Dynamics of a Single-File Pore: Non-Fickian Behavior

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The dynamics of an infinite one-dimensional system of hard rods is generalized to include the effects of a random background. Each rod follows a trajectory which is described by a generalized random function and when two rods collide they interchange velocities (and trajectories). An exact solution is obtained for the distribution $f_s(x, v, t/v')$ which is the probability of finding a particle at x with velocity v at time t that was at $x=0$ with velocity v' at $t=0$. The most interesting result is that in the long-time limit $p(x, t)$, which is the probability of finding a particle at x at time t that was at $x=0$ at $t=0$, is of the form $t^{-1/4}\exp(-x^2/t^{1/2})$. Thus, the spatial distribution does not become Gaussian and Fick's law is not valid. It is suggested that this qualitative behavior might be expected whenever single-file effects become important and that it is not dependent on the details of the one-dimensional hard-rod collisions which have been used in the derivation.

I. INTRODUCTION

Jepson[1] and Lebowitz and Percus[2] have obtained exact solutions for $f_s(x, v, t/v')$ (the probability that a particle that was at $x=0$ with velocity v' at time $t=0$ is at x with velocity v at time t) and $p(x, t)$ (the probability that the particle initially at the origin is now at x) for an infinite one-dimensional system of hard rods. In the long-time limit, $p(x, t)$ reduces to a Gaussian with a diffusion coefficient given by

$$D=(1/\rho)\int_0^\infty vg(v)\,dv, \tag{1}$$

where $g(v)$ is the distribution of the initial velocities and ρ is the density of the points [if rods of length a are used, one gets the same result simply by using $\rho=\rho'/(1-\rho'a)$, where ρ' is the density of the rods]. In this paper, a generalization of this process will be described in which the one-dimensional dynamics are combined with a randomized background. The exact solutions for $f_s(x, v, t/v')$ and $p(x, t)$ will be obtained. The most interesting result of this analysis is that, under rather general conditions, the long-time limit of $p(x, t)$ is given by

$$p(x, t)=\frac{\sqrt{\rho}}{2(\pi Dt)^{1/4}}\exp\{-\rho x^2[\pi/(16Dt)]^{1/2}\}, \tag{2}$$

where D is the diffusion coefficient the particle would have if it were the only particle in the infinite one-dimensional system. It can be seen from Eq. (2) that the spread in x goes as $t^{1/4}$ rather than $t^{1/2}$ and the process cannot be described by a diffusion coefficient (Fick's law does not apply). Although Eq. (2) is derived for a one-dimensional system of hard rods, the qualitative ($t^{1/4}$) behavior predicted by this equation probably applies to much more general systems and might be expected in most physical systems in which single-file effects are important.

II. LONG-TIME LIMIT

Since the results in this limit are the most interesting and straightforward, they will be obtained first and the general result will be derived in Sec. III. The derivation is based on a small modification of a method that the author used in a previous paper.[3] The dynamics of the model are shown in Fig. 1. The points have a given set of positions and velocities at $t=0$ and an ensemble average over these initial conditions will be taken. In the one-dimensional dynamics studied by Jepsen, the initial velocities are described by straight lines (trajectories). From the dynamics of one dimension it is easy to show that when two points collide, they simply interchange velocities or, in other words, the labels of the particles on the trajectories are interchanged. In the model described in Fig. 1 the dynamics of the one-dimensional collision is retained, that is, the trajectories simply pass through one another, but now the path of each trajectory is assumed to be an independent random function which is described by the distribution $h(x-x', v, t/v')$, where x' and v' is the initial position and velocity. For the case studied by Jepson

$$h(x-x', v, t/v')=\delta(v-v')\delta(x-x'-v't). \tag{3}$$

In this section, only the long-time limit of h is needed and it will be assumed that in this limit,

$$h(x-x', v, t/v')\to(4\pi Dt)^{-1/2}e^{-(x-x')^2/4Dt}g(v), \tag{4}$$

where $g(v)$ is any normalized function of velocity.

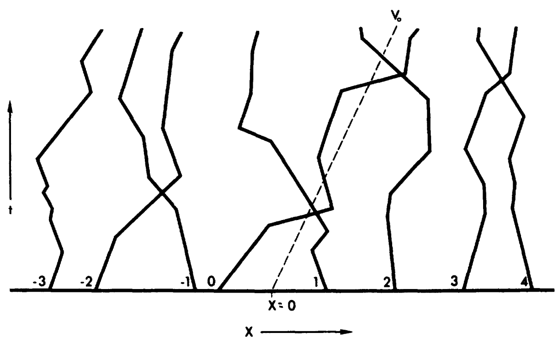

FIG. 1. Diagram showing the dynamics of the system. When two rods collide, they exchange velocities so that the trajectories seem to pass through one another. The kinks in the trajectories result from the interactions with the random background. The dashed line is a "test" trajectory with velocity v_0.

