Diffusion and velocity relaxation of a Brownian particle immersed in a viscous compressible fluid confined between two parallel plane walls

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Many processes in physical chemistry and biology are dominated by the process of **diffusion**.

In geometry on a small scale, i. e. membranes, thin liquid fims, pores, one has to worry about the influence of geometry on the diffusion coefficient.

Near a wall diffusion becomes anisotropic and one has to deal with a diffusion tensor $\overleftrightarrow{\mathbf{D}}(h)$ dependent on the distance h to the wall.

In bulk $D = \frac{kT}{\zeta}$ Einstein 1905

with friction coefficient $\zeta = 6\pi\eta a$ Stokes 1850

η shear viscosity a particle radius

Near a wall $\overleftrightarrow{\mathbf{D}}(h) = kT\overleftrightarrow{\mu}(h)$ with mobility tensor $\overleftrightarrow{\mu}(h) = \overleftrightarrow{\zeta}(h)^{-1}$

parallel xy-plane

$$\overleftrightarrow{\mu}(h) = \mu_{xx}(h)(\mathbf{e}_x\mathbf{e}_x + \mathbf{e}_y\mathbf{e}_y) + \mu_{zz}(h)\mathbf{e}_z\mathbf{e}_z$$

$\mu_{xx}(h) = \mu_0[1 - \frac{9}{16}\frac{a}{h}]$ $\mu_{zz}(h) = \mu_0[1 - \frac{9}{8}\frac{a}{h}]$ Lorentz 1907

$\mu_0 = \frac{1}{6\pi\eta a}$ Higher order correction terms first worked out by Faxén 1925

At present the mobilities $\mu_{xx}(h)$ and $\mu_{zz}(h)$ are known very precisely.

Similar results for a particle between two plane walls

$\mu_{xx}(h,L)$ and $\mu_{zz}(h,L)$

To first order in $\frac{a}{h}$

$\mu_{xx}(\frac{L}{2},L) = \mu_0[1 - 1.004\frac{a}{h}]$ Faxén 1925

$\mu_{zz}(\frac{L}{2},L) = \mu_0[1 - 1.452\frac{a}{h}]$ BUF 2005

So far we considered static diffusion tensor $\overleftrightarrow{\mathbf{D}}(h,L)$

For fast processes it may be necessary to generalize to a frequency-dependent tensor $\overleftrightarrow{\mathbf{D}}(h,L,\omega)$

Again there is an Einstein-type relation $\overleftrightarrow{\mathbf{D}}(h,L,\omega)=kT\overleftrightarrow{\mathbf{y}}(h,L,\omega)$

where $\overleftrightarrow{\mathbf{y}}(h,L,\omega)$ is the admittance tensor for the geometry h, L at frequency ω

For applied force $\mathbf{E}(t)=\operatorname{Re}\mathbf{E}_\omega e^{-i\omega t}$

the particle velocity is $\mathbf{U}(t)=\operatorname{Re}\mathbf{U}_\omega e^{-i\omega t}$

with

$$\mathbf{U}_\omega=\overleftrightarrow{\mathbf{y}}(h,L,\omega)\cdot\mathbf{E}_\omega$$

The diffusion process is related to velocity relaxation by

$$\overleftrightarrow{\mathbf{D}}(\omega)=\int_0^\infty e^{i\omega t}\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle dt$$

with velocity correlation function $\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle$

For $\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle=\left\langle\mathbf{v}(0)\mathbf{v}(0)\right\rangle e^{-\zeta t/m_p}$ with $\left\langle\mathbf{v}(0)\mathbf{v}(0)\right\rangle=\frac{kT}{m_p}\mathbf{1}$

this gives the Einstein relation $D(0)=\frac{kT}{\zeta}$

t

More generally $D(\omega)=\frac{kT}{-i\omega m_p+\zeta(\omega)}$

Corresponding to admittance $\mathsf{y}_t(\omega)=\frac{kT}{-i\omega m_p+\zeta(\omega)}$

