Anomalous transport and onset of diffusive behaviour in confined systems

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Outline

Local Thermodynamic Equilibrium, based on separation of scales

$$N \gg 1 \;, \qquad \ell \ll \delta L \ll L \;, \qquad \tau \ll \delta t \ll t$$

δL^3 contains thermodynamic system (P, V, T);
δt suffices for system in δL^3 to reach equilibrium.

Hydrodynamic laws are given; container shape does **NOT** matter (only boundary conditions).

Differently, in microporous media, walls play a significant role in determining transport law: inter-particle and particle-wall interactions equally likely.

- How does transition take place?
- What if it does not take place (e.g. in bio- nano-systems)?

Introduce Transport Exponent γ as: $\langle \mathbf{r}^2(t) \rangle \sim t^{2\nu}$

Inter-particle interactions have stronger influence on transition than defocussing particle-wall interactions: not bound to occur at fixed positions, efficiently break correlations.

Chaos neither sufficient nor necessary.

How does liner response need to be modified?

Given that

$$D_{ii} = \lim_{t\to\infty} \frac{\langle (x_i(t) - x_i(0))^2 \rangle}{2t} = \int_0^\infty C_{ii}(t)\, dt \;, \quad C_{ii}(t) = \langle v_i(t) v_i(0) \rangle$$

anomalous diffusion occurs if

- variance of velocity is not finite ($\langle v^2 \rangle = \infty$)
- correlations persist ($C_{ii}(t) \sim t^{-\beta}$, $\beta < 1$)

FDR relates mean velocity and position responses to an external perturbing force **F**, to the velocity autocorrelation:

$$\langle v(t) \rangle_{\mathbf{F}} \propto \int_0^t C_v(t') dt'$$

$$\langle x(t) \rangle_{\mathbf{F}} = \int_0^t \langle v(t') \rangle_{\mathbf{F}} \propto \int_0^t \int_0^t C_v(t' - t'') dt' dt'' = \langle x(t)^2 \rangle_0 \sim t^{2\nu}$$

Although the above argument is correct in the case of normally diffusing systems, in general it is not rigorous, and in the case of anomalous diffusion it easily leads to inconsistencies.

In some subdiffusive case, however, its conclusions have been theoretically, numerically and experimentally confirmed [MBK99,GSGWS96,VPV08].

Various works show that transient anomalous diffusion is often realized, even when asymptotically normal diffusion sets in. It is then to be seen whether the asymptotic regime is experimentally relevant.

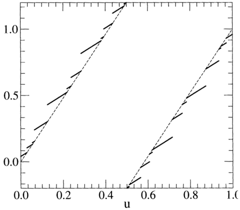
Many reports on fast diffusion, e.g. of water in carbon natubes.

Well known slow transport in *single-file diffusion*.

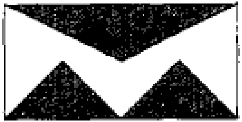
Let us invetsigate some simple model, to see how various transport regimes may be realized.

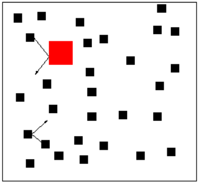
Studies concerning minimal requirements for $\langle \mathbf{r}^2(t) \rangle \sim t$.
In particular, non-chaotic systems:

quenched disorder



irrational angles ⇒ ergodicity(?)

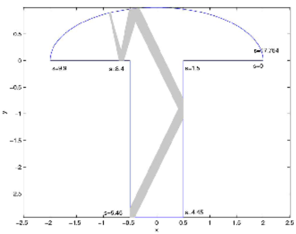




dynamical disorder

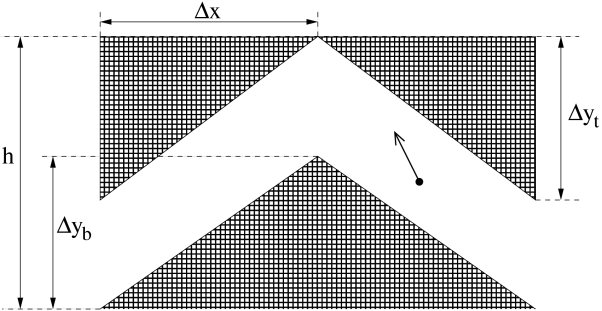
Alonso, Artuso, van Beijeren, Casati, Cohen, Dettmann, Klages, Larralde, Prosen, Sanders, Vulpiani, ...

