Self-Diffusion in a Nonuniform Model System

Detlef Dürr
Bibos, Universität Bielefeld, D-4800 Bielefeld 1, West Germany

and

Sheldon Goldstein and Joel L. Lebowitz[(a)]
Department of Mathematics, Rutgers University, New Brunswick, New Jersey 08903
(Received 10 April 1986)

We prove that the motion of a tagged particle in a one-dimensional fluid of hard point particles in an external potential U may be asymptotically described by a diffusion process. The process is spatially homogeneous or inhomogeneous according to whether U varies on a microscopic or macroscopic scale. The latter process can still be described by a simple Langevin equation, provided that one interprets it in the sense of Stratonovich.

PACS numbers: 05.60.+w, 66.30.Dn

The motion of a tagged particle (TP) in an equilibrium fluid is one of the most studied problems in statistical mechanics.[1-5] It is a paradigm for the extraction of stochastic simplicity from deterministic complexity, that is, for finding a simple stochastic description for a small subsystem of a large (formally infinite) system undergoing a deterministic evolution. The latter is for a classical fluid given by the Hamiltonian equations of motion while the former is known only approximately in the absence of some coarse graining.[5] We can achieve simplicity by examination of the trajectories of the TP on a space and time scale which is very large (macroscopic) compared with the time scale on which the (microscopic) velocity of the TP changes. This is generally expected to yield a universal diffusive process in which the precise nature of the fluid interactions enter only through the diffusion constant.

An actual derivation of this expected result exists, despite the efforts of many, only for the simplest model systems. Chief among them is the fluid of hard rods or point particles on a line in which the TP is identical with (has the same mass as) the other particles.[1-3] In all these studies the fluid was taken to be spatially uniform so that the resulting diffusion process was independent of the position of the TP.

In the present work we consider for the first time the case where the fluid is not spatially uniform. We show that the resulting motion of the TP still converges asymptotically to a diffusion process. This diffusion process can be either homogeneous or inhomogeneous depending on whether the external potential varies on a "microscopic" or a "macroscopic" scale. In the former case the effect of the external potential is merely to change (reduce) the diffusion constant in a simple explicitly calculable way (an exact form of the Arrhenius law). In the latter case the asymptotic motion is described by a spatially varying diffusion coefficient and drift.

As is well known, diffusion processes can be described by Langevin-type equations [stochastic differential equations (SDE's)]. When the "noise" is multiplicative, as happens in the case when the diffusion coefficient depends on the position of the tagged particle, the SDE can be written in various equivalent mathematical forms. The two best known are the Itô and Stratonovich forms,[6] which can be given simple physical interpretations. These can play an important role when one has to "derive heuristically" a diffusive behavior for a physical process.

We find interestingly that in our case, where we derive the diffusion equation rigorously, the Stratonovich form is definitely *simpler*—it involves no drift terms—and more *natural.* This gives weight to a general belief that heuristic approximations are better done in the more symmetric Stratonovich form than in the mathematically simpler Itô form. We emphasize, however, that any process which can be described by one of these forms can *always* also be described by the other form. So all we are talking here about is which form is more *natural* for a given *physical* process.

We describe our results and give an outline of the proof below. The complete proof (which turns out to be fairly simple) will be presented elsewhere.[7]

We consider an infinite system of identical point particles on the line moving in an external potential U. The only interactions between the particles are elastic collisions, i.e., in a collision velocities are exchanged. These prevent particles from crossing, without affecting the infinite-system motion if labeling is ignored. The particles are distributed according to the stationary grand canonical ensemble, i.e., their positions and velocities are Poisson with "density" $(\beta/2\pi)^{1/2}\rho_0\exp\{-\beta[U+\frac{1}{2}v^2]\}$. ($\beta$ is the inverse temperature.) As in Ref. 3, we study the position $y(t)$ of a tagged particle for large times, i.e.,

© 1986 The American Physical Society

we consider the scaled process

$$y_A(t) = A^{-1/2} y(At), \quad t \geq 0$$

in the limit $A \to \infty$. $y_A(t)$ should be regarded as describing the motion on macroscopic length and time scales.

