J Stat Phys (2010) 138: 40–50
DOI 10.1007/s10955-009-9917-8

On Tagged Particle Dynamics in Highly Confined Fluids

J.K. Percus

Received: 9 November 2009 / Accepted: 28 December 2009 / Published online: 13 January 2010

Abstract Heuristic approaches to the statistics of tagged particle motion in a one-dimensional hard point particle fluid are discussed. An exact expression is obtained for the finite N case with arbitrary single-particle interactionless dynamics. This is extended to the mean over tagged particles as $N \to \infty$, and a simple form presented in terms of elementary physical quantities. Extension to single-file flow under quasi-one-dimensional confinement is initiated.

Keywords Single file · Confined fluids · Self dynamics

1 Introduction

Sophisticated experimental [1], theoretical [2], and computational [3] techniques have combined with industrial importance [4] and biological necessity [5] to motivate the recent surge in the study of highly confined fluids. It is of course difficult to create a vehicle capable of encompassing the diverse phenomenology put in evidence as the parameters controlling such systems are varied, and we will not attempt to do so. We will rather focus—with a good deal of bias- on perhaps the extreme of quasi-one-dimensional confinement, in which the molecules of the fluid in question do not have the physical space to pass each other, creating so-called single file flow. The fact that a particle, to move substantially, must carry a cloud of particles with it, is an enormous impediment to motion, producing anomalously slow identified particle dynamics. We will here narrow our attention to circumstances under which classical physics suffices as theoretical underpinning; other specializations will arise in due course.

Based loosely on talks given at Ben-Gurion University, Jan 2007, Rutgers University, Dec 2008, and Beijing Institute of Theoretical Physics, Jan 2009.

J.K. Percus (✉)
Courant Institute and Physics Department, New York University, 251 Mercer St., New York, 10012 NY, USA
e-mail: jerome.percus@nyu.edu

The major characteristics of the system we study will be

1. Blocking of motion by neighboring particles.
2. Small (molecular scale) volume/surface ratio of the confining substrate.
3. Crucial—but non-trivial—background information will be assumed, that of the dynamics of an isolated particle in the same confining environment. This itself is a newly revivified [6] very active field, building upon the dynamics of a free totally unimpeded particle, which can be imagined to run the spectrum from inertial, based upon the Liouville equation

$$\partial f/\partial t + v \cdot \nabla f = 0 \tag{1}$$

to the overdamped extreme of diffusion

$$\partial \rho/\partial t - D\nabla^2 \rho = 0 \tag{2}$$

and we will when feasible make no explicit assumption as to this dynamics.

In this study, we will aim at the dynamics of a specified particle, one of the assumed identical particles comprising the fluid; this "tagged particle" dynamics is to be regarded as the signature of fluid transport properties, a relationship that is somewhat indirect [7]. We will throughout take advantage of the separation of time scales between free particle motion and that of the surrounding fluid. In summary, we will start with a review of the case of field-free hard point particles on the full 1-D line, eliciting much of the phenomenology of interest. We then proceed to an exact solution of the same system in an arbitrary external field and with arbitrary isolated particle dynamics, introducing a number of physically relevant concepts. Specialization to equilibrium and steady state systems is immediate. Extension to hard rods on the line is trivial in the field-free case, and this gives us sufficient parameter control to construct a leading order map to a next neighbor interacting fluid in a cylindrical container with wall interactions.

2 Point Particles on a Line: Heuristics

If we cannot readily analyze the dynamics of a tagged particle in a system of identical hard point particles on an unbounded line, then we cannot do anything! First, let us settle on the meaning of "hard point particle". For the usual Newtonian inertial dynamics, we are referring to the interaction responsible for elastic collisions, in which case energy and momentum conservation tell us at once that incoming velocities v_1 and v_2 produce outgoing velocities $v_1' = v_2$, $v_2' = v_1$. A pictorial interpretation is that the pair of velocities is unchanged—as with no interaction—but the "tag" #1 is transferred to particle #2 by their collision.

