S10.G.3. Velocity Autocorrelation Function

Mathematica code for the graphics in this section can be found in file "graph.nb".

Taking the inverse Fourier transform of (10.372) gives

$$\begin{aligned}\boldsymbol{F}(t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t}\, 6\pi\eta\, \boldsymbol{u}_\omega R\left(1 - i k R - \frac{k^2 R^2}{9}\right) \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t}\, 6\pi\eta \int_{-\infty}^{\infty} dt'\, e^{i\omega t'}\, \boldsymbol{u}(t')\, R\left(1 - i k R - \frac{k^2 R^2}{9}\right) \\ &= \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')}\, 6\pi\eta R\left(1 - i k R - \frac{k^2 R^2}{9}\right) \boldsymbol{u}(t') \\ &= \int_{-\infty}^{\infty} dt'\, \alpha(t-t')\, \boldsymbol{u}(t')\end{aligned}$$

(10.373a)

where

$$\begin{aligned}\alpha(t-t') &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')}\, 6\pi\eta R\left(1 - i k R - \frac{k^2 R^2}{9}\right) \\ &\equiv \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')}\, \tilde{\alpha}(\omega)\end{aligned}$$

(10.373b)

$$\rightarrow \qquad \tilde{\alpha}(\omega) = 6\pi\eta R\left(1 - i k R - \frac{k^2 R^2}{9}\right)$$

(10.374)

Since it takes $\boldsymbol{F}(t)$ to drag the particle into moving with $\boldsymbol{u}(t)$, the fluid must be exerting a friction force $\boldsymbol{F}(t)$ on the particle. The corresponding Langevin equation is therefore [see §5.E.1]

$$m \frac{d\,\boldsymbol{u}(t)}{dt} = -\int_{-\infty}^{\infty} dt'\, \alpha(t-t')\, \boldsymbol{u}(t') + \boldsymbol{F}_{\text{rand}}(t)$$

(10.373)

where

$$\langle \boldsymbol{F}_{\text{rand}}(t) \rangle_{\boldsymbol{F}} = 0$$

with

$\langle \ldots \rangle_{\boldsymbol{F}}$ = average over the probability distribution of the stochastic variable $\boldsymbol{F}_{\text{rand}}(t)$.

(10.373a) describe a force with memory. Causality then demands

$$\boldsymbol{F}(t) = \int_{-\infty}^{t} dt'\, \alpha(t-t')\, \boldsymbol{u}(t')$$

(10.374b)

so that

$$\alpha(t) = 0 \qquad \forall\ t < 0$$

Also, owing to the memory effect, $\boldsymbol{F}_{\text{rand}}(t)$ is not a white noise [see (5.78)], i.e.,

$$\langle \boldsymbol{F}_{\text{rand}}(t)\, \boldsymbol{F}_{\text{rand}}(t') \rangle_F \neq g\, \delta(t-t')$$

Now,

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t} \int_{-\infty}^{\infty} dt'\, \alpha(t-t')\, \boldsymbol{u}(t')$$

$$= \int_{-\infty}^{\infty} d\,t\, e^{i\,\omega\,t} \int_{-\infty}^{\infty} d\,t' \int_{-\infty}^{\infty} \frac{d\,\omega'}{2\,\pi}\, e^{-i\,\omega'\,(t-t')}\, \tilde{\alpha}\,(\omega)\, \boldsymbol{u}(t')$$ [(10.373b) used.]

$$= \int_{-\infty}^{\infty} d\,t\, e^{i\,\omega\,t} \int_{-\infty}^{\infty} \frac{d\,\omega'}{2\,\pi}\, e^{-i\,\omega'\,t}\, \tilde{\alpha}(\omega)\, \tilde{\boldsymbol{u}}\,(\omega')$$

$$= \int_{-\infty}^{\infty} d\,\omega'\, \delta(\omega - \omega')\, \tilde{\alpha}(\omega)\, \tilde{\boldsymbol{u}}(\omega')$$

$$= \tilde{\alpha}(\omega)\, \tilde{\boldsymbol{u}}(\omega)$$

so that the Fourier transform of (10.373) gives

$$-i\,m\,\omega\,\tilde{u}(\omega) + \tilde{\alpha}(\omega)\,\tilde{\boldsymbol{u}}(\omega) = \tilde{\boldsymbol{F}}_{\text{rand}}(\omega)$$