Starting from non-interacting point particles
What happens when they become disks?
Bunimovich, Lansel, Porter for billiards with with regular, chaotic and mixed regular-chaotic pointlike particle dynamics.



Interacting particles:
some integrals of motion survive,
phase space subdivides in ergodic
components of positive measure.

Shape of container matters also for ergodic properties of interacting particles (also Swinney et al.)



If particles don't interact inside polygonal pores, consider them as point-like. Vanishing Lyapunov exp. slow correlation decays. Trajectories slowly separate.

Uniform phase space probability distribution is invariant, but system does not need to be ergodic.

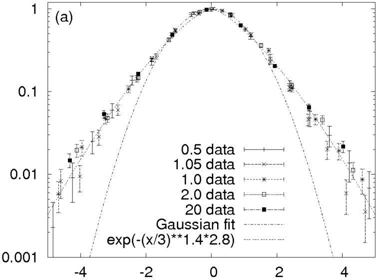
γ for parallel walls. 5000 particles, 10^7 collisions.

$\frac{\Delta y}{\Delta x}$	$h = \Delta y/2$	$h = \Delta y$	$h = 1.05\Delta y$	$h = 2\Delta y$	$h = 20\Delta y$
0.25	1.85	1.83	1.82	1.85	1.85
1	1.66	1.64	1.62	1.67	1.68
2	1.83	1.85	1.82	1.80	1.79
3	1.86	1.87	1.84	1.80	1.70

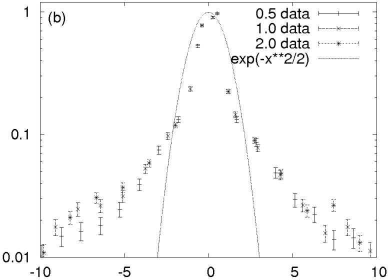
For $h \geq 2\Delta y$: infinite horizon.
Error estimated to ± 0.03. Clearly superdiffusive, not ballistic.
Note reduction of γ with h, for steepest walls.

1-flat wall: only longer transients, and even slightly smaller γ !

Total x-dispalcement after 10^6 collisions.

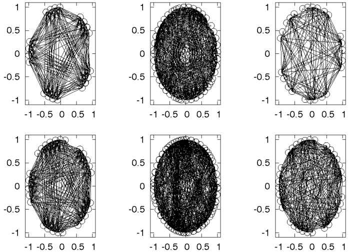


$\Delta y / \Delta x = 2$ i.e.
irrational polygon.
Gaussian only close to peak. Exponential tails.



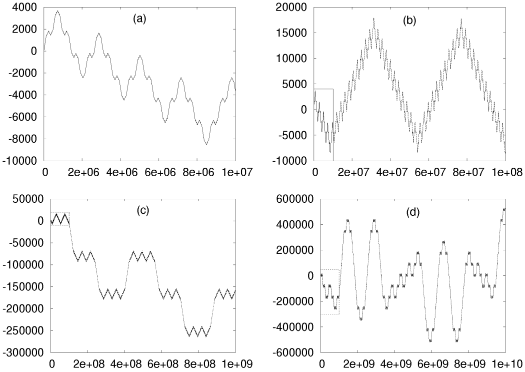
$\Delta y / \Delta x = 1$ i.e.
rational polygon.

Very slow decay of correlations.



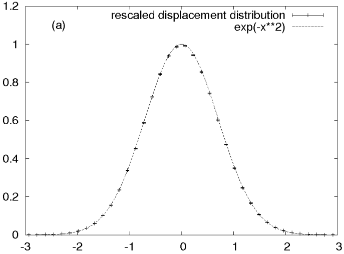
$\Delta y/\Delta x = 3$, pore height$= 2\Delta y$.
10^3 momenta,
sampled every 10^4 steps
6 different initial conditions.

Particle displacement
for $\Delta y/\Delta x = 1$, $d = 2\Delta y$.



Light gas in pore ~ 1 nm, room T, $v \sim 400m/s$, $\tau \sim 1ps$
$\Longrightarrow$ correlations over 1 μs and 1 mm.

Unparallel walls. Apparent diffusion.



$\Delta y_t / \Delta x = 0.62$,
$\Delta y_b / \Delta x = 0.65$,
i.e. irrational polygons,
10^6 time units ($10^6 - 10^7$ coll.),
10^4 initial conditions.