In confined geometry $\overleftrightarrow{\mathbf{D}}(\omega)=kT\overleftrightarrow{\mathbf{y}}(\omega)$

$$\overleftrightarrow{\mathbf{y}}(\omega)=\frac{1}{kT}\int_0^\infty e^{i\omega t}\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle dt$$ fluctuation-dissipation theorem

By inverse Fourier transform

$$\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle=\frac{kT}{2\pi}\int_{-\infty}^{\infty}\overleftrightarrow{\mathbf{y}}(\omega)e^{-i\omega t}d\omega$$

$t>0$

This may be used to calculate $\left\langle\mathbf{v}(t)\mathbf{v}(0)\right\rangle$ in confined geometry.

At high frequency $\overset{\leftrightarrow}{\mathbf{y}}(\omega) \approx \frac{1}{-i\omega m_p}\mathbf{1}$ as $\omega \to \infty$

The behavior at low frequency is of particular interest,
since it is related to the long-time behavior. This is affected by the geometry.

Alder and Wainwright found 1970 in computer simulation

$$\langle \mathbf{v}(t)\mathbf{v}(0) \rangle \square\, t^{-3/2} \qquad \text{as} \qquad t \to \infty$$

This was first understood from kinetic theory, later from hydrodynamics.

The admittance of a sphere in an incompressible fluid
behaves at low frequency as

$$\mathrm{y}_t(\omega) = \frac{1}{6\pi\eta a}\left[1 + \alpha a + O(\alpha^2)\right] \qquad \alpha = \sqrt{\frac{-i\omega\rho}{\eta}}$$

This yields by Tauberian theorem

$$\langle \mathbf{v}(t)\mathbf{v}(0) \rangle \approx kT\mathbf{1}\frac{1}{12\pi\rho(\pi\nu)^{3/2}}t^{-3/2} \qquad \text{as} \qquad t \to \infty$$

$\nu = \frac{\eta}{\rho}$ kinematic viscosity

Quite generally for $\hat{f}(\omega) = \int_0^\infty e^{i\omega t} f(t)\,dt$

Tauberian theorem small ω behavior of $\hat{f}(\omega)$ ⟺ large t behavior of $f(t)$

conversely large ω behavior of $\hat{f}(\omega)$ ⟺ small t behavior of $f(t)$

The converse theorem has also played a role in physics.
Following earlier remarks by Lorentz, and work by H. Weyl,
there is a famous paper by Mark Kac

„Can one hear the shape of a drum?“

CAN ONE HEAR THE SHAPE OF A DRUM?

MARK KAC, The Rockefeller University, New York

To George Eugene Uhlenbeck on the occasion of his sixty-fifth birthday

> "La Physique ne nous donne pas seulement l'occasion de résoudre des problèmes . . . , elle nous fait presentir la solution." H. POINCARÉ.

Before I explain the title and introduce the theme of the lecture I should like to state that my presentation will be more in the nature of a leisurely excursion than of an organized tour. It will not be my purpose to reach a specified destination at a scheduled time. Rather I should like to allow myself on many occasions the luxury of stopping and looking around. So much effort is being spent on streamlining mathematics and in rendering it more efficient, that a solitary transgression against the trend could perhaps be forgiven.

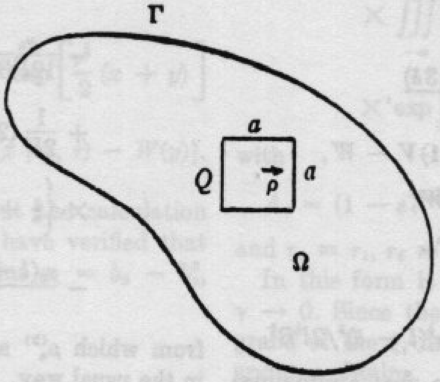


FIG. 1

1. And now to the theme and the title.

It has been known for well over a century that if a membrane Ω, held fixed along its boundary Γ (see Fig. 1), is set in motion its displacement (in the direction perpendicular to its original plane)

$$F(x, y; t) \equiv F(\vec{\rho}; t)$$

obeys the wave equation

$$\frac{\partial^2 F}{\partial t^2} = c^2 \nabla^2 F,$$

where c is a certain constant depending on the physical properties of the membrane and on the tension under which the membrane is held.