Using (10.374), we have

$$-i\,m\,\omega\,\tilde{u}(\omega) + 6\,\pi\,\eta\,R\left(1 - i\,k\,R - \frac{k^2\,R^2}{9}\right)\tilde{\boldsymbol{u}}(\omega) = \tilde{\boldsymbol{F}}_{\text{rand}}(\omega) \qquad (10.375a)$$

Setting

$$\zeta = 6\,\pi\,\eta\,R$$

(10.375b)

$$M = \frac{4}{3}\,\pi\,\rho_0\,R^3 = \text{mass of fluid displaced by the Brownian particle} \qquad (10.375c)$$

$$\rightarrow \qquad \frac{M}{\zeta} = \frac{2\,\rho_0\,R^2}{9\,\eta} = \frac{2}{9}\,\Delta^2 \qquad \text{where} \qquad \Delta = \sqrt{\frac{\rho_0\,R^2}{\eta}}$$

(10.375d)

we have [see (10.360b)]

$$k\,R = \sqrt{\frac{\omega\,\rho_0\,R^2}{2\,\eta}}\,(1+i) = \sqrt{\frac{3\,\pi\,R^3\,\omega\,\rho_0}{\zeta}}\,(1+i) = \frac{3}{2}\sqrt{\frac{M\,\omega}{\zeta}}\,(1+i)$$

$$= \Delta\sqrt{\frac{\omega}{2}}\,(1+i) = \Delta\sqrt{i\,\omega}$$

where

$$\sqrt{i} = e^{i\,\pi/4} = \frac{1}{\sqrt{2}}\,(1+i)$$

$$\rightarrow \qquad 1 - i\,k\,R - \frac{k^2\,R^2}{9} = 1 - i\,\Delta\sqrt{i\,\omega} - \frac{1}{9}\,i\,\omega\,\Delta^2 = 1 - \Delta\sqrt{-i\,\omega} - i\,\frac{M\,\omega}{2\,\zeta}$$

(10.375a) then becomes

$$-i\,m\,\omega\,\tilde{\boldsymbol{u}}(\omega) + \zeta\left(1 - \Delta\sqrt{-i\,\omega} - i\,\frac{M\,\omega}{2\,\zeta}\right)\tilde{\boldsymbol{u}}(\omega) = \tilde{\boldsymbol{F}}_{\text{rand}}(\omega)$$

$$-i\,m'\,\omega\,\tilde{\boldsymbol{u}}(\omega) + \zeta\,\tilde{\boldsymbol{u}}(\omega) - \zeta\,\Delta\sqrt{-i\,\omega}\;\tilde{\boldsymbol{u}}(\omega) = \tilde{\boldsymbol{F}}_{\text{rand}}(\omega) \qquad (10.375)$$

where

$$m' = m + \frac{M}{2} = \text{effective mass of Brownian particle} \qquad (10.375e)$$

The inverse Fourier transform of (10.375) is trivial except for the term proportional to $\sqrt{-i\,\omega}$, which involves

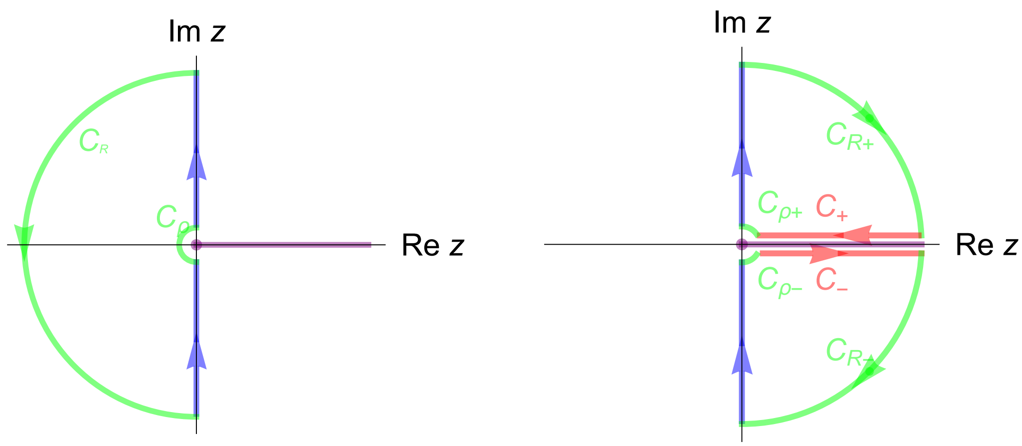
$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\sqrt{-i\omega}\;\tilde{\mathbf{u}}(\omega)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega t}\sqrt{-i\omega}\int_{-\infty}^{\infty}ds\,e^{i\omega s}\,\mathbf{u}(s)$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\sqrt{-i\omega}\int_{-\infty}^{\infty}\frac{d\,e^{i\omega(s-t)}}{i\omega}\,\mathbf{u}(s)$$
$$=-\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{i}{\sqrt{i\omega}}\int_{-\infty}^{\infty}ds\,e^{i\omega(s-t)}\frac{d\mathbf{u}}{ds} \qquad (10.376a)$$