The dotted line shown in Fig. 1 is a "test" trajectory with a velocity v_0 that originates from the origin ($x=0$). Since the rods are impenetrable, every time a trajectory crosses the test trajectory from the right, the particle number of the rod immediately to the left and immediately to the right of the test trajectory will be raised by 1 (assuming the rods are originally numbered consecutively and increasing to the right). Similarly, if a trajectory crosses the test trajectory from the left the number of the nearest rod on each side of the test trajectory will be lowered by 1. Thus, as was first pointed out by Jepsen, the number of the rod immediately to the right (or left) of the trajectory at time t will be changed by an integer amount α (positive, negative, or zero) if the test trajectory is crossed α more times from the right than from the left in time t. Then, define $A_\alpha(v_0, t)$ as equal to the probability that the number of the rod immediately adjacent to the test trajectory with a velocity v_0 has been changed by an amount α in time t. Define $P_R(v_0, n, t)$ as the probability that n trajectories which started to the right of the test trajectory ($x>0$) end up at time t on the left ($x<v_0 t$). Similarly, define P_L for the particles which start to the left and end up on the right. Then (for $\alpha>0$),

$$A_\alpha(v_0, t) = \sum_{n=0}^{\infty} P_R(v_0, n+\alpha, t) P_L(v_0, n, t). \qquad (5)$$

Although the derivation will be given only for $\alpha>0$, it is easy to show that the final result is also valid for $\alpha<0$. These probabilities are ensemble averages over the initial conditions. To obtain P_R consider the probability $B_R(x_0)$ that a trajectory originates from the position between x_0 and x_0+dx_0 where $x_0>0$ and ends up to the left of the test trajectory at time t ($x<v_0 t$):

$$B_R(x_0)dx_0 = \rho dx_0 (4\pi D t)^{-1/2} \int_{-\infty}^{v_0 t} e^{-(x-x_0)^2/4Dt} dx$$
$$= \rho dx_0/\sqrt{\pi} \int_{-\infty}^{\beta} e^{-\alpha^2} d\alpha, \qquad (6)$$

where

$$\beta = (v_0 t - x_0)/2(Dt)^{1/2}.$$

In Eq. (6), ρdx_0 is the probability that a trajectory originates in the interval dx_0, and the integral is the probability [in the long-time limit, Eq. (4)] that the trajectory ends up on the left. Since each trajectory moves independently of the other trajectories, Eq. (6) applies to each dx_0 and the probability that exactly n trajectories start at $x_0>0$ and end at $x<v_0 t$ is given by a Poisson distribution with a mean of

$$\bar{B}_R = \int_0^{\infty} B_R(x_0) dx_0.$$

Integrating by parts

$$\bar{B}_R = 2\rho(Dt/\pi)^{1/2} \int_{-\infty}^{\gamma} (\gamma-\beta)^{-\beta^2} d\beta,$$

where $\gamma = v_0 t/(4Dt)^{1/2}$ and

$$P_R(v_0, n, t) = e^{-\bar{B}_R}[(\bar{B}_R)^n/n!]. \qquad (7)$$

Similarly

$$P_L(v_0, n, t) = e^{-\bar{B}_L}[(\bar{B}_L)^n/n!], \qquad (8)$$

where

$$\bar{B}_L = 2\rho(Dt/\pi)^{1/2} \int_{\gamma}^{\infty} (\beta-\gamma) e^{-\beta^2} d\beta. \qquad (9)$$

Substituting Eqs. (7) and (8) into Eq. (5) one obtains

$$A_\alpha(v_0, t) = \sum_{n=0}^{\infty} e^{-\bar{B}_R} \frac{(\bar{B}_R)^{n+\alpha}}{(n+\alpha)!} e^{-\bar{B}_L} \frac{(\bar{B}_L)^n}{n!}$$
$$= e^{-(\bar{B}_R+\bar{B}_L)} (\bar{B}_R/\bar{B}_L)^{\alpha/2} [2(\bar{B}_R \bar{B}_L)^{1/2}], \qquad (10)$$

where I_α is the imaginary Bessel function of order α and for integer α, $I_\alpha(x) = I_{-\alpha}(x)$.