I shall choose units to make $c^2 = \frac{1}{2}$.

In his paper Kac actually reduces the acoustic problem to a diffusion problem:

Consider the conditional probability of finding a particle at **r** at time t when it starts out at **0** at time 0

$$P(\mathbf{r},t\,|\,\mathbf{0},0)$$

P behaves like particle density and therefore satisfies $\frac{\partial P}{\partial t} = D\nabla^2 P$

The fundamental solution is $P(\mathbf{r},t\,|\,\mathbf{0},0) = \frac{1}{(4\pi Dt)^{3/2}}\exp[\frac{-r^2}{4Dt}]$

Mean square displacement $\langle r^2 \rangle = \int r^2 P(\mathbf{r},t\,|\,\mathbf{0},0)\,d\mathbf{r} \quad = 6Dt$

i.e. size of probability cloud grows as $\sqrt{t}$

Kac considered $P(\mathbf{0},t\,|\,\mathbf{0},0) = \frac{1}{(4\pi Dt)^{3/2}} \qquad t > 0$

Write this as integral of decaying exponentials

$$\int_0^\infty g(\lambda)\exp[-\lambda t]d\lambda = \frac{1}{(4\pi Dt)^{3/2}}$$

then $g(\lambda) = \frac{1}{(4\pi D)^{3/2}}\frac{\sqrt{\lambda}}{\Gamma(3/2)} \qquad \Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$

in agreement with Tauberian theorem $\frac{\sqrt{\lambda}}{\Gamma(3/2)} \Longleftrightarrow \frac{1}{t^{3/2}}$

large λ small t

small λ large t

In this case both types of behavior are realized at the same time.

Similarly in a viscous incompressible fluid $\mathbf{v}(\mathbf{r},t)$ satisfies the linearized Navier-Stokes equation

$$\rho\frac{\partial\mathbf{v}}{\partial t}=\eta\nabla^2\mathbf{v}-\nabla p \qquad \nabla\cdot\mathbf{v}=0$$

For δ- impulse at t=0 $$\rho\frac{\partial\mathbf{v}}{\partial t}-\eta\nabla^2\mathbf{v}+\nabla p=\mathbf{P}\delta(\mathbf{r})\delta(t)$$

fundamental solution $$\mathbf{v}(\mathbf{r},t)=\frac{1}{4\pi\eta}\mathbf{T}(\mathbf{r},t)\cdot\mathbf{P} \qquad t>0$$

At the origin $$\mathbf{v}(\mathbf{0},t)=\frac{1}{4\pi\eta}\frac{1}{3\sqrt{\pi\nu}}t^{-3/2}\mathbf{P}$$ all t

$$=\frac{1}{12\rho(\pi\nu)^{3/2}}t^{-3/2}\mathbf{P}$$

corresponds precisely to the long-time behavior of Brownian particle found from $\sqrt{\omega}$ term in $\Upsilon_t(\omega)$

This shows that the velocity correlation function of a Brownian particle is closely related to the Green function of the hydrodynamic equations of motion.
But the Green function depends on geometry.
One can expect that in particular the long-time behavior is strongly dependent on geometry.

