy}; open triangles, C_{xx}; open inverted triangles, C_{yy}. (Online version in colour.)

because the situation is very different from that in figure 4. We also see that all quantities are symmetric under $A\to -A$. Indeed, reversing the force is the same as translating the whole system, which has no effect on the long time behaviour.

5. The symmetrized mobility

We now consider the symmetric part of the mobility matrix, i.e. we rewrite equation (2.5) as

$$\frac{M_{ij}(t)+M_{ji}(t)}{2}=\frac{1}{T}D_{ij}(t)+\frac{1}{4\gamma mTt}\left[\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;\boldsymbol{\Psi}_j\rangle+\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_j;\boldsymbol{\Psi}_i\rangle\right].$$

The last term can be rewritten using elementary algebra,

$$\begin{aligned}&\frac{1}{m\gamma}\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;\boldsymbol{\Psi}_j\rangle+\frac{1}{m\gamma}\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_j;\boldsymbol{\Psi}_i\rangle\\&=\left\langle\left[(\boldsymbol{r}_t-\boldsymbol{r}_0)_i+\frac{\boldsymbol{\Psi}_i}{m\gamma}\right];\left[(\boldsymbol{r}_t-\boldsymbol{r}_0)_j+\frac{\boldsymbol{\Psi}_j}{m\gamma}\right]\right\rangle\\&\quad-\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;(\boldsymbol{r}_t-\boldsymbol{r}_0)_j\rangle-\frac{1}{m^2\gamma^2}\langle\boldsymbol{\Psi}_i;\boldsymbol{\Psi}_j\rangle.\end{aligned}$$

The second term on the right-hand side is proportional to the diffusion function. Furthermore, the first of the terms on the right-hand side of the last equation can be simplified; for that, let us write the Langevin equation in its integral form,

$$\boldsymbol{v}_t-\boldsymbol{v}_0=-\gamma(\boldsymbol{r}_t-\boldsymbol{r}_0)+\int_0^t\mathrm{d}s\left[\frac{\boldsymbol{F}(\boldsymbol{r}_s,\boldsymbol{v}_s)}{m}+\sqrt{\frac{2\gamma T}{m}}\boldsymbol{\xi}_s\right].$$

Using definition (2.6) of the functional $\boldsymbol{\Psi}$, we substitute

$$\frac{1}{m\gamma}\boldsymbol{\Psi}+\boldsymbol{r}_t-\boldsymbol{r}_0=\sqrt{\frac{2T}{m\gamma}}\int_0^t\mathrm{d}s\,\boldsymbol{\xi}_s.$$

The right-hand side involves Gaussian white noise and $\langle\xi_{u,i}\xi_{s,j}\rangle=\delta(s-u)\delta_{i,j}$. The result is the following expression for the symmetric part of the mobility:

$$\frac{M_{ij}(t)+M_{ji}(t)}{2}=\frac{D_{ij}(t)}{2T}+\frac{\delta_{i,j}}{2\gamma m}-\frac{1}{4\gamma^2m^2Tt}\langle\boldsymbol{\Psi}_i;\boldsymbol{\Psi}_j\rangle. \tag{5.1}$$

Using exponential relaxation in large time limits (see appendix A) one can see that in the long time limit this relation becomes (2.10). However, even for finite times when $i=j$, the third term on the right-hand side in equation (5.1) is minus a variance, yielding the following bound for the mobility (diagonal elements):

$$M_{ii}(t)\le\frac{D_{ii}(t)}{2T}+\frac{1}{2m\gamma}. \tag{5.2}$$

6. Conclusions

This work investigates the relation between diffusion and mobility for Langevin particles. The particles are independent and passive, undergoing white noise and friction from the fluid in thermal equilibrium. The total force on the particles is periodic but is not compatible with a periodic potential, bringing the system out of equilibrium. We have studied the modified Sutherland–Einstein relation. The new mobility–diffusion relation remains explicit and we have visualized the typical dependencies on the non-equilibrium driving and other parameters. In the future, we hope that the inverse analysis will also be possible, i.e. that our formulae will enable us to obtain useful information about unknown aspects of diffusive non-equilibria exactly by measuring the correction to the Sutherland–Einstein relation and by comparing it with equation (2.7) or with equation (2.10). In many cases, however, we expect that further extensions to non-Markovian evolutions will be necessary to meet the physics of small systems immersed in viscoelastic media.