The potential U we wish to consider is of the form $U(x/\lambda)$ where the scale parameter λ may depend upon A. Hence the density is of the form $\rho(x/\lambda)$.

The macroscopic motion of a tagged particle is determined by the *macroscopic density*

$$\tilde{\rho}(x) = \text{weak limit of } \rho(\sqrt{A}x/\lambda)$$

as $A \to \infty$, which defines naturally the *macroscopic potential* $\tilde{U}(x)$ by

$$\tilde{\rho}(x) = \rho_0 e^{-\beta \tilde{U}(x)},$$

and the *macroscopic force*

$$\tilde{F}(x) = -d\tilde{U}(x)/dx.$$

In fact we show that provided $\tilde{\rho}$ exists the macroscopic process $y_A(t)$, $t \geq 0$, converges weakly as $A \to \infty$ to a diffusion process $Z(t)$, $t \geq 0$, whose probability density $p(z,t)$ is governed by

$$\partial p(z,t)/\partial t = \tfrac{1}{2}(\partial/\partial z)[-\beta D(z)\tilde{F}(z)p + D(z)(\partial/\partial z)p], \quad (1)$$

where

$$D(z) = \rho_0 \exp[-\beta U_{\max}]\langle |v| \rangle \tilde{\rho}^{-2}(z),$$

$$U_{\max} = \sup_x \{U(x)\} \text{ and } \langle |v| \rangle = (2/\beta\pi)^{1/2}.$$

We discuss the result now for two special choices of the scale λ.

If $\lambda = \sqrt{A}$, then U varies on the macroscopic scale, i.e., $\tilde{U}(x) = U(x)$ and $\tilde{\rho}(x) = \rho(x)$. Then (1) is a *bona fide* Smoluchowski equation with spatially varying diffusion term. Note that the mobility $\beta D(x)$ satisfies the Einstein relation as it must[8] for the equilibrium distribution to be a stationary solution of (1).

As a second choice we set $\lambda = 1$, i.e., we consider a potential which varies on the microscopic scale. Then the macroscopic density is constant

$$\tilde{\rho} = \lim_{L \to \pm\infty} L^{-1} \int_0^L \rho(x)\, dx, \quad (2)$$

provided both limits agree. In this case (1) reduces to

$$\partial p(z,t)/\partial t = \tfrac{1}{2} D \partial^2/\partial z^2 p. \quad (3)$$

In particular we have (2) and hence (3) for periodic or quasiperiodic and, more generally, for ergodic random potentials. Here the result holds (with the same value of D) for almost every realization of the potential.

Note that the diffusion constant D may be written as

$$(\langle |v| \rangle/\tilde{\rho})(e^{-\beta U_{\max}}/\langle e^{-\beta U}\rangle),$$

where

$$\langle e^{-\beta U}\rangle = \lim_{L \to \infty} \frac{1}{2L} \int_{-L}^{L} e^{-\beta U(x)}\, dx.$$

It behaves for $\beta U_{\max} \gg 1$ as in the Arrhenius law[9]; e.g., if $U(x) = \sum_{n=-\infty}^{\infty} \phi(x-n)$, where

$$\phi(x) = \varepsilon, \quad |x| \leq \delta/2, \quad \delta < 1,$$

$$\phi(x) = 0, \quad |x| > \delta/2, \quad \delta < 1,$$

we have that

$$\tilde{\rho} = \rho_0[1 - \delta(1 - e^{-\beta\varepsilon})],$$

and

$$D = (\langle |v| \rangle/\tilde{\rho}) e^{-\beta\varepsilon}/[1 - \delta(1 - e^{-\beta\varepsilon})] \sim e^{-\beta U_{\max}} \text{ for } \beta\varepsilon \gg 1.$$

Also, in the limit $\delta \to 0$ ($\tilde{\rho} \to \rho_0$) the formula for D becomes $(\langle |v| \rangle/\rho_0)e^{-\beta\varepsilon}$.

If the macroscopic density on the left $\tilde{\rho}^-$ $(L \to \infty)$ and on the right $\tilde{\rho}^+$ $(L \to \infty)$ exist but do not agree, then

$$\tilde{\rho}(x) = \begin{cases} \tilde{\rho}^+, & x > 0 \\ \tilde{\rho}^-, & x < 0 \end{cases}$$

is discontinuous. In this case the macroscopic process should be regarded as having a δ function at the origin as drift term.