where we have assumed

$$e^{i\omega(s-t)}\,\mathbf{u}(s)\Big|_{-\infty}^{\infty}=0$$

Setting $z=i\omega$, we have

$$\mathcal{I}=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{i\,e^{i\omega(s-t)}}{\sqrt{i\omega}}=\int_{-i\infty}^{i\infty}\frac{dz}{2\pi}\frac{e^{z(s-t)}}{\sqrt{z}}$$



Contour for $s>t$. Contour for $t>s$.

Let the branch cut of $\sqrt{z}$ to be the positive Re z axis [see Figure above].

For $s>t$, the contour closes on the LHS of the z-plane. Hence

$$\mathcal{I}+\mathcal{I}_R+\mathcal{I}_\rho=0 \qquad (10.376b)$$

where

$\mathcal{I}_R=0$ is the integral over the great half-circle at infinity.

$$\mathcal{I}_\rho=\int_{C_\rho}\frac{dz}{2\pi}\frac{e^{z(s-t)}}{\sqrt{z}}$$

C_ρ is the half-circle of radius $\rho\to 0$ that goes around the origin on its LHS.

Since

$$\mathcal{I}_\rho\le\left|\int_{C_\rho}\frac{dz}{2\pi}\frac{e^{z(s-t)}}{\sqrt{z}}\right|\le\frac{\pi\rho}{2\pi}\frac{e^{\rho(s-t)}}{\sqrt{\rho}}\xrightarrow[\rho\to 0]{}0$$

(10.376b) becomes

$$\mathcal{I}=0 \qquad \text{for} \qquad s>t$$

(10.376c)

For $t>s$, the contour closes on the RHS of the z-plane. Owing to the branch cut, we have

$$\mathcal{I}+\mathcal{I}_{R+}+\mathcal{I}_{\rho+}+\mathcal{I}_{+}+\mathcal{I}_{\rho-}+\mathcal{I}_{-}+\mathcal{I}_{R-}=0 \qquad (10.376d)$$

where the subscript ± denotes a path on the $\begin{matrix}\text{upper}\\\text{lower}\end{matrix}$ half of the z-plane and

$$\mathcal{I}_\pm = \int_{C_\pm} \frac{dz}{2\pi} \frac{e^{z(s-t)}}{\sqrt{z}}$$

$$= \mp \lim_{\delta\to 0} \int_0^\infty \frac{dz}{2\pi} \frac{e^{z(s-t)}}{\sqrt{z}} \bigg|_{z = x \pm i\delta} \qquad x = \operatorname{Re} z$$

As for the case $s > t$,

$$\mathcal{I}_{R\pm} = \mathcal{I}_{\rho\pm} = 0$$

$$\to \qquad \mathcal{I} + \mathcal{I}_+ + \mathcal{I}_- = 0 \tag{10.376e}$$

Using

$$\sqrt{z} = e^{\ln\sqrt{z}} = e^{(\ln z)/2}$$

$$\to \qquad \sqrt{z}\,\bigg|_{z = x\pm i\delta} = \begin{cases} e^{(\ln x)/2} \\ e^{(\ln x + i 2\pi)/2} \end{cases} = \begin{cases} e^{(\ln x)/2} \\ -e^{(\ln x)/2} \end{cases} = \pm\sqrt{x}$$

$$\therefore \qquad \mathcal{I}_\pm = \mp \int_0^\infty \frac{dx}{2\pi} \frac{e^{-x(t-s)}}{\pm\sqrt{x}}$$

$$= -\int_0^\infty \frac{dx}{2\pi} \frac{e^{-x(t-s)}}{\sqrt{x}}$$

$$= -\int_0^\infty \frac{dy}{\pi} e^{-y^2(t-s)} \qquad y = \sqrt{x}$$

$$= -\frac{1}{2\sqrt{\pi(t-s)}}$$

Hence, (10.376e) gives

$$\mathcal{I} = \frac{1}{\sqrt{\pi(t-s)}} \qquad \text{for} \qquad t > s \tag{10.376f}$$