Next, let us decide on just how we want to describe the tagged particle dynamics. Since we will be dealing with a stochastic context, i.e. averaging over an ensemble of trajectory realizations, we will regard this as specified by

$$p(x, t; y, 0) \tag{3}$$

the probability density of the particle being at x at time t, as well as being at y at time 0. Consider an isolated particle. Probability then enters in two different ways: (a) via the initial velocity distribution of the particle, but thereafter deterministically, including the possibility of a damping mechanism; here the initial velocity of the trajectory is "frozen" in. (b) via random forces applied to the trajectory, which is "annealed" in the sense that a new random

Fig. 1 Basic collision

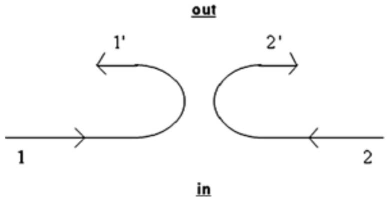
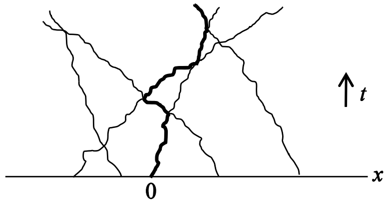


Fig. 2 Tagged particle trajectory (*bold*) in model fluid of non-interacting particles



force is applied at each instant of time. In each case, there results a "phase space" density $p_0(x, v, t; y, u, 0)$, and the corresponding marginal density

$$p_0(x, t; y, 0) = \int p_0(x, v, t; y, u, 0)\, dv\, du \tag{4}$$

Inertial dynamics is one extreme, in which random forces and damping are absent. Diffusion is an opposite extreme, in which, on suitable scaling, the inertial $m\ddot{x}$ forces vanish and only damping and random forces remain.

In the whole dynamical clan just described, only the infinite contact forces matter during the infinitesimal time of a collision, and so the prescription of Fig. 1 remains valid. Proceeding to a tagged particle in a fluid, we can regard all particles as free and non-interacting, but then the tag is to be transferred each time its carrier meets another particle, resulting in the bold piecewise trajectory of Fig. 2 (implicit in the work of Harris [8], Jepsen [9], and Levitt [2]). A quick heuristic analysis might then go like this:

The tagged particle, hemmed in by its neighbors, will have net motion on a much longer time scale than that of the particles of the surrounding fluid, which can be regarded as non-interacting. So on the latter time scale, we can "pessimistically" imagine the tagged particle as stuck near its initial location, say 0, but able to pick up fluctuations (their nature is where the physics lies) from its collisions. We will feel free to replace variables by their averages—a mean field reduction—when convenient. Thus, if the mean particle density is $n = \frac{1}{l}$, where l is the specific 1-D volume, a tag will move $\pm l$ from its local mean position when a collision (just a crossing) with a neighbor takes place. Regarding successive collisions as independent (but see Ref. [10]), the mean square displacement at time t would then be

$$\langle \Delta x(t)^2 \rangle = l^2 Q(t) \tag{5}$$

where $Q(t)$ is the number of collisions up to time t.

Now on the scale on which we take the default location of the tag as the origin, a collider initially at distance y from the origin (location $\pm y$) will arrive at the origin at a time t_y estimated as the function of y inverse to

$$y_t = \int |y| p_0(0, t|y, 0)\, dy = \langle |y(t)| \rangle_0 \quad \text{where } p_0(x, t|y, 0) \equiv \frac{p_0(x, t; y, 0)}{p_0(y)} \tag{6}$$

but y_t, in units of l, is precisely the number of collisions that have occurred until t, $y_t = l\,Q(t)$ (half from each of $\pm y$, the other half going away from the origin). We conclude [11] that

$$\langle \Delta x(t)^2 \rangle = l \langle |x(t)| \rangle_0 \tag{7}$$

In inertial motion, $\langle |\Delta x(t)| \rangle_0 \propto t$, so that the tagged particle moves diffusively; in diffusive motion, $\langle |\Delta x(t)| \rangle_0 \propto t^{\frac{1}{2}}$ and then $\langle \Delta x(t)^2 \rangle \propto t^{\frac{1}{2}}$ exhibits subdiffusion, or anomalous diffusion.