Equivalently to (1) we may describe the macroscopic process Z by a stochastic differential equation.[6,10]

In case $\lambda = \sqrt{A}$ and the process has a spatially varying diffusion term, the form of the Itô equation will differ from that of the Stratonovich equation. The Stratonovich equation is very simple and natural, namely

$$dZ(t) = \tilde{\rho}^{-1}(Z(t)) \circ dW(t), \quad (4)$$

with $W(t)$ a Wiener process with diffusion constant $\rho_0 e^{-\beta U_{\max}}\langle |v| \rangle$. As a matter of fact, our proof directly yields (4), not the more familiar (1).

The Itô equation corresponding to (1) contains the "spurious drift" and reads

$$dZ(t) = -\tfrac{1}{2}\beta\tilde{F}(Z(t))D(Z(t))dt + \tilde{\rho}^{-1}(Z(t))\, dW(t). \quad (5)$$

As in Ref. 3, we study the motion of the tagged particle by the relation of its position at time t to the signed number $n(t)$ of crossings of the origin by particles before time t: $n(t)$ is the number of particles crossing the origin from left to right minus the number of particles crossing from right to left, which, of course, is the same as for the "free" motion, i.e., the motion without collisions.

To describe the essence of our approach consider first the much studied case $U \equiv 0$.[1,3] Then without collisions particles move in straight lines. As tagged particle we choose for simplicity the first particle to the left of the origin at $t=0$. Following the path $y(t)$, $t\geq 0$, of this particle one finds easily that (i) $y(t)=x^t_{n(t)}\equiv$the position of the $n(t)$-th particle to the right of the origin at time t. Next observe that (ii) $n(t)$, $t\geq 0$, is a simple random walk with "± 1" jumps and jump rate $\rho\langle|v|\rangle$, where ρ is the density of the ideal gas and $\langle|v|\rangle$ the first absolute moment of the velocity distribution of the particles. This follows from the fact that in the free motion (a) particles cannot cross the origin more than once, and (b) in the ideal-gas Gibbs state, which is stationary, "distinct particles are independent." Therefore $n(t)$, $t\geq 0$, obeys the classical (functional) central limit theorem (Donsker's invariance principle)[11] with variance $\rho\langle|v|\rangle t$: The process $n(At)/\sqrt{A}$, $t\geq 0$, converges in distribution as $A\to\infty$ to $W(t)$, a Wiener process with diffusion constant $D_n=\rho\langle|v|\rangle$. Finally, for the ideal-gas Gibbs state we have that (iii) $x^t_{n(t)}\sim\rho^{-1}n(t)$. Therefore we obtain by (i) the invariance principle for $y(t)$, $t\geq 0$, with variance $\rho^{-1}\langle|v|\rangle t^3$: $y(At)/\sqrt{A}$, $t\geq 0$, converges in distribution to $\rho^{-1}W(t)$, a Wiener process with diffusion constant $D_0=\langle|v|\rangle/\rho$.

Now suppose the particles are moving in an external potential $U(x)$. Then the equilibrium density will be spatially varying: $\rho(x)=\rho_0 e^{-\beta U(x)}$. Just as for the case $U=0$, $y(t)=x^t_{n(t)}$, where $n(t)$, now the "crossing process" at the maximum of U (which to simplify notation we assume to be at the origin—our results do not require this assumption), obeys the invariance principle: $n(At)/\sqrt{A}$, $t\geq 0$, converges in distribution to $W(t)$, a Wiener process with diffusion constant $D_n=\rho_{\min}\langle|v|\rangle$, where $\rho_{\min}$ $[=\rho(0)]=\rho_0 e^{-\beta U_{\max}}$. Moreover, if $U(x)$, $x\in R$, is a (translate of) a sample of a translation invariant random bounded potential, then we have that $x^t_{n(t)}\sim\tilde{\rho}^{-1}n(t)$ and hence that $y(At)/\sqrt{A}$, $t\geq 0$, converges in distribution to $\tilde{\rho}^{-1}W(t)$, a Wiener process with diffusion constant

$$(\rho_{\min}/\tilde{\rho})(\langle|v|\rangle/\tilde{\rho})=(\rho_{\min}/\tilde{\rho})D_0,$$

where

$$\tilde{\rho}=\langle\rho\rangle=\lim_{L\to\pm\infty}L^{-1}\int_0^L\rho(x)\,dx,$$

the average density.