Now consider $A_0(v_0, t)$. This is the probability that the same particles which were initially to the right and left of $x=0$ are now just to the right and left of $x=v_0 t$. Thus A_0 is the spatial probability distribution of the line segment which connects the two neighboring particles which were initially on opposite sides of the origin. After long times, this distribution (with a different normalization) is the same as $p(x, t)$, because after a long time the difference in position between the point $x=v_0 t$ and the position of either of its nearest neighbors is negligible compared to x.

As t goes to infinity so do $\bar{B}_R$ and $\bar{B}_L$ and $I_\alpha(z) \to e^z/(2\pi z)^{1/2}$ where $z = 2(\bar{B}_R\bar{B}_L)^{1/2}$. Thus, as $t \to \infty$

$$A_0(t) \to (4\pi\bar{B}_L\bar{B}_R)^{-1/2} e^{-(\bar{B}_L^{1/2}-\bar{B}_R^{1/2})^2}. \qquad (11)$$

It is easy to show that if $x/(4Dt)^{1/2} = \gamma > \epsilon$ for any ϵ, then $A_0(x, t)$ goes to zero as t becomes infinite. That is, it is only necessary to consider values of γ for which $\gamma \ll 1$. This assumption will be shown to be self-consistent. Thus we have

$$\bar{B}_R = 2\rho(Dt/\pi)^{1/2}\left[\int_{-\infty}^{0}(\gamma-\beta)e^{-\beta^2}d\beta + \int_0^{\gamma}(\gamma-\beta)e^{-\beta^2}d\beta\right],$$

where the first integral equals $\frac{1}{2}+\frac{1}{2}(\sqrt{\pi})\gamma$ and since $\gamma \ll 1$ the second integral $\approx \int_0^\gamma(\gamma-\beta)\,d\beta = \frac{1}{2}\gamma^2$. Thus

$$\begin{aligned}\bar{B}_R &= \rho(Dt/\pi)^{1/2}[1+(\sqrt{\pi})\gamma+\gamma^2]\\ &\approx \rho(Dt/\pi)^{1/2}[1+(\sqrt{\pi})\gamma]\\ &= K(1+a),\end{aligned} \qquad (12)$$

where $K = \rho(Dt/\pi)^{1/2}$ and $a = (\sqrt{\pi})\gamma \ll 1$. Similarly,

$$B_L = K[1-a]. \qquad (13)$$

Substituting Eqs. (12) and (13) into Eq. (11),

$$A_0(x, t) \to [1/(\sqrt{4\pi K})]\,e^{-Ka^2}. \qquad (14)$$

This result is consistent with the initial assumption that $\gamma << 1$ or $x \ll (Dt)^{1/2}$. As was shown in the previous paper,[3] the integral of A_0 over all space (normalization) should be equal to the average separation between particles, $1/\rho$. Integrating Eq. (14) over all space shows that this is correct. Thus at long times the normalized probability distribution is given by Eq. (2).

III. GENERAL CASE

The system is identical to that shown in Fig. 1 except that now it is known that there is a particle (and, therefore, a trajectory) at the origin at $t=0$ with velocity v' and the problem is to calculate the probability that this particle is in the interval between x and $x+dx$ at time t with a velocity v. The distributions and notation that are used in this section are summarized: $g(v)$ is the initial velocity distribution; $h(x-x', v, t/v')$ is the probability that the trajectory that originated from x' with velocity v' (at $t=0$) is at x with velocity v at t; $E_R(x, t/v')$ is the probability that the trajectory that is initially at the origin with velocity v' is at $x' > x$ at t,

$$E_R = \int_{-\infty}^{\infty} dv \int_x^{\infty} h(x', v, t|v')dx'; \qquad (15)$$

E_L is defined analogously.

In this section the most important probabilities will be terms of the type $S_{RL}^0(x, v, t)\,dx\,dv$ which is the probability of finding a trajectory in the interval between $x-dx$ and x with velocity v at t that was at $x' > 0$ at $t=0$, conditional on the knowledge that there have been no net crossings at time t. This can be written in the form

$$S_{RL}^0 = \sum_{n=0}^{\infty} nC_R D_R^0(n), \qquad (16)$$

where $D_R^0(n)$ is the probability that n trajectories have started at $x' > 0$ and ended up at $x' < x$ conditional on the knowledge that there have been no net crossings at time t; and $C_R(x, v, t)\,dx$ is the probability that a trajectory starting from $x' > 0$ and known to be at $x' < x$ at t, will be in the interval $x-dx$, x with velocity v at t. The unconditional probability that a trajectory ends up in $x-dx$, dx that was $x' > 0$ at $t=0$, is

$$p_R(x, v, t) = \int_0^{\infty} dx' \int_{-\infty}^{\infty} h(x-x', v, t/v')g(v')dv', \qquad (17)$$

and C_R is equal to

$$C_R = (\rho/\bar{B}_R)p_R, \qquad (18)$$

where $\bar{B}_R/\rho$, the probability that a trajectory started from $x' > 0$ and is at $x' < x$ at t, is given by

$$\bar{B}_R/\rho = \int_{-\infty}^{\infty} dv \int_{-\infty}^{x} p_R(x', v, t)\,dx'. \qquad (19)$$

