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 films, 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 $\tilde{D}(h)$ 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

$\eta$ shear viscosity $a$ particle radius

Near a wall $\tilde{D}(h) = kT \tilde{\mu}(h)$ with mobility tensor $\tilde{\mu}(h) = \tilde{\zeta}(h)^{-1}$ parallel xy-plane

$$\tilde{\mu}(h) = \mu_{xx}(h)(e_x e_x + e_y e_y) + \mu_{zz}(h)e_z e_z$$

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

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

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 $\tilde{D}(h, L)$

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

Again there is an Einstein-type relation

$$\tilde{D}(h, L, \omega) = kT\tilde{y}(h, L, \omega)$$

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

For applied force

$$E(t) = \text{Re} \ E_\omega e^{-i\omega t}$$

$$U(t) = \text{Re} \ U_\omega e^{-i\omega t}$$

the particle velocity is with

$$U_\omega = \tilde{y}(h, L, \omega) \cdot E_\omega$$

The diffusion process is related to velocity relaxation by

$$\tilde{D}(\omega) = \int_0^\infty e^{i\omega t} \left< v(t) v(0) \right> dt$$

with velocity correlation function $\left< v(t) v(0) \right>$

For $\left< v(t) v(0) \right> = \left< v(0) v(0) \right> e^{-\zeta t/m_p}$ with $\left< v(0) v(0) \right> = \frac{kT}{m_p}$

this gives the Einstein relation

$$D(0) = \frac{kT}{\zeta}$$

More generally

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

Corresponding to admittance

$$\gamma_i(\omega) = \frac{kT}{-i\omega m_p + \zeta(\omega)}$$

In confined geometry

$$\tilde{D}(\omega) = kT\tilde{y}(\omega)$$

$$\tilde{y}(\omega) = \frac{1}{kT} \int_0^\infty e^{i\omega t} \left< v(t) v(0) \right> dt$$

fluctuation-dissipation theorem

By inverse Fourier transform

$$\left< v(t) v(0) \right> = \frac{kT}{2\pi} \int_{-\infty}^\infty \tilde{y}(\omega) e^{-i\omega t} d\omega$$

$t > 0$

This may be used to calculate $\left< v(t) v(0) \right>$ in confined geometry.
At high frequency \( \ddot{y}(\omega) \approx \frac{1}{-i\omega m_p} \) 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
\[
\langle \mathbf{v}(t)\mathbf{v}(0) \rangle \propto t^{-3/2} \quad \text{as} \quad t \to \infty
\]

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

The admittance of a sphere in an incompressible fluid behaves at low frequency as
\[
y_t(\omega) = \frac{1}{6\pi\eta a} \left[ 1 + \alpha a + O(\alpha^2) \right] \quad \alpha = \sqrt{\frac{-i\omega \rho}{\eta}}
\]

This yields by Tauberian theorem
\[
\langle \mathbf{v}(t)\mathbf{v}(0) \rangle \approx kT \frac{1}{12\pi \rho (\pi \nu)^{3/2}} t^{-3/2} \quad \text{as} \quad t \to \infty
\]

\( \nu = \frac{\eta}{\rho} \) kinematic viscosity

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

Tauberian theorem

small \( \omega \) behavior \( \leftrightarrow \) large \( t \) behavior

of \( \hat{f}(\omega) \)

conversely

large \( \omega \) behavior \( \leftrightarrow \) small \( t \) behavior

of \( \hat{f}(\omega) \)

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?“
1. And now to the theme and the title.
It has been known for well over a century that if a membrane $\Omega$, held fixed along its boundary $\Gamma$ (see Fig. 1), is set in motion its displacement (in the direction perpendicular to its original plane)

$$F(x, y; t) = F(\vec{r}; t)$$

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 $c^2 = \frac{1}{4}$. 