Gotoh and Kaneda (1982) found that in the presence of a single plane wall the long-time behavior is

$$\langle v_x(t)v_x(0)\rangle \square\, t^{-5/2} \qquad \langle v_z(t)v_z(0)\rangle \square\, t^{-7/2}$$

I found (2005) that the latter result is incorrect. Both correlation functions behave as

$$C_{xx}(t)\approx A_{xx}t^{-5/2} \qquad C_{zz}(t)\approx A_{zz}t^{-5/2}$$

with coefficients A_{xx} A_{zz}

The second coefficient may be <0, depending on particle mass.

Velocity correlation function for a fluid with a single wall
was studied in computer simulation by Pagonabarraga, Hagen, Lowe,
Frenkel 1998

It turned out that fluid compressibility has a significant effect.

In bulk compressible fluid one can calculate the velocity correlation function again from the admittance $\mathsf{Y}_t(\omega)$

Result:

$$\langle v_x(t)v_x(0)\rangle \approx \frac{kT}{12\pi\rho(\pi\nu)^{3/2}}t^{-3/2} + At^{-5/2}$$

with a coefficient A that is negative if the fluid is sufficiently compressible, i.e. the decay is not monotonic, but can change sign

BUF, JChemPhys 2005

$$\mathsf{Y}_t(\omega) = \frac{1}{-i\omega m_p + \zeta(\omega)}$$

with a complicated expression for the friction coefficient

Zwanzig, Bixon 1970
Bedeaux, Mazur 1974
Metiu et al. 1977

$\zeta(\omega)$ depends on shear viscosity, bulk viscosity, density, compressibility

Again a wall causes modification of the behavior, but I found that the coefficients A_{xx} and A_{zz} of the $t^{-5/2}$ long-time behavior are independent of compressibility, BUF 2005
(limit to bulk behavior not simple)

For a fluid confined between two walls Pagonabarraga et al. found a dramatic change of behavior (1997,1998)

$$C_{xx}(t) = \langle v_x(t)v_x(0)\rangle \approx At^{-2} \qquad \text{with} \qquad A<0$$

no details were shown

They made more elaborate analysis in 2D: fluid between two lines. In that case

$$C_{xx}(t) = \langle v_x(t)v_x(0)\rangle \approx At^{-3/2} \qquad \text{with} \qquad A<0$$

They gave expression for A.

Recently I have calculated the coefficient A of the $t^{-3/2}$ long-time tail in 3D. Result:

$$C_{xx}(t) = \langle v_x(t) v_x(0) \rangle \approx -\frac{9}{2\pi}\frac{h^2(L-h)^2}{L^5}\frac{kT}{\rho c_0^2 t^2}$$

c_0 is the adiabatic (long-wave) sound velocity

Note the result is independent of viscosity.

Again the behavior follows from a Tauberian theorem.

The admittance tensor in any geometry can be expressed as

$$\overleftrightarrow{\mathbf{y}}(\mathbf{r}_0,\omega) = \mathrm{y}_t(\omega)\left[1 + A(\omega)C(\omega)\overleftrightarrow{\mathbf{F}}_a(\mathbf{r}_0,\omega)\right]$$

bulk

Faxén type coefficents calculated
by Bedeaux, Mazur 1974

$\overleftrightarrow{\mathbf{F}}_a(\mathbf{r}_0,\omega)$ is the reaction field tensor, depends on geometry.

In point approximation $\overleftrightarrow{\mathbf{F}}(\mathbf{r}_0,\omega) = \lim_{\mathbf{r}\to\mathbf{r}_0}[\mathbf{G}(\mathbf{r},\mathbf{r}_0) - \mathbf{G}_0(\mathbf{r}-\mathbf{r}_0)]$

Bulk Green function $\mathbf{G}_0(\mathbf{r}-\mathbf{r}_0,\omega)$ is known.

I have calculated $\mathbf{G}(\mathbf{r},\mathbf{r}_0,\omega)$ for compressible viscous fluid between two planes.