$\Delta y_t / \Delta x$	$\Delta y_b / \Delta x$	$0.5 \Delta y$	$1.0 \Delta y$	$1.05 \Delta y$	$2.0 \Delta y$	$20 \Delta y$
0.62	0.63	1.00(2)	1.02(2)	0.97(3)	1.03(7)	0.72(3)
0.62	0.64	1.00(1)	1.2(1)	1.03(3)	1.19(7)	1.10(5)
0.62	0.65	0.99(2)	1.02(2)	1.02(3)	0.97(6)	1.13(5)

Individual ≈ collective behaviour, excpet for rare apparently ballistic trajectories, which may affect collective behaviour.

$\Delta y_t/\Delta x$	$\Delta y_b/\Delta x$	γ	$\Delta y_t/\Delta x$	$\Delta y_b/\Delta x$	γ
1	1.01	0.71(4)	2	2.02	1.04(2)
1	1.001	0.35(6)	2	2.002	1.01(2)
1	1.0001	0.66(5)	2	2.0002	1.04(2)
1	1.00001	0.58(3)	2	2.00002	1.02(2)
1	1.000001	0.53(5)	2	2.000002	0.98(2)
1	1	1.66(3)	2	2	1.83(3)

Apparently, no trend towards super-diffusion, close to (rational or irrational) parallel cases, for fixed simulation times.
Sanders and Larralde show that the crossover time from normal to anomalous diverges as walls become parallel.

Macroscopically less predictable,
though microscopically more unstable than chaotic systems;
sensitive dependence of transport on geometry:
not just transport coefficient but transport law appears highly irregular.

Definition. Geometry determined by $y \in [0, h]$.
Transport law: $\lim_{t\to\infty} \langle s_x^2(t) \rangle / t^\gamma = A$.
$\Delta\gamma(y_m, y_M) =$ largest γ variation for $y \in (y_m, y_M) \subset [0, h]$.
Fix simulation time $t_{\max}$.

i. *Transport complexity of first kind in (y_m, y_M):*

$$\mathcal{C}_1(y_m, y_M) = \frac{h\Delta\gamma(y_m, y_M)}{2(y_M - y_m)}$$

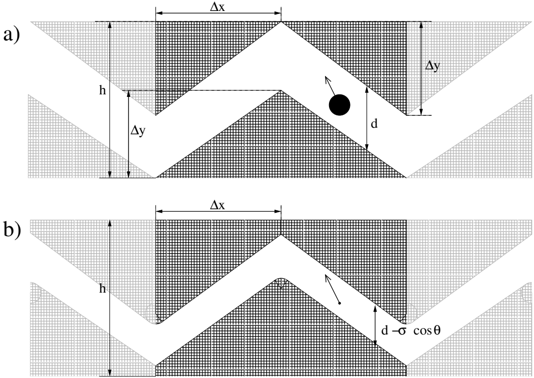
ii. *Transport complexity of second kind for $y = \hat{y}$: $\mathcal{C}_2(\hat{y})$ such that*

$$\lim_{\varepsilon\to 0} \frac{\mathcal{C}_1(\hat{y}-\varepsilon, \hat{y}+\varepsilon)}{\varepsilon^{\mathcal{C}_2(\hat{y})}} < \infty$$

iii. *Transport complexity of third kind for $y = \hat{y}$:*

$$\mathcal{C}_3(\hat{y}) = \lim_{\varepsilon\to 0} \Delta\gamma(\hat{y}-\varepsilon, \hat{y}+\varepsilon)$$

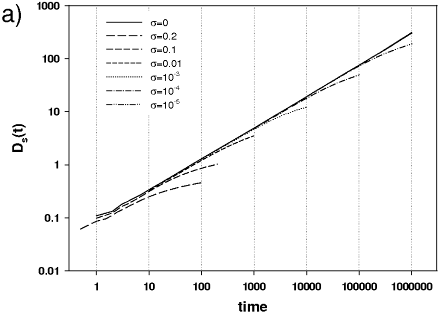
Anomalous point-like diffusion: $\Delta y/\Delta x = 1$ or 2. $\sigma =$ particle diameter.