Appendix A. Smoothness and mixing

We argue here why the diffusion matrix $D_{ij}(t)$ has a finite limit and why certain terms do not contribute in the long time limit; that is, the vanishing of equations (2.9) and (3.4). We do not want to go into full technical details but it should be clear that our results depend on good exponential mixing properties of the dynamics with propagation of smooth densities. Of course, there is no stationary regime in unbounded diffusive systems, but this problem is irrelevant whenever expectations are considered of quantities that have the same periodicity as the dynamics (forces) of the system. (This gives no restriction on the velocity dependence of these quantities.) In that case, we can restrict the dynamics of the system to one period, with periodic boundary conditions (reducing the infinite space to a torus). Taken on a torus, our system does have a stationary regime, i.e. the Fokker–Planck equation (2.2) with periodic boundary conditions can, in principle, be solved with left-hand side zero. The solution is assumed to be the smooth density $\rho(\boldsymbol{r}, \boldsymbol{v})$, giving the stationary distribution of positions (on the torus) and velocities. By assumption then, any function g with the same periodicity as the dynamics satisfies

$$\lim_{t\to\infty} \langle g(\boldsymbol{r}_t, \boldsymbol{v}_t)\rangle = \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{v} \rho(\boldsymbol{r}, \boldsymbol{v})\, g(\boldsymbol{r}, \boldsymbol{v}) \equiv \langle g\rangle_\rho,$$

and there exist finite constants C and $\alpha > 0$ such that for large enough times $t \geq 0$,

$$|\langle g(\boldsymbol{r}_t, \boldsymbol{v}_t)\rangle - \langle g\rangle_\rho| \leq C\sqrt{\langle g^2\rangle_\rho}\mathrm{e}^{-\alpha t}.$$

From the above bound, one can deduce bounds on truncated correlation functions. For example, writing $g(t) = g(\boldsymbol{r}_t, \boldsymbol{v}_t)$, for $t \geq s$,

$$\langle f(s); g(t)\rangle = \langle f(s)[\langle g(t)\rangle_s - \langle g\rangle_\rho]\rangle + \langle f(s)\rangle[\langle g\rangle_\rho - \langle g(t)\rangle],$$

where $\langle g(t)\rangle_s$ stands for the conditional expectation of g at time t, given the state at time s. We can then insert the exponential bounds,

$$\begin{aligned}\langle f(s); g(t)\rangle &\leq \langle |f(s)|\rangle\, C\sqrt{\langle g^2\rangle_\rho}[\mathrm{e}^{-\alpha(t-s)} + \mathrm{e}^{-\alpha t}]\\ &\leq \left[\langle |f(s)|\rangle_\rho + C'\sqrt{\langle f^2\rangle_\rho}\mathrm{e}^{-\alpha' s}\right] C\sqrt{\langle g^2\rangle_\rho}\left[\mathrm{e}^{-\alpha(t-s)} + \mathrm{e}^{-\alpha t}\right]\\ &\leq \sqrt{\langle f^2\rangle_\rho\langle g^2\rangle_\rho}[1 + C'\mathrm{e}^{-\alpha' s}]\, C[\mathrm{e}^{-\alpha(t-s)} + \mathrm{e}^{-\alpha t}].\end{aligned} \tag{A 1}$$

With this bound, one obtains that the diffusion matrix has a finite limit,

$$\lim_{t\to\infty}|D_{ij}(t)| \le \lim_{t\to\infty}\frac{1}{2t}\int_0^t \mathrm{d}s\int_0^s \mathrm{d}u[|\langle \boldsymbol{v}_{i,s}\boldsymbol{v}_{j,u}\rangle| + |\langle \boldsymbol{v}_{i,u}\boldsymbol{v}_{j,s}\rangle|]$$
$$\le \sqrt{\langle \boldsymbol{v}_i^2\rangle_\rho\langle \boldsymbol{v}_j^2\rangle_\rho}\,\frac{C'\alpha + C\alpha'}{2\alpha\alpha'}.$$

Similarly, for equation (2.9), we find that

$$\left|\frac{1}{t}\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;(\boldsymbol{v}_t-\boldsymbol{v}_0)_j\rangle\right| \le \lim_{t\to\infty}\frac{1}{2t}\int_0^t \mathrm{d}u[|\langle \boldsymbol{v}_{i,u}\boldsymbol{v}_{j,t}\rangle| + |\langle \boldsymbol{v}_{i,u}\boldsymbol{v}_{j,0}\rangle|]$$

goes to zero, by the direct use of equation (A 1).