An "optimistic" viewpoint is interesting as well [12]. Here, the default is that of the tagged particle moving with complete freedom. But of course, it can only proceed as rapidly as the particles in the direction of its motion retreat, while those on the other side move into the vold created. There is then a cluster surrounding the tagged particle, which can be approximately identified with the center of mass of the correlation cluster—similar to diffusion in polymer melts [13]. What will be the dynamics of this center of mass? Suppose that the cluster contains $M(t)$ particles, of course an increasing function of time, now asymmetrically enclosing the origin, and that $M^-(t)$ particles are to the left of o, $M^+(t)$ to the right, with $M^+(t) + M^-(t) = M(t)$. The center of mass is clearly given—again assuming fixed interparticle separation l, by

$$x_{cm}(t) = \frac{l}{2} \sum_1^{M(t)} \operatorname{sgn} x_i(t) \tag{8}$$

and so, using $(\operatorname{sgn} x)^2 = 1$, the independence of the $x_i(t)$, and the mean field assertion that $\langle x_i(t) \rangle = 0$, we conclude that

$$\langle x_{cm}(t)^2 \rangle = \frac{l^2}{4} M(t) \tag{9}$$

Equation (9) is independent of explicit dynamics, which then enters when we try to calculate $M(t)$. For this purpose, it suffices to look at $\langle x_{cm}(t)^2 \rangle$ from another viewpoint. Rather than use the approximate representation (8), we have by definition

$$x_{cm}(t) = \Delta x_{cm}(t) = \frac{1}{M(t)} \sum_1^{M(t)} \Delta x_i(t) \tag{10}$$

where the $\Delta x_i(t)$ follow isolated particle dynamics. Then from $\langle \Delta x_i(t) \rangle_0 = 0$ and independence (and $x_{cm}(0) = 0$), we see that

$$\langle \Delta x_{cm}(t)^2 \rangle = \frac{1}{M(t)^2} (M(t) \langle \Delta x(t)^2 \rangle_0) \tag{11}$$

Eliminating $M(t)$ between (9) and (10), then

$$\langle \Delta x(t)^2 \rangle = \frac{l}{2} \langle \Delta x(t)^2 \rangle_0^{\frac{1}{2}} \tag{12}$$

not quite the same as (7), but yielding the same power of time dependence.

3 Hard Point Particles on a Line: Exact Self-dynamics

It is not hard to extend the above to include space and time varying external fields—which have implicitly been ignored—but rather than do so in the context of a hand-waving treatment, we now turn to an exact solution of this rather elementary many-body problem. Suppose then that we have $N = 2M + 1$ hard point particles in one-dimensional space, confined as desired by an external field, and that we know the isolated particle stochastic dynamics $p_0(x,t;y,0)$. For definiteness, we will imagine that the *central particle*, denoted by x_c, is tagged (other *ordinal* locations are just a bit more complicated). The particle x_c must then be picked out from the unordered particle set whose free dynamics is equivalent to our set of contact-reflecting particles. There are many ways of doing so, but for our purposes, an indirect approach is more convenient. To set the stage, we first ask for the tagged particle distribution at time t, not conditioned on $t = 0$, and choose to work with

$$s_0(x,t) \equiv \langle \mathrm{sgn}(x - x_i(t)\rangle_0 \tag{13}$$

which is a sensitive indicator of deviations from uniformity. Of course, we then have

$$p_0(x,t) = \frac{1}{2}\frac{\partial}{\partial x} s_0(x,t) \tag{14}$$

Now to find the density $p_c(\xi)$ of the central particle x_c at location ξ (time implicit), we note that x_i will be the central particle if

$$\sum_j \mathrm{sgn}(x_i - x_j) = 0 \tag{15}$$

it follows that any function $f(x_c)$can be represented as

$$f(x_c) = \sum_i f(x_i)\delta_{kr}\left(\sum_j \mathrm{sgn}(x_1 - x_j)\right) \tag{16}$$

where δ_{kr} denotes the Kronecker δ-function. Hence

$$f(x_c) = \sum_i f(x_i) \int_{-\pi}^{\pi} \exp\left(i\phi \sum_j \mathrm{sgn}(x_1 - x_j)\right) \frac{d\phi}{2\pi} \tag{17}$$