Putting (10.376c, f) into (10.376a) gives

$$\int_{-\infty}^\infty \frac{d\omega}{2\pi} e^{-i\omega t} \sqrt{-i\omega}\; \tilde{\boldsymbol{u}}(\omega) = -\int_{-\infty}^t ds \frac{1}{\sqrt{\pi(t-s)}} \frac{d\boldsymbol{u}}{ds}$$

so that the inverse Fourier transform of (10.375) becomes

$$m' \frac{d\boldsymbol{u}(t)}{dt} + \zeta\,\boldsymbol{u}(t) + \frac{\zeta\Delta}{\sqrt{\pi}} \int_{-\infty}^t ds \frac{1}{\sqrt{t-s}} \frac{d\boldsymbol{u}}{ds} = \boldsymbol{F}_{\text{rand}}(t) \tag{10.376}$$

which is the Langevin equation for a sticky Brownian particle in an incompressible fluid.

Taking the average over $\boldsymbol{F}_{\text{rand}}$ gives

$$m' \frac{d\langle \boldsymbol{u}(t)\rangle_{\boldsymbol{F}}}{dt} + \zeta\,\langle \boldsymbol{u}(t)\rangle_{\boldsymbol{F}} + \frac{\zeta\Delta}{\sqrt{\pi}} \int_{-\infty}^t ds \frac{1}{\sqrt{t-s}} \frac{d\langle \boldsymbol{u}(t)\rangle_{\boldsymbol{F}}}{ds} = 0 \tag{10.377}$$

which will be solved by means of a Laplace transform in Exercise 10.9.

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Exercise 10.9.

Take the Laplace transform of

$$m' \frac{d f(t)}{d t} + \zeta f(t) + \frac{\zeta \Delta}{\sqrt{\pi}} \int_{-\infty}^{t} d s \frac{1}{\sqrt{t-s}} \frac{d f(s)}{d s} = 0 \qquad \text{(1a)}$$

Answer

Setting

$$f(t) = \int_{-i\infty}^{i\infty} \frac{d z}{2\pi i} e^{z t} \tilde{f}(z) \qquad \tilde{f}(z) = \int_{0}^{\infty} d t\, e^{-z t} f(t) \qquad \text{(1)}$$

$$\rightarrow \quad \frac{d f(t)}{d t} = \int_{-i\infty}^{i\infty} \frac{d z}{2\pi i} z e^{z t} \tilde{f}(z) \qquad \text{(2)}$$

$$\int_{0}^{\infty} d t\, e^{-z t} \frac{d f(t)}{d t} = f(t) e^{-z t} \Big|_{0}^{\infty} + z \int_{0}^{\infty} d t\, e^{-z t} f(t)$$

$$= -f(0) + z \tilde{f}(z) \qquad [\operatorname{Re} z > 0] \qquad \text{(2a)}$$

Let

$$\mathcal{I}(t) = \int_{-\infty}^{t} d s \frac{1}{\sqrt{t-s}} \frac{d f(s)}{d s}$$

$$\rightarrow \quad \tilde{\mathcal{I}}(z) = \int_{0}^{\infty} d t\, e^{-z t} \int_{-\infty}^{t} d s \frac{1}{\sqrt{t-s}} \frac{d f(s)}{d s}$$

$$= \int_{0}^{\infty} d t\, e^{-z t} \int_{-\infty}^{t} d s \frac{1}{\sqrt{t-s}} \int_{-i\infty}^{i\infty} \frac{d z'}{2\pi i} z' e^{z' s} \tilde{f}(z') \qquad [\text{ (2) used. }] \qquad \text{(3a)}$$