At $\omega = 0$ this gives results mentioned earlier:

$$\mu_{xx}(0) = \mu_0[1 + 6\pi\eta a F_{xx}(0)] \qquad \mu_{zz}(0) = \mu_0[1 + 6\pi\eta a F_{zz}(0)]$$

$\mu_{xx}(h,L) = \frac{1}{6\pi\eta a}[1 - 1.004\frac{a}{h}]$ at $h = L/2$ Faxén 1925

$\mu_{zz}(h,L) = \frac{1}{6\pi\eta a}[1 - 1.452\frac{a}{h}]$ at $h = L/2$ BUF 2005

Tauberian theorem is applied to the low frequency behavior

$$F_{xx}(h,L,\omega)=\frac{1}{4\pi\eta h}\left[X_0+\frac{2}{3}\alpha h-36\xi^2\frac{h^2(L-h)^2}{L^5}\alpha^2 h\ln\alpha+O(\alpha^2)\right]$$

$$\alpha=\sqrt{\frac{-i\omega\rho}{\eta}}$$

Here X_0 is given by a complicated integral over wavenumber q, coming from Fourier expansion in the xy-plane.
This gives the steady-state results.

The next term $\frac{2}{3}\alpha h$ leads to cancellation of the bulk $t^{-3/2}$ tail.

The mathematical origin of this term is already quite subtle.
Usually the term linear in $\sqrt{\omega}$ comes from an integral over wavenumber of the form

$$f(\alpha)=\int_0^\infty e^{-gq^2}\frac{q^2}{q^2+\alpha^2}dq$$

cutoff for large q

diffusion pole

$$f(\alpha)=\frac{1}{2}\sqrt{\frac{\pi}{g}}-\frac{\pi}{2}\alpha\exp[g\alpha^2]erfc[\sqrt{g}\alpha]$$

Expansion in powers of α yields

$$f(\alpha)=\frac{1}{2}\sqrt{\frac{\pi}{g}}-\frac{\pi}{2}\alpha+O(\alpha^2)$$

independent of the cutoff, such a term gives rise to the bulk $t^{-3/2}$ tail.

Instead the term $\frac{2}{3}\alpha h$ comes from a branch cut in the complex q-plane, rather than a simple pole.

In the last term $\xi=\frac{\eta}{\rho c_0}=\frac{\nu}{c_0}$ is the acoustic damping length.

The $\alpha^2\ln\alpha$ singularity comes from an acoustic diffusion pole (overdamped sound wave), but with weight q rather than q^2

The corresponding diffusion coefficient is $D = \dfrac{c_0^2 L^2}{12\nu}$

The xx element of the reaction field tensor can be expressed as

$$F_{xx}(h,L,\omega) = \frac{1}{4\pi\eta}\int_0^\infty f_x(q,\omega)q\,dq$$

The function $f_x(q,\omega)$ behaves for small q and ω as

$$f_x(q,\omega) \approx \frac{q\sqrt{q^2+\alpha^2} - q^2 - 2\alpha^2}{2\alpha^2\sqrt{q^2+\alpha^2}} + \frac{h^2(L-h)^2}{L^3}\,\frac{36\alpha^2\xi^2}{q^2L^2 + 12\alpha^2\xi^2}$$

branch cut same as for single wall

diffusion pole

In the pole term we use the integral

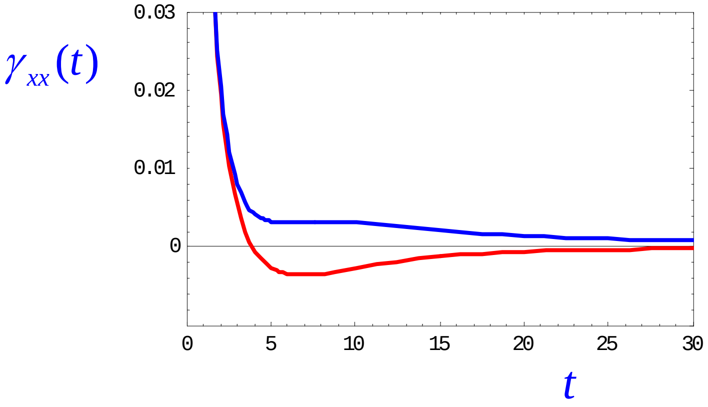
$$\int_0^\infty \frac{q}{q^2+\alpha^2}\exp[-gq^2]\,dq = \frac{1}{2}e^{g\alpha^2}E_1(g\alpha^2)$$