In particular, the per configuration probability density of x_c, $\hat{p}_c(\xi) = \delta(\xi - x_c)$, is given by

$$\hat{p}_c(\xi) = \sum_1 \delta(\xi - x_i) \int_{-\pi}^{\pi} \exp\left(i\phi \sum_j \mathrm{sgn}(\xi - x_i)\right) \frac{d\phi}{2\pi} \tag{18}$$

This is most simply evaluated [14] by observing that as ξ goes from x_j^- to x_j^+, $e^{i\phi\,\mathrm{sgn}(\xi - x_j)}$ goes from $e^{-i\phi}$ to $e^{i\phi}$, a jump of $2i \sin\phi$. Hence

$$\frac{\partial}{\partial \xi} e^{i\phi \sum_i \mathrm{sgn}(\xi - x_i)} = 2i \sin\phi \sum_j \delta(\xi - x_j) e^{i\phi \sum_i \mathrm{sgn}(\xi - x_i)} \tag{19}$$

We can therefore (exercising caution for $\phi \sim 0$) rewrite (18) as

$$\hat{p}_c(\xi) = \int \frac{1}{2\sin\phi} \frac{\partial}{\partial \xi} e^{i\phi \sum_j \operatorname{sgn}(\xi - x_j)} \frac{d\phi}{2\pi} \tag{20}$$

Taking the expectation of the independent $\{x_i\}$, with common distribution $p_0(x)$, and recalling that $\langle \operatorname{sgn}(\xi - x)\rangle_0 = s_0(\xi)$, we then have

$$\begin{aligned} p_c(\xi) &= \frac{\partial}{\partial \xi} q_c(s_0), \\ \text{where } \frac{\partial q_c}{\partial s_0} &= \frac{N}{2^N}\left(\int_{-\pi}^{\pi} (\cos\phi + i s_0(\xi)\sin\phi)^{N-1} \frac{d\phi}{2\pi}\right) \\ &= \frac{N}{2^N}\binom{2M}{M}(1 - s_0^2)^M \end{aligned} \tag{21}$$

Integration is routine, and so

$$p_c(\xi) = p_0(\xi)\left(N\binom{2M}{M}\Big/2^{2M}\right)(1 - s_0(\xi)^2)^M \tag{22}$$

which for large M reduces to

$$p_c(\xi) = p_0(\xi)\left(\frac{2N}{\pi}\right)^{\frac{1}{2}} e^{-\frac{N}{2}s_0(\xi)^2} \tag{23}$$

The dramatic narrowing of p_0 as we depart from the center of the distribution p_0—signaled by the vanishing of $s_0(\xi)$—is hardly a surprise, since x_0 approximates the mean particle position, and the central limit theorem then takes over.

With this introduction, we proceed next to the central particle space-time autocorrelation $p_c(x, t; y, 0)$. We must now impose the time 0 and t conditions

$$\sum_j \operatorname{sgn}(x_i(0) - x_j(0)) = 0 = \sum_j \operatorname{sgn}(x_i(t) - x_j(t)) \tag{24}$$

Following the above pattern, we have at once

$$\begin{aligned} \hat{p}_c(x, t; y, 0) = \sum_{i,j} &\delta(x - x_1(t))\delta(y - x_j(0)) \\ &\times \int \int_{-\pi}^{\pi} \exp \sum_k [i\phi \operatorname{sgn}(x - x_k(t)) + i\phi' \operatorname{sgn}(y - x_k(0))] \\ &\times \frac{d\phi}{2\pi}\frac{d\phi'}{2\pi} \end{aligned} \tag{25}$$

which we rewrite, as we did (18),

$$\begin{aligned} \hat{p}_c(x, t; y, 0) = \frac{-\partial^2}{\partial x \partial y} &\iint \exp \sum_k [i\phi \operatorname{sgn}(x - x_k(t)) + i\phi' \operatorname{sgn}(y - x_k(0)] \\ &\times \frac{d\phi}{2\pi}\frac{d\phi'}{2\pi}/4\sin\phi\sin\phi' \end{aligned} \tag{26}$$