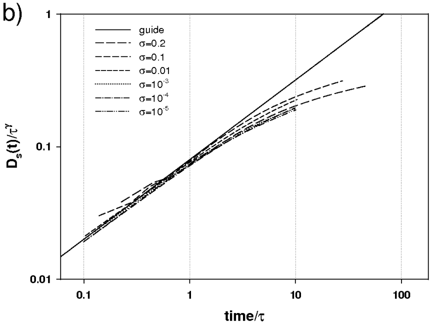


Semidispersive billiard with bumps ergodicity not known. Collisions with rounded corners and interactions may lead to positive Lyapunov exponents.

$$D_s(N;t) = \sum_{i=1}^{N} \int_0^t \frac{\langle \mathbf{v}_i(0)\mathbf{v}_i(s)\rangle}{2dN} ds \,, \quad D_0(N;t) = \sum_{i,j=1}^{N} \int_0^t \frac{\langle \mathbf{v}_i(0)\mathbf{v}_j(s)\rangle}{2dN} ds$$

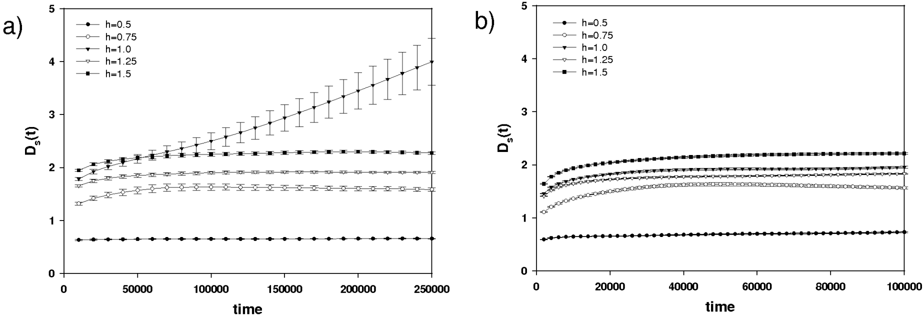
Let f_{apex} = apex collision frequency;
τ_{apex} = mean apex collision time.
Initially: point-like transport in pores of reduced heigh;
super-diffusive, γ determined by wall angle.
Slow departure to apparently diffusive behaviour [O(10) τ_{apex}].





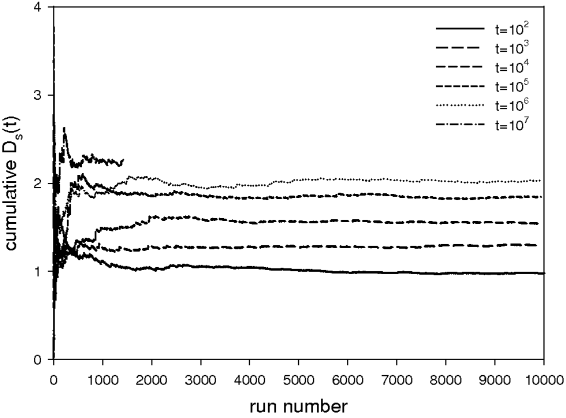
Departure points overlap if time rescaled by $t' = tf_{\text{apex}}$.

Convergence to diffusive behaviour not obvious. Even if departure from pointlike case occurs after 10 τ_{apex}, $10^3\tau_{\mathrm{apex}}$ and averaging over 10^5 initial conditions are not sufficient.



Do bursts due to very long very few ballistic trajectory segments affect asymptotic result?

Even removing the bursts, convergence is problematic:
convergence at fixed times is almost achieved,
but convergence at fixed ensemble size is not obvious:
D grows with t.



Defocussing collisions
do contribute to decay
of correlations,
but is it enough?
Larger particles,
i.e. shorter τ_{apex} help
(dispersive limit).

Interparticle collisions introduce further randomizing, decorrelating, mechanisms: defocussing collisions occur at random positions (hence impair the "bursts").

Departure from polygonal billiard phase takes place on the shortest time scale between $1/f_{\rm apex}$ and $1/f_{\rm coll}$. Convergence towards diffusion, now common, is determined by $f_{\rm coll}$.

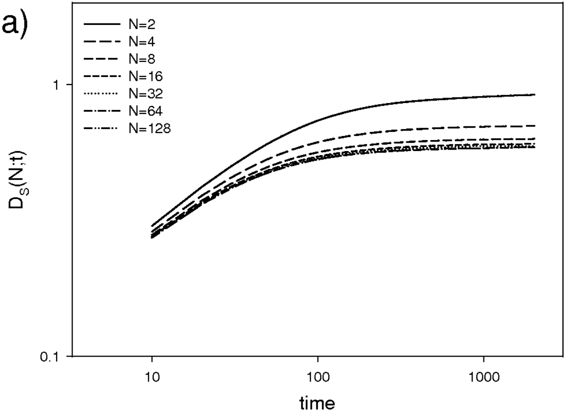
However, for $N \leq 10$, kinetic theory prediction

$$D_s^{(\text{2D-Enskog})} = \frac{1}{2n\sigma g(\nu)} \sqrt{\frac{kT}{\pi m}} \; ; \quad g(\nu) = \frac{1 - 7\nu}{16(1-\nu)^2} \; ; \quad \nu = \frac{\pi n \sigma^2}{4}$$

and even simply $1/n$ behaviour are not verified.