$\bar{B}_R$ is the generalized mean of the Poisson distribution used previously [Eq. (7)]. From Eq. (5), which was used to derive A_0, it is easy to see that D_R^0 is equal to

$$D_R^0(n) = (1/A_0)P_R(n)P_L(n).$$

Thus

$$\begin{aligned}S_{RL}^0 &= \sum_{n=1}^{\infty}\frac{n\rho p_R}{A_0\bar{B}_R}e^{-\bar{B}_R}\frac{(\bar{B}_R)^n}{n!}e^{-\bar{B}_L}\frac{(\bar{B}_L)^n}{n!}\\ &= \frac{\rho p_R}{A_0}\sum_{n=0}^{\infty}e^{-\bar{B}_R}\frac{(\bar{B}_R)^{n-1}}{(n-1)!}e^{-\bar{B}_L}\frac{(\bar{B}_L)^n}{n!}\\ &= \frac{\rho p_R A_{-1}}{A_0}.\end{aligned} \qquad (20)$$

Following a similar procedure it can be shown that

$$S_{RL}^1 = \rho p_R A_0/A_1, \qquad (21)$$

where 1 refers to the conditional knowledge of one extra crossing from the right. One can carry out a similar derivation for terms of the form S_{LR}^0 which is the probability of finding a trajectory in the interval x, $x+dx$ at time t that was at $x' < 0$

at $t=0$. One finds that

$$S^{0}_{LR}=\rho p_L A_1/A_0, \quad S^{-1}_{LR}=\rho p_L A_0/A_{-1}, \tag{22}$$

where

$$P_L=\int_{-\infty}^{0} dx' \int_{-\infty}^{\infty} h(x-x', v, t/v')g(v')dv'. \tag{23}$$

The A's in Eqs. (20)–(22) are given by Eq. (10) with the mean $\bar{B}_R$ given by Eq. (19) with a similar equation for $\bar{B}_L$.

Now terms of the form S^{0}_{RR} (the probability of finding a trajectory in the interval x, $x+dx$ at time t that was at $x'>0$ at $t=0$ given that there are no net crossings) or S^{0}_{LL} cannot be obtained in the same way since no exact conditions are placed on the trajectories which end up on the same side of the test trajectory that they start on. However, if a trajectory with velocity v is in the interval x, $x+dx$ (on the right of the test trajectory with $v_0=x/t$) at time t and there have been no net crossings then in an infinitesimal time $d\tau=dx(v-v_0)$ in the future or past, it will be in the interval dx on the left and there will have been one extra crossing from the right. That is

$$\begin{aligned} A_0(x,t)S^{0}_{RR}(x,v,t) &= A_1(x',t')S^{1}_{RL}(x',t') \\ &= \rho p_R(x',t')A_0(x',t'), \end{aligned} \tag{24}$$

where $x'=x+v_0 d\tau$, and $t'=t+d\tau$. Since all the terms in Eq. (22) are continuous in x and t, $S^{0}_{RR}=\rho p_R$ is just the unconditional probability of finding a trajectory in dx about x that started at $x'>0$. This result might have been anticipated since the conditional knowledge about the number of net crossings does not place any restrictions on the number of trajectories which have not crossed. In a similar manner it can be shown that

$$S^{\pm 1}_{RR}=\rho p_R, \quad S^{0,\pm 1}_{LL}=\rho p_L. \tag{25}$$

Having derived these probabilities, the exact expression for $f_s(x, v, t/v')$ can be obtained easily. Consider the case in which the trajectory initially at the origin starts off to the right of the test trajectory ($v'>v_0=x/t$) and is on the right ($x'>x$) at time t. Then, if at time t there have been no net crossings by all the other trajectories (with a probability given by A_0) the particle that was initially at the origin must now be the nearest neighbor on the right and if there is a trajectory in the interval between x and $x+\frac{1}{2}dx$ this particle must be on it. Thus the contribution to f_s for this case is