To carry out the expectation of (26), we first add to the definition (13):

$$C_0(x,t;y,0) \equiv \langle \operatorname{sgn}(x - x_c(t)) \operatorname{sgn}(y - x_c(0)) \rangle_0 \tag{27}$$

and then reduce the exponentials in (26) by the identity $\exp(i\phi \operatorname{sgn}) = \cos\phi + i \sin\phi \operatorname{sgn}$ that was also used in (21):

$$\begin{aligned}
&\langle \exp[i\phi \operatorname{sgn}(x - x(t)) + i\phi' \operatorname{sgn}(y - x(0)]\rangle_0 \\
&\quad = \frac{1}{2}[(1 + C_0)\cos\Psi + (s_0 + \bar{s}_0)i \sin\Psi \\
&\qquad + (1 - C_0)\cos\Psi' + (s_0 - \bar{s}_0)i \sin\Psi'] \\
&\quad \text{where } s_0 \equiv s_0(x,t),\ \bar{s}_0 \equiv s_0(y,0),\ \Psi \equiv \phi + \phi',\ \Psi' \equiv \phi - \phi'
\end{aligned} \tag{28}$$

Furthermore, $-4\sin\phi \sin\phi' = 2(\cos\Psi - \cos\Psi')$, and we can write

$$p_c(x,t;y,0) = \frac{-\partial^2}{\partial x \partial y} \frac{1}{2} Q_c(s_0, \bar{s}_0, c_0) \tag{29}$$

where, dropping the 0 subscripts, (the denominator now cancels)

$$\frac{\delta Q_c}{\delta C} = \frac{N}{2^{N+1}} \langle [(1 + C)\cos\Psi + (s + \bar{s})i \sin\Psi + (1 - C)\cos\Psi' + (s - \bar{s})i \sin\Psi']^{2M} \rangle \tag{30}$$

$\langle\,\rangle$ denoting average over Ψ and Ψ', identical with that over ϕ and ϕ'. The evaluation of (30) is direct. We have

$$\begin{aligned}
\frac{\delta Q_c}{\delta C} &= \sum \binom{2M}{k} \frac{N}{2^{N+1}} \langle [(1 + C)\cos\Psi + (s + \bar{s})i \sin\Psi]^k \rangle \\
&\quad \times \langle [(1 - C)\cos\Psi + (s - \bar{s})i \sin\Psi']^{2M-k} \rangle \\
&= \frac{N}{2^{2N}} \sum \binom{2M}{2K} (1 + C + s + \bar{s})^k (1 + C - s - \bar{s})^k \binom{2K}{K} \\
&\quad \times (1 - C + s - \bar{s})^{M-K} (1 - C - s + \bar{s})^{M-K} \binom{2(M-K)}{M-K}
\end{aligned} \tag{31}$$

But (see Ref. [15] p. 38), we know that

$$\sum \binom{M}{K}^2 A^K B^{M-K} = (A - B)^M P_M\left(\frac{A + B}{A - B}\right), \tag{32}$$

and so, conclude that

$$\begin{aligned}
&\frac{\delta Q_c}{\delta C} = \frac{N}{2^{2N}} \binom{2M}{M} (A - B)^M P_M\left(\frac{A + B}{A - B}\right) \\
&\quad \text{where } A = (1 + C)^2 - (s + \bar{s})^2,\ B = (1 - C)^2 - (s - \bar{s})^2
\end{aligned} \tag{33}$$

We also know that in the special case in which the (x,t) and $(y,0)$ distributions are independent, we will have $C_0(x,t;y,0) = s_0(x,t)s_0(y,0) = s\bar{s}$, as well as $Q_c(x,t;y,0) = q_c(x,t)q_c(y,0) = q_c(s)q_c(\bar{s})$. Thus, to (33) we can add the initial condition

$$Q_c(s,\bar{s},C)_{c=s\bar{s}} = q_c(s)q_c(\bar{s}) \tag{34}$$

This suffices in principle to determine $Q_{c,}$ and consequently the desired p_c.