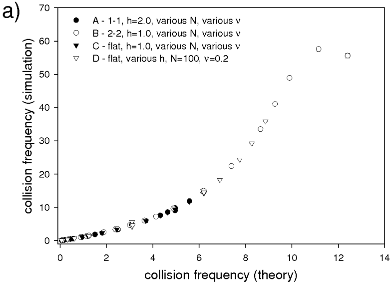
Convergence rather quick ($N \geq 16$):

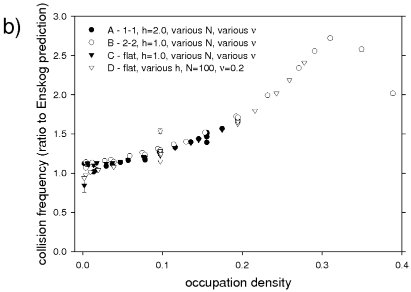
a)

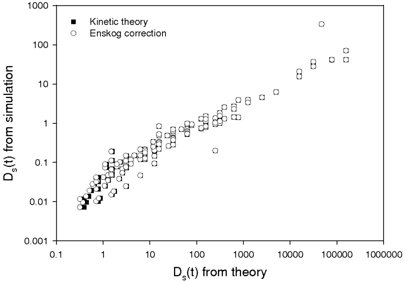


$D_s \neq D_0$ and
$D_s \to D_0$ as $\sigma \to 0$,
but $D_s \not\to D_0$ if $n \to 0$.
D_s closer to D_0
for large D.

Correlations of particles persist because of rare or ineffective (due to boundaries) mutual interactions.







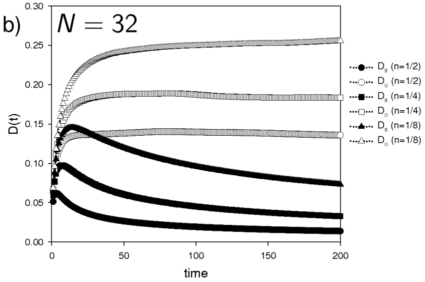
$$f_{\text{coll}}^{(2\text{D})} = 2n\sigma g(\nu)\sqrt{\frac{\pi k T}{m}}$$

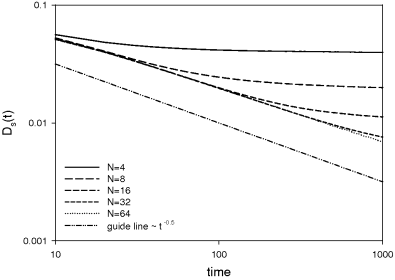
$g = 1$ in ideal case.

Frequency discrepancies independent of geometry: low density as from kinetic theory; high density $\ell \ll L$.

Theories overestimate D_s.

Single File Transport ($\sigma > d/2$, cannot overtake); some correlation persists (particles order); expected $\gamma = 1/2$, for $N \to \infty$.
Self diffusion surely affected, D_0 may be not.





Finite N, D_s only reduced, but $\gamma \to 1/2$ as $N \to \infty$; D_0 differs from corresponding point-like D_s values; single file D_s reached within $O(10^3)$, while 10^5 not enough for $N = 1$. Yet $f_{\text{apex}} \sim f_{\text{coll}}$.
Stable phenomenon due to low dimensionality.

- Point particles enjoy peculiar properties, but finite-sized particles behave similarly within given space and time scales. Can be diffusive (chaos not necessary).
- Single particle with $\sigma > 0$: **a)** initial point-like phase of duration $O(1/\sigma)$; **b)** asymptotic regime appears diffusive.
- $N \geq 2$: diffusion sets in even for $f_{\text{coll}} \ll f_{\text{apex}}$; randomness of interactions counts more than chaos for normal transport (faster correlations decay). $D \approx$ kinetic theory if $N \geq 16$, $\sigma \ll L$.
- Single file: self-sub-diffusive; collectively diffusive even for $f_{\text{coll}} \ll f_{\text{apex}}$, because of low dimensionality (chaos not sufficient).

Geometry effects and correlations lasting over scales comparable with medium size, interesting even if not asymptotic: e.g. relevance for nano- bio-sciences.