Our result does not, in fact, require full translation invariance, but merely that the "average density on the left" and on the right exist and agree, i.e., that the "macroscopic density" $\tilde{\rho}(x)$ [the (weak) limit as $A\to\infty$ of $\rho(\sqrt{A}x)$] be constant. If they do not agree, so that the macroscopic density $\tilde{\rho}$ has different values on the left and on the right of the origin, it remains true that $x^t_{n(t)}\sim\tilde{\rho}^{-1}(n(t))n(t)$ and hence that $y(At)/\sqrt{A}$, $t\geq 0$, converges in distribution to $Z(t)=\tilde{\rho}^{-1}(W(t))W(t)$. $Z(t)$ formally can be described by the stochastic differential equation $dZ=\tilde{\rho}^{-1}(Z(t))\circ dW$ provided that the differential is interpreted in the sense of Stratonovich.[10]

We obtain the same result even if the potential varies on the macroscopic scale A, i.e.,

$$U=U(x/\sqrt{A})\text{ and hence }\rho=\rho(x/\sqrt{A}),$$

and we consider now again the rescaled displacement of the test particle $y_A(t)=y(At)/\sqrt{A}$. (Note that as $A\to\infty$ the scale of the potential changes in just such a way as to make the external force on the TP, which is the same as that on any other fluid particle, have a finite nonvanishing effect over the macroscopic time scale At.) Moreover, on the macroscopic scale the density varies as $\rho(x)=\rho_0\exp[-\beta U(x)]$, i.e., the macroscopic density $\tilde{\rho}(x)=\rho(x)$ in this case.

Furthermore, since $n(t)$ is the number of particles between the origin and $y(t)=x^t_{n(t)}$, we should have that $dn=\rho(y/\sqrt{A})\,dy$ and hence that $y(At)/\sqrt{A}$, $t\geq 0$, converges in distribution to a process $Z(t)$ satisfying $dZ=\tilde{\rho}^{-1}(Z)\circ dW$. As we shall soon see, this turns out to be correct provided the stochastic differential is interpreted in the sense of Stratonovich.

The reader should note that the preceding analysis is not very convincing in the case where the potential varies on a macroscopic scale (e.g., nothing in the argument given for this case distinguishes between Itô and Stratonovich integrals). The rigorous derivation of our results is based on the simple change of variables

$$\bar{x}=\int_0^x\rho(x')\,dx'=f(x),$$

which converts our system to one with uniform unit density. Thus for $\bar{y}(t)=f(y(t))=f(x^t_{n(t)})=\bar{x}^t_{n(t)}$ we have that $\bar{y}(t)\sim n(t)$ behaves like $W(t)$ on macroscopic length and time scales: $\bar{y}_A(t)\equiv A^{-1/2}\bar{y}(At)$, $t\geq 0$, converges in distribution to $W(t)$ as $A\to\infty$. Undoing the change of variables, we have that $y(t)=g(\bar{y}(t))$, $g=f^{-1}$, so that

$$\begin{aligned}y_A(t)\equiv A^{-1/2}y(At)&=A^{-1/2}g(\bar{y}(At))\\&=A^{-1/2}g(A^{1/2}A^{-1/2}\bar{y}(At))\\&=A^{-1/2}g(A^{1/2}\bar{y}_A(t))\\&\equiv g_A(\bar{y}_A(t)).\end{aligned}$$

Now in all the cases we consider, the function $g_A(u)$ converges (uniformly on compacts) as $A\to\infty$ to a function $\tilde{g}(u)$, so that $y_A(t)$ converges in distribution to $\tilde{g}(W(t))$ in that limit. Moreover, when $U(x)$ varies on the microscopic scale (i.e., does not depend upon A) we have that $\tilde{g}(u)=\tilde{\rho}^{-1}(u)u$.