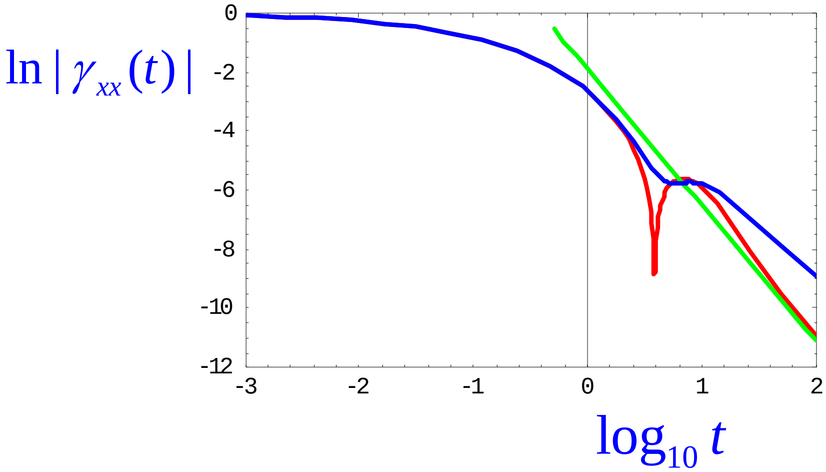
Expansion yields the $\alpha^2 \ln\alpha$ term, and this gives the t^{-2} tail.

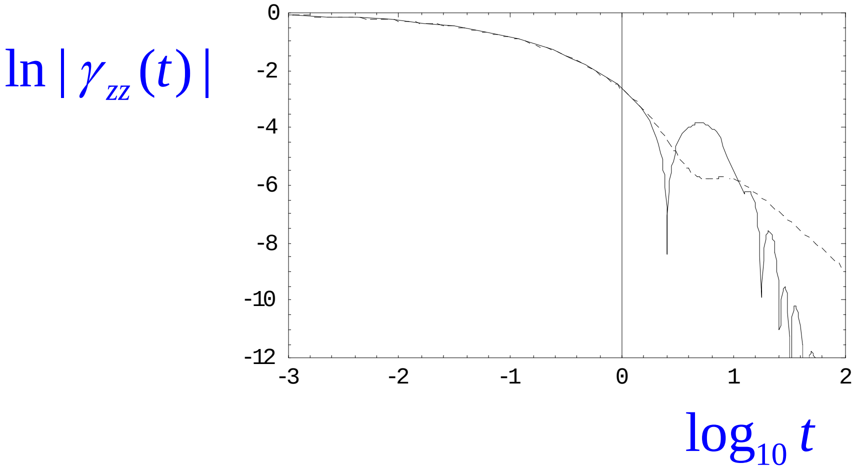
Define relaxation functions $\gamma_{xx}(t)$ and $\gamma_{zz}(t)$ from

$$C_{xx}(t) = \frac{kT}{m_p}\gamma_{xx}(t) \qquad C_{zz}(t) = \frac{kT}{m_p}\gamma_{zz}(t)$$

$$\gamma_{xx}(0) = 1 \qquad \gamma_{zz}(0) = 1$$




ln | $\gamma_{xx}(t)$ |
0
-2
-4
-6
-8
-10
-12
-3
-2
-1
0
1
2
$\log_{10} t$


ln | $\gamma_{zz}(t)$ |
0
-2
-4
-6
-8
-10
-12
-3
-2
-1
0
1
2
$\log_{10} t$