The proof of equation (3.4) is similar to the one for equation (2.9), with one extra element; namely, the fact that the dynamics in this case is an equilibrium dynamics, meaning that the associated stationary distribution ρ is the equilibrium distribution. Equilibrium is characterized by time-reversal invariance. This means in particular that the expectation value of a time-antisymmetric quantity is zero in equilibrium. In our case, this means that

$$\left\langle(\boldsymbol{r}_t-\boldsymbol{r}_0)_i;\int_0^t \mathrm{d}s\nabla_{r_j}U(\boldsymbol{r})\right\rangle_\rho = 0.$$

The rest of the proof of (3.4) is quite straightforward.

Appendix B. The mobility for one-dimensional diffusions

We give a short proof of formula (3.5). Consider the stationary probability current j_ρ^f for one-dimensional overdamped diffusion on the circle in the presence of a constant force f,

$$j_\rho^f = \chi[f - U']\rho - \chi T\rho',$$

where ρ is the stationary distribution. Because of stationarity, the current does not depend on the spatial coordinate x. We divide the last equation by ρ and integrate over the circle,

$$j_\rho^f\int\frac{\mathrm{d}x}{\rho(x)} = R\chi f.$$

Up to first order in f, the stationary current is thus given by

$$j_\rho^f = \frac{R\chi f}{\int \mathrm{d}x/\rho_0(x)},$$

where $\rho_0 = \mathrm{e}^{-U(x)/T}/\int \mathrm{e}^{-U(x)/T}$ is the equilibrium distribution. This gives the mobility

$$M = R\left.\frac{\partial}{\partial f}j_\rho^f\right|_{f=0} = \frac{R^2\chi}{\int \mathrm{e}^{+U(x)/T}\int \mathrm{e}^{-U(x)/T}}$$

because

$$M = \lim_{t\to\infty}\frac{1}{t}\left.\frac{\partial}{\partial f}\langle x_t - x_0\rangle^f\right|_{f=0} = \lim_{t\to\infty}\frac{1}{t}\left.\frac{\partial}{\partial f}\int_0^t\langle \mathrm{d}x_t\rangle^f\right|_{f=0}.$$

Appendix C. About the simulations

All graphs in this paper are the result of simulations made with the programming language C++ by directly applying the Langevin equation. This means (taking the simple example of one dimension) taking variables x and v, which at each time step of length $\mathrm{d}t$ change by the operations

$$x \to x + v\,\mathrm{d}t$$

and

$$v \to v + F(x, v)\,\mathrm{d}t - \gamma v\,\mathrm{d}t + \sqrt{2m\gamma T\,\mathrm{d}t}\xi,$$

where ξ is a random number drawn with a standard normal distribution (mean zero and variance 1). In this way, a trajectory of consecutive positions and velocities is generated. In the same way, trajectories are generated for a dynamics where a small constant force is added. The relevant quantities (diffusion, integrated forces, displacement of the particle) are then computed at each time step by averaging over many simulated trajectories. The size of the time step, the force and the number of simulated trajectories varied between the different examples in this text to find, each time, a good compromise between statistical accuracy and computation time. The length of the trajectories was taken such that the quantities showed a clear convergence to a constant value. As an example, for the case of the non-periodic potential, we took $\mathrm{d}t = 0.002$, $f = 0.03$, the number of time steps 15 000 and the number of trajectories 160 000. As the goal of this paper was not to provide accurate quantitative information, but rather a qualitative visualization of the relation between mobility and diffusion, we did not compute the statistical and systematical errors. Rather, we checked each time that the mobility equals the sum of the terms on the right-hand side of equation (2.5). The mobility needs much more computation time (number of simulated trajectories) than the other quantities. The problem with this is that one subtracts two quantities that are close to each other, and then divides by a small number. Furthermore, for the mobility one needs to simulate two systems: the perturbed one and the unperturbed one. This also means that our results are numerically useful, as one does not need to compute the mobility separately. We used this fact in the simulations where the force was varied, as in figures 4, 5 and 8. These simulations took longer, as each different value of the force required a different simulation. By leaving out the mobility, the number of trajectories could however be reduced (e.g. for the non-periodic force the number was 8000).

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