The preceding analysis covers the case in which the potential U, and hence ρ, depends on A; in this case f, g, y, and $\bar{y}$ also have an implicit dependence on A. When $U=U(x/\sqrt{A})$ varies on the macroscopic scale, the scaling involved in the definition of g_A cancels the implicit $\sqrt{A}$ scaling involved in g, so that $g_A=\tilde{g}$, where $\tilde{g}=\tilde{f}^{-1}$ and $\tilde{f}=\int_0^x\tilde{\rho}(x')\,dx'$. Thus $y_A(t)$ converges in distribution to $Z(t)=\tilde{g}(W(t))$. Since the usual rules of calculus are valid for Stratonovich integrals, we have that $dZ=\tilde{g}'(W(t))\circ dW$ if the Stratonovich convention is adopted. Since $\tilde{g}'(W)=[\tilde{f}'(Z)]^{-1}=[\tilde{\rho}(Z)]^{-1}$, our result follows.

We note that the fact that Z is most simply expressed as a Stratonovich integral can be understood in terms of symmetry properties under time reversal: Both $n(t)$, whose asymptotic law is $W(t)$, and $\int\tilde{\rho}^{-1}(Z)\circ dW$ are antisymmetric.

We conclude this section by noting the following consequence of the way the diffusion constant D depends upon the macroscopic density $\tilde{\rho}$: If $U=U(x)$ is quasiperiodic then D exhibits sensitive dependence on the modulation parameters. For example, if $U(x)=\cos x+\cos x(kx)$, then $D=D(k)=D^*$, independent of k, for k irrational and is unequal to D^* for k rational; in fact, D is continuous at all irrational k and discontinuous at rational k. These facts follow from the corresponding facts about $\tilde{\rho}=\tilde{\rho}(k)$. Similar results were discussed in the work of Golden, Goldstein, and Lebowitz[12] for diffusion in a quasiperiodic potential (Smoluchowski equation). Here the source of the discontinuity is perhaps more concrete since it lies in the density.

This work was supported in part by National Science Foundation Grants No. DMS-85-12505 and No. DMR-81-14726. One of us (D.D.) acknowledges receipt of a Heisenberg fellowship.

[a]Also at the Department of Physics.

[1]F. Spitzer, J. Math. Mech. **18**, 973–989 (1968).

[2]D. W. Jepsen, J. Math. Phys. (N.Y.) **6**, 405 (1965); J. L. Lebowitz and J. K. Percus, Phys. Rev. **155**, 122 (1967).

[3]D. Dürr, S. Goldstein, and J. L. Lebowitz, Comm. Pure Appl. Math. **38**, 573 (1985).

[4]A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1965); S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1934); G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930).

[5]Cf. R. Kubo, M. Toda, and N. Hashitsume, in *Statistical Physics II*, edited by M. Cardona, P. Fulde, H. Queisser, and K. von Klitzing, Springer Series in Solid-State Science Vol. 31 (Springer-Verlag, Berlin, 1985); N. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[6]Cf. N. G. van Kampen, J. Stat. Phys. **24**, 175 (1981).

[7]D. Dürr, S. Goldstein, and J. L. Lebowitz, "Self-diffusion in a non-uniform system of point particles with collisions" (to be published).

[8]P. A. Ferrari, S. Goldstein, and J. L. Lebowitz, in *Statistical Physics and Dynamical Systems*, edited by J. Fritz, A. Jaffe, and D. Szasz (Birkhauser, Cambridge, 1985).

[9]E. N. da C. Andrade, Philos. Mag. **17**, 497, 698 (1934), and Nature (London) **170**, 794 (1952), and Proc. Roy. Soc., Ser. A **215**, 36 (1952).

[10]L. Arnold, in *Stochastic Differential Equations*, edited by R. Oldenbourg (Springer-Verlag, Berlin, 1973).

[11]P. Billingsley, *Convergence of Probability Measures* (Wiley, New York, 1968).

[12]K. Golden, S. Goldstein, and J. L. Lebowitz, Phys. Rev. Lett. **55**, 2629 (1985).