Onset of diffusive behaviour in confined transport systems

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Local Thermodynamic Equilibrium, based on separation of scales

\[ N \gg 1 , \quad \ell \ll \delta L \ll L , \quad \tau \ll \delta t \ll t \]

\( \delta L^3 \) contains thermodynamic system \((P, V, T)\);
\( \delta t \) suffices for system in \( \delta L^3 \) 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 $\gamma$ as: $\langle r^2(t) \rangle \sim t^\gamma$

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

- **quenched disorder**
- **irrational angles** $\implies$ **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 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.
\( \gamma \) for parallel walls. 5000 particles, \( 10^7 \) collisions.

<table>
<thead>
<tr>
<th>( \Delta y )</th>
<th>( h = \Delta y / 2 )</th>
<th>( h = \Delta y )</th>
<th>( h = 1.05\Delta y )</th>
<th>( h = 2\Delta y )</th>
<th>( h = 20\Delta y )</th>
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</thead>
<tbody>
<tr>
<td>0.25</td>
<td>1.85</td>
<td>1.83</td>
<td>1.82</td>
<td>1.85</td>
<td>1.85</td>
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<tr>
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<td>1.66</td>
<td>1.64</td>
<td>1.62</td>
<td>1.67</td>
<td>1.68</td>
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<tr>
<td>2</td>
<td>1.83</td>
<td>1.85</td>
<td>1.82</td>
<td>1.80</td>
<td>1.79</td>
</tr>
<tr>
<td>3</td>
<td>1.86</td>
<td>1.87</td>
<td>1.84</td>
<td>1.80</td>
<td>1.70</td>
</tr>
</tbody>
</table>

For \( h \geq 2\Delta y \): infinite horizon.

Error estimated to \( \pm 0.03 \). Clearly superdiffusive, not ballistic.

Note reduction of \( \gamma \) with \( h \), for steepest walls.

1-flat wall: only longer transients, and even slightly smaller \( \gamma \)!
Total $x$-displacement 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. 

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

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

Light gas in pore $\sim 1$ nm, room $T$, $v \sim 400 m/s$, $\tau \sim 1 ps$ $\Rightarrow$ correlations over $1 \mu s$ and $1$ mm.
The problem
Pointlike particles
Finite size particles
Conclusions

Parallel walls
Unparallel walls
Transport complexity

Unparallel walls.

Apparent diffusion.

\[ \Delta y_t / \Delta x = 0.62, \]
\[ \Delta y_b / \Delta x = 0.65, \]
i.e. irrational polygons,
10⁶ time units (10⁶ – 10⁷ coll.),
10⁴ initial conditions.

<table>
<thead>
<tr>
<th>(\Delta y_t / \Delta x)</th>
<th>(\Delta y_b / \Delta x)</th>
<th>0.5(\Delta y)</th>
<th>1.0(\Delta y)</th>
<th>1.05(\Delta y)</th>
<th>2.0(\Delta y)</th>
<th>20(\Delta y)</th>
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<tbody>
<tr>
<td>0.62</td>
<td>0.63</td>
<td>1.00(2)</td>
<td>1.02(2)</td>
<td>0.97(3)</td>
<td>1.03(7)</td>
<td>0.72(3)</td>
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<tr>
<td>0.62</td>
<td>0.64</td>
<td>1.00(1)</td>
<td>1.2(1)</td>
<td>1.03(3)</td>
<td>1.19(7)</td>
<td>1.10(5)</td>
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<tr>
<td>0.62</td>
<td>0.65</td>
<td>0.99(2)</td>
<td>1.02(2)</td>
<td>1.02(3)</td>
<td>0.97(6)</td>
<td>1.13(5)</td>
</tr>
</tbody>
</table>

Individual \(\approx\) collective behaviour, except for rare apparently ballistic trajectories, which may affect collective behaviour.
<table>
<thead>
<tr>
<th>$\Delta y_t/\Delta x$</th>
<th>$\Delta y_b/\Delta x$</th>
<th>$\gamma$</th>
<th>$\Delta y_t/\Delta x$</th>
<th>$\Delta y_b/\Delta x$</th>
<th>$\gamma$</th>
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<td>0.71(4)</td>
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<td>2.02</td>
<td>1.04(2)</td>
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<tr>
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<td>2</td>
<td>2.002</td>
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<tr>
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<td>0.58(3)</td>
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<td>1.02(2)</td>
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<td>1</td>
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<td>0.53(5)</td>
<td>2</td>
<td>2.000002</td>
<td>0.98(2)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.66(3)</td>
<td>2</td>
<td>2</td>
<td>1.83(3)</td>
</tr>
</tbody>
</table>

No trend toward super-diffusion, arbitrarily close to (rational or irrational) parallel cases.

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: $\lim_{t \to \infty} \left\langle s_x^2(t) \right\rangle / t^\gamma = A$. 
$\Delta \gamma(y_m, y_M) =$ largest $\gamma$ variation for $y \in (y_m, y_M) \subset [0, h]$.

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

$$C_1(y_m, y_M) = \frac{h \Delta \gamma(y_m, y_M)}{2(y_M - y_m)}$$

ii. **Transport complexity of second kind for** $y = \hat{y}$: $C_2(\hat{y})$ such that

$$\lim_{\varepsilon \to 0} \frac{C_1(\hat{y} - \varepsilon, \hat{y} + \varepsilon)}{\varepsilon C_2(\hat{y})} < \infty$$

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

$$C_3(\hat{y}) = \lim_{\varepsilon \to 0} \Delta \gamma(\hat{y} - \varepsilon, \hat{y} + \varepsilon)$$
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 $f_{\text{apex}} = \text{apex collision frequency};$
$\tau_{\text{apex}} = \text{mean apex collision time}.$
Initially: point-like transport in pores of reduced height;
super-diffusive, $\gamma$ determined by wall angle.
Slow departure to apparently diffusive behaviour $[O(10) \tau_{\text{apex}}].$

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 $10 \tau_{\text{apex}}, 10^3 \tau_{\text{apex}}$ 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 $\tau_{\text{apex}}$ 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 $1/f_{\text{apex}}$ and $1/f_{\text{coll}}$. Convergence towards diffusion, now common, is determined by $f_{\text{coll}}$.

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

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

and even simply $1/n$ behaviour are not verified.
Convergence rather quick ($N \geq 16$):

$$D_s \neq D_0 \text{ and } D_s \to D_0 \text{ as } \sigma \to 0,$$

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.
The problem
Pointlike particles
Finite size particles
Conclusions

Single particle
Multiparticle systems

\[ f^{(2D)}_{\text{coll}} = 2n \sigma g(\nu) \sqrt{\frac{\pi kT}{m}} \]

\[ g = 1 \text{ in ideal case.} \]

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

Theories overestimate \( D_s \).

Onset of diffusive behaviour
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.