$$\tfrac{1}{2}dx\,\eta(v't-x)E_R A_0[S^{0}_{RR}+S^{0}_{LR}+(h/E_R)], \tag{26}$$

where η is the unit step function and specifies that the trajectory starts off to the right, E_R [Eq. (12)] is the probability that the trajectory is still on the right, A_0 is the probability that there have been no net crossings, and the term in brackets is the probability of finding a trajectory in the interval x, $x+\frac{1}{2}dx$ for these conditions. S^{0}_{RR} and S^{0}_{LR} are the probabilities of finding a trajectory in this interval that was at $x'>0$ and $x'<0$ at $t=0$, respectively, and h/E_R is the probability of finding the trajectory that was initially at the origin in this interval, conditional on the knowledge that it is at $x'>x$ at t. Similarly, consider the case in which the trajectory again starts off to the right, is still on the right at t, but that there has been one extra crossing from the right. Then the particle initially at the origin must be the nearest neighbor on the left and the term in f_s is

$$\tfrac{1}{2}dx\,\eta(v't-x)E_R A_1(S^{1}_{RL}+S^{1}_{LL}). \tag{27}$$

If one carries out the same sort of procedure for the six other combinations of conditions and then substitutes from Eqs. (17)–(25) for the S's, the final expression for f_s is obtained,

$$\begin{aligned} f_s(x,v,t/v') = \rho[E_R(A_0 p_R+A_1 p_L)+E_L(A_{-1}p_R+A_0 p_L)] \\ +A_0 h(x,v,t/v'). \end{aligned} \tag{28}$$

The general result for $p(x,t)$ is obtained simply from

$$p(x,t)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_s(x,v,t/v')g(v')dv'dv. \tag{29}$$

If the expression for h used by Jepson [Eq. (3)] is substituted into Eqs. (15)–(19) then it is easy to show that

$$\begin{aligned} &E_R=\eta(v't-x), \quad E_L=\eta(x-v't), \\ &p_R=g(v)\eta(x-vt), \quad p_L=g(v)\eta(vt-x), \\ &\bar{B}_R=\rho\int_{-\infty}^{x/t}(x-vt)g(v)dv, \\ &\bar{B}_L=\rho\int_{x/t}^{\infty}(vt-x)g(v)dv. \end{aligned} \tag{30}$$

If these expressions are substituted in Eqs. (28) and (29) the results of Jepson are obtained immediately.[3]

Another simplification of Eqs. (28) and (29) can be obtained if it is assumed that $h(x-x', v, t/v')=g(v)f(x-x',t)$ where, for example, g might be Maxwellian and f Gaussian with a diffusion coefficient D [Eq. (4)]. This form of h would be valid for times which are long with respect to the random process and yet still not long enough that the average displacement of a particle is long with respect to the interparticle distance. With this simplification it can be shown that

$$p(x, t) = \rho[2A_0H(1-H) + A_1(1-H)^2 + A_{-1}H^2] + A_0 f(x, t), \tag{31}$$

where

$$H(x, t) = \int_{-\infty}^{x} f(x', t)dx'.$$

As t becomes infinite, $A_0 = A_{-1} = A_1$ and $p(x, t) = \rho A_0$ which was the limit considered in Sec. II.

IV. RELATIONSHIP TO PHYSICAL SYSTEMS

Although these results were based on the assumption of one-dimensional collisions of hard rods, the qualitative behavior predicted by Eq. (2) may have much more general applications. That is, if the collisions with the random background occur with a much higher frequency than the interparticle collisions, then it seems reasonable to assume that the exact details of the interparticle collisions are unimportant and that the hard-sphere collisions are only a convenient mathematical way of preventing the particles from passing each other. Consider, for example, a gas in a pore so narrow that the molecules cannot pass each other. Then the random background would correspond to the collisions of the gas with the wall, and D in Eq. (2) could be obtained from the equations used to describe Knudsen flow. Another possible application would be, for example, the movement of large solute particles through narrow water-filled pores. In this case, the random motion would be the result of the collisions of the solute molecule with the wall and with the solvent background. The h of the model would correspond to the solution of the Fokker-Planck equation and D would be the solute diffusion coefficient if only one particle were present in the pore.

It would be of interest to test the predictions of Eq. (2) in some physical system. There is good evidence for the existence of pores with a radius of about 3 Å in biological membranes in which solutes would have to pass single file.[4] However, since these pores are less than 50 Å long, no more than one or two molecules would be in the pore at a time (at normal solute concentrations); the condition that the distance moved must be long relative to the intersolute distance could not be met and any single-file effect would be negligible.

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