4 Limiting Cases

Equations (29), (33), (34) do constitute an exact solution, but they are hardly transparent. A form in which no further integrations have to be performed is also available by computing $\frac{\delta Q_c}{\delta y}$ directly, and so canceling the unwieldly denominator. It is also rather involved. And a formally exact solution for the case in which the isolated particle dynamics is diffusive, with no external field, is available as well [16], but is exceedingly complicated.

Under these circumstances, limiting cases give us more of a feeling as to the basic character of the process. We will now review, quote, and analyze one that has been considered in detail [17]. It is that in which $N \to \infty$ under an external potential that confines the system longitudinally, say to distance L, but then $L \to \infty$ as well at the same rate. To further simplify matters, we focus not on a specified initial particle, but rather on any particle initially at y and then at x at time t, and average over the number of particles. This must dilute any conclusions, but not as much as it might seem to start with, because the probability of a particle being at y at $t=0$ is weighted heavily by a small set of nearby particles, all of which are far from the boundary if y is.

That said, we only have to make sure that we are following the same particle from y to x, meaning that the index (with integer values in the range $[-M,M]$)

$$I(x,t) = \frac{1}{2}\sum_{j=1}^{N} \mathrm{sgn}(x - x_j(t)) \tag{35}$$

remains the same. Hence, we now include the weight

$$\delta_{kn}(I(x,t) - I(y,0)) \tag{36}$$

in any system expectation over all system trajectories. In particular, the self-density auto correlation $n_s = Np_s$($c =$ central has become $s =$ self) is

$$\begin{aligned} n_s(x,t;y,0) = \int \sum_{(i)} \Big\langle \delta(x - x_i(t))\delta(y - x;(0)) \\ \times II_k e^{i\phi\frac{1}{2}(\mathrm{sgn}(x-x_k(t))-\mathrm{sgn}(y-x_k(0)))}\frac{d\phi}{2\pi}\Big\rangle, \end{aligned} \tag{37}$$

which yields by the technique of (25). The Nth power included becomes, in this limit, an exponential, and we readily obtain

$$\begin{aligned} Q_s(x,t;y,0) = \frac{1}{N}\int \{\exp[Q_0(x,t;y,0)(\cos\phi - 1)] \\ \times \cos(W_0(x,t;y,0) - 1\}\frac{d\phi}{4\pi}(\cos\phi - 1), \end{aligned} \tag{38}$$

where

$$
\begin{aligned}
Q_0(x,t;y,0) &= \frac{1}{2}\langle 1-\operatorname{sgn}(x-x(t))(y-x(0))\rangle_0 \\
&= \frac{1}{2}(1-C_0(x,t;y,0)) \\
W_0(x,t;y,0) &= \frac{1}{2}\langle \operatorname{sgn}(x-x(t))-\operatorname{sgn}(y-x(0))\rangle_0 \\
&= \frac{1}{2}(s_0(x,t)-s_0(y,0))
\end{aligned}
\tag{39}
$$

in the notation of (13) and (27).