1
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 \( 0 \)

\[ P(r, t \mid 0, 0) \]

\( P \) behaves like particle density and therefore satisfies

\[ \frac{\partial P}{\partial t} = D \nabla^2 P \]

The fundamental solution is

\[ P(r, t \mid 0, 0) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left[-\frac{r^2}{4Dt}\right] \]

Mean square displacement

\[ \langle r^2 \rangle = \int r^2 P(r, t \mid 0, 0) \, dr = 6Dt \]

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

Kac considered

\[ P(0, t \mid 0, 0) = \frac{1}{(4\pi Dt)^{3/2}} \quad t > 0 \]

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

\[ g(\lambda) = \frac{1}{(4\pi D)^{3/2}} \frac{\sqrt{\lambda}}{\Gamma(3/2)} \quad \Gamma(3/2) = \frac{1}{2}\sqrt{\pi} \]

in agreement with Tauberian theorem

\[ \frac{\sqrt{\lambda}}{\Gamma(3/2)} \quad \leftrightarrow \quad \frac{1}{t^{3/2}} \]

large \( \lambda \) small \( t \)

small \( \lambda \) 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

\[
\rho \frac{\partial \mathbf{v}}{\partial t} = \eta \nabla^2 \mathbf{v} - \nabla p \quad \quad \nabla \cdot \mathbf{v} = 0
\]

For \( \delta \)- 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

\[
\mathbf{v}(\mathbf{r}, t) = \frac{1}{4\pi \eta} \mathbf{T}(\mathbf{r}, t) \cdot \mathbf{P} \quad t > 0
\]

At the origin

\[
\mathbf{v}(0, t) = \frac{1}{4\pi \eta} \frac{1}{3\sqrt{\pi \nu}} t^{-3/2} \mathbf{P}
\]

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

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

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

\[
\left\langle v_x(t)v_x(0) \right\rangle \propto t^{-5/2} \quad \quad \left\langle v_z(t)v_z(0) \right\rangle \propto t^{-7/2}
\]

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

\[
C_{xx}(t) \approx A_{xx} t^{-5/2} \quad \quad C_{zz}(t) \approx A_{zz} t^{-5/2}
\]

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 $\mathcal{Y}_t(\omega)$

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

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

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)

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

no details were shown

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

In that case

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

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

$$\tilde{y}(r_0, \omega) = \mathbf{y}_i(\omega) \left[ 1 + A(\omega)C(\omega)\tilde{F}_a(r_0, \omega) \right]$$

bulk Faxén type coefficients calculated by Bedeaux, Mazur 1974

$\tilde{F}_a(r_0, \omega)$ is the reaction field tensor, depends on geometry.

In point approximation

$$\tilde{F}(r_0, \omega) = \lim_{r \to r_0} [\mathbf{G}(r, r_0) - \mathbf{G}_0(r - r_0)]$$

Bulk Green function $\mathbf{G}_0(r - r_0, \omega)$ is known.

I have calculated $\mathbf{G}(r, r_0, \omega)$ for compressible viscous fluid between two planes.

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

$$\mu_{xx}(0) = \mu_0[1 + 6\pi\eta a \mathcal{F}_{xx}(0)] \quad \mu_{zz}(0) = \mu_0[1 + 6\pi\eta a \mathcal{F}_{zz}(0)]$$

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

Faxén 1925

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

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

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

Expansion in powers of \( \alpha \) yields

\[ f(\alpha) = \frac{1}{2} \sqrt{\frac{\pi}{g}} \left( -\frac{\pi}{2} \alpha + O(\alpha^2) \right. \]

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

\[ D = \frac{c_0 L^2}{12 \nu} \]

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 \( \omega \) as

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

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

\[ C_{xx}(t) = \frac{kT}{m_p} \gamma_{xx}(t) \quad \gamma_{xx}(0) = 1 \]

\[ C_{zz}(t) = \frac{kT}{m_p} \gamma_{zz}(t) \quad \gamma_{zz}(0) = 1 \]