Qualitative information then resides in the properties of Q_0 and W_0, and for clarity we here restrict ourselves to steady state. $W_0(x,y)=W_0(x,t;y,0)$ does not depend on time, and is just the single particle (signed) total density between x and y. On the other hand, $Q_0(x,t;y,0)$ is still time-dependent. But, at long enough time, where $x(t)-x(0)$ is diverging at the single particle rate, we will be interested (see (21)) in much smaller differences between x and y. If we choose $y=0$, then necessarily $x\sim 0$, and so $Q_0(x,t;y,0)$ is replaced by

$$
Q_0(t)=\frac{1}{2}\langle 1-\operatorname{sgn} x(t)x(0)\rangle_0 \tag{40}
$$

Q_0 being a function only of time, W_0 only of x and y simplifies matters substantially, and it is easy to show by direct evaluation that, introducing the current density j, which satisfies

$$
\frac{\partial j_0}{\partial x}+\frac{\partial n_0}{\partial t}=0, \tag{41}
$$

then the dimensionless (self) density and current density

$$
\begin{aligned}
g(x,t;y,0) &= \frac{n(x,t;y,0)}{n_0(x)n_0(y)} \\
k(x,t;y,0) &= \frac{j(x,t;y,0)}{Q(t)n_0(y)}
\end{aligned}
\tag{42}
$$

obey

$$
\frac{\partial g}{\partial Q}+\frac{\partial k}{\partial F}=0, \qquad \frac{\partial k}{\partial Q}+\frac{\partial g}{\partial F}+2k=0 \tag{43}
$$

where $Q=Q_0(t)$, $F=\frac{1}{2}s_0(x)$, independently of dynamics and external fields. In fact, it is clear that both g and k obey

$$
\frac{\partial^2 g}{\partial Q^2}+2\frac{\partial g}{\partial Q}=\frac{\partial^2 g}{\partial F^2}, \tag{44}
$$

the classical telegrapher's equation, wavelike at small "time" Q, diffusive at large Q.

The "stretched time" Q is also readily shown to satisfy

$$
\langle \Delta F(x(t))^2\rangle = Q+\frac{1}{2}(1-e^{-2Q})\to Q \quad \text{at large } Q, \tag{45}
$$

as in bare particle inertial dynamics, which is then the prototype for all. For a uniform system, where $\Delta F=n\Delta x$, (50) also tells us that $Q(t)$ can be identified as the collision number $Q(t)$ of (5). But what is Q in other dynamical cases, and can we explicitly validate the independence of x and y? This must be done separately for each dynamics. An artificial dynamics illustrates what is involved. It is deterministic, with no external field, but with a Hamiltonian

$$H = c|p| \tag{46}$$

So that $v = c\,\mathrm{sgn}\,p,\ \dot{p} = 0$. Hence $v = \pm c$, the equilibrium state is uniform of density n_0, and

$$\begin{aligned} n_0(x,t;y,0) &= \int \frac{1}{2} n_0 \delta(x-y-vt)\,dv \\ &= \frac{n_0}{2}(\delta(x-y-ct)+\delta(x-y+ct)), \end{aligned} \tag{47}$$

from which

$$Q_0(x,t;y,0) = n_0 Max(|x-y|, ct) \tag{48}$$

For small t, this is just $n_0|x-y|$, but in the region of interest $|x-y| \propto t^{\frac{1}{2}}$ so that $Q_0 = n_0 ct$ is independent of x and y. Further analyses [17] show that both in inertial dynamics and diffusion, this conclusion continues to hold. Note that if we specialize to uniform systems, then it is easily verified quite generally that from (40),

$$Q(t) = n_0 \langle |x(t) - x(0)| \rangle_0, \tag{49}$$

and so (7) is validated.

5 Brief Extension to Quasi 1-D

Let us again specialize to uniform systems. Suppose however instead of point cores, our particles have hard cores of diameter a. Insofar as the tagged particle is concerned, the only change is that the mean spacing between adjacent contacting faces has fallen from l to $l-a$, but collision occurs at precisely the same rate. Thus, (7) is modified to

$$\langle \Delta x(t)^2 \rangle = (l-a)\langle |\Delta x(t)| \rangle_0. \tag{50}$$

Recalling that in thermal equilibrium for a hard rod system at reciprocal temperature β, the 1-D equation of state is given by $\beta P = \frac{n}{(1-na)} = \frac{1}{(l-a)}$ [no matter what dimension, P is the mean force per unit boundary cross-section required], so that (50) can also be written

$$\langle \Delta x(t)^2 \rangle = \frac{1}{\beta P}\langle |\Delta x(t)| \rangle_0, \tag{51}$$

which one is tempted to generalize to any single-file fluid, with longitudinal coordinate x in a longitudinally invariant container. Although this is a very weak argument, it agrees reasonably well with a number of numerical simulations of single-file fluids. But (51) is hardly unique: we could equally well make the replacement $\frac{1}{(l-a)} \to (-\frac{\partial \beta P}{\partial l})^{\frac{1}{2}}$ which is also valid for hard rods. We should do better.

A general technique might go like this. We would really like to know the distribution of $\Delta x(t)$, and if we could ignore correlations between successive collisions, this would be related to the distribution $f(\xi)$ of the next neighbor longitudinal separation ξ. The strategy would then be to select K characteristics of $f(\xi)$, determine these parameters for a solvable model system with K parameters to match these, and use the asymptotic relation between $\langle \Delta x(t)^2 \rangle$ and $\langle |\Delta x(t)| \rangle_0$ of the model system to mimic the system under study. Prototypically, the solvable hard rod reference system has known $\langle \xi \rangle_{ref} = l$, $\langle \xi^2 \rangle_{ref} - \langle \xi \rangle_{ref}^2 = (l-a)^2$, which can be determined instead for the system of interest, and the two mapped into each other,

$$l = \langle \xi \rangle, \quad (l-a)^2 = \sigma^2(\xi). \tag{52}$$

The solvable Toda model [18] has 3 parameters and could be used similarly in the approximation in which particle passing can be neglected. Of course, finding even $\sigma^2(\xi)$ analytically for a given fluid is not trivial, and we might instead use the (uniform cross-section profile) approximation $l - a = (\frac{-\partial l}{\partial \beta P})^{\frac{1}{2}}$. If this is done, we would then have the prediction

$$\langle \Delta x(t)^2 \rangle = \left(\frac{-\partial l}{\partial \beta P} \right)^{\frac{1}{2}} \langle |\Delta x(t)^2| \rangle_0 \tag{53}$$

with P determined to produce the desired l. And even this improves the empirical (51).

References

1. Cao, D., Wu, J.: Langevin **20**, 3769 (2004)
2. Levitt, D.G.: Phys. Rev. A **8**, 3050 (1972)
3. Mon, K.K., Percus, J.K.: J. Chem. Phys. **112**, 3457 (2000)
4. Karger, J., Ruthven, D.M.: Diffusion in Zeolites and Other Microporous Solids. Wiley, New York (1992)
5. Finkelstein, A.: Water Movement through Lipid Bilayers, Pores, and Plasma Membranes. Wiley, New York (1987)
6. Zhou, H.X., Zwanzig, R.: J. Chem. Phys. **94**, 6147 (1991)
7. Darken, L.S.: Trans AIME **175**, 184 (1948)
8. Harris, T.E.: J. Appl. Prob. **2**, 323 (1965)
9. Jepsen, D.W.: J. Math. Phys. **6**, 405 (1965)
10. Marchesoni, F., Taloni, A.: Phys. Rev. Lett. **97**, 106101 (2006)
11. Percus, J.K.: Phys. Rev. A **9**, 557 (1974)
12. Mon, K.K., Percus, J.K., Yan, J.: Mol. Sim. **29**, 721 (2003)
13. Doi, M.: Introduction to Polymer Physics. Clarendon Press, Oxford (1996)
14. Lebowitz, J.L., Percus, J.K.: Phys. Rev. **155**, 122 (1967)
15. Gould, H.W.: Combinatorial Identities. Morgantown Printing and Binding, Morgantown (1972)
16. Lizana, L., Armbjornsson, T.: Phys. Rev. Lett. **109**, 200601 (2008)
17. Kalinay, P., Percus, J.K.: Phys. Rev. E **76**, 041111 (2007)
18. Percus, J.K.: In: Lebowitz, J.L. (ed.) Studies in Statistical Mechanics. North-Holland, Amsterdam (1982)