Setting

$$x = t - s$$

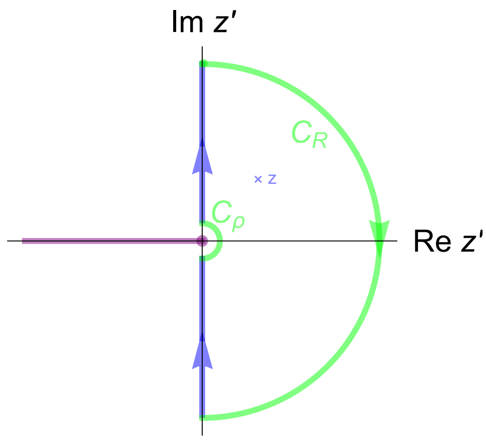
we have

$$\int_{-\infty}^{t} d s \frac{1}{\sqrt{t-s}} e^{z' s} = \int_{0}^{\infty} d x \frac{1}{\sqrt{x}} e^{z'(t-x)} = 2 e^{z' t} \int_{0}^{\infty} d \sqrt{x}\, e^{-z' x} = e^{z' t} \sqrt{\frac{\pi}{z'}} \qquad \text{(4)}$$

so that (3a) becomes

$$\tilde{\mathcal{I}}(z) = \int_{0}^{\infty} d t \int_{-i\infty}^{i\infty} \frac{d z'}{2\pi i} e^{-(z - z') t} \sqrt{\pi z'}\, \tilde{f}(z') \qquad \text{(5)}$$

$$= \int_{-i\infty}^{i\infty} \frac{d z'}{2\pi i} \frac{\sqrt{\pi z'}}{z' - z} \tilde{f}(z') \qquad \text{(6)}$$



As is implicit in (1), $t > 0$ so that the contour for obtaining $\tilde{\mathcal{I}}(z)$ is to be closed on the RHS of the z-plane [see Figure above]. Placing the branch cut of $\sqrt{z'}$ on the negative real axis, (6) becomes [with $\mathcal{I}_\rho = \mathcal{I}_R = 0$ as in (10.376b)],

$$\tilde{\mathcal{I}}(z) = -\text{Res}\left[\frac{\sqrt{\pi z'}}{z - z'}\tilde{f}(z');\ z' = z\right] = \sqrt{\pi z}\ \tilde{f}(z) \tag{7}$$

where the negative sign in front of Res is due to the contour being clockwise.

Using (1), (2a) & (7), the Laplace transform of (1a) is therefore

$$m'\left[-f(0) + z\,\tilde{f}(z)\right] + \zeta\,\tilde{f}(z) + \zeta\,\Delta\sqrt{z}\ \tilde{f}(z) = 0$$

$$\rightarrow \qquad \tilde{f}(z) = \frac{m'\ f(0)}{m'\ z + \zeta + \zeta\,\Delta\sqrt{z}} \tag{8}$$

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Since $\boldsymbol{u}(t)$ remains in the $\hat{\mathbf{z}}$ direction for all t, (10.377) is a 1-D equation of a particle with effective mass m'. We therefore define the velocity autocorrelation function as

$$C_{u\,u}(t) = C_{u\,u}(\mid t \mid) \equiv \langle\langle u(\mid t \mid)\rangle_F\, u(0)\rangle_T \qquad \text{where} \qquad \boldsymbol{u}(t) = u(t)\,\hat{\mathbf{z}}$$

(10.378)

Putting (8) into (1), we have

$$\langle u(\mid t \mid)\rangle_F = \int_{-i\infty}^{i\infty}\frac{d\,z}{2\,\pi\,i}\,e^{z\,|t|}\,\frac{m'\,u(t)}{m'\ z + \zeta + \zeta\,\Delta\sqrt{z}} \tag{10.378a}$$

so that (10.378) becomes

$$C_{u\,u}(t) = \int_{-i\infty}^{i\infty}\frac{d\,z}{2\,\pi\,i}\,e^{z\,|t|}\,\frac{m'\,\langle u(0)^2\rangle_T}{m'\ z + \zeta + \zeta\,\Delta\sqrt{z}}$$

$$= \int_{-i\infty}^{i\infty}\frac{d\,z}{2\,\pi\,i}\,e^{z\,|t|}\,\frac{k_B\,T}{m'\ z + \zeta + \zeta\,\Delta\sqrt{z}} \quad \text{[Equipartition theorem used.]} \tag{10.380}$$

$$\rightarrow \qquad \tilde{C}_{u\,u}(z) = \frac{k_B\,T}{m'\ z + \zeta + \zeta\,\Delta\sqrt{z}} \tag{10.381}$$

$$\xrightarrow[z\to 0]{} \frac{k_B\,T}{\zeta} = D = \text{Einstein's diffusion coefficient [see §5.E.1]}.$$

(10.381a)

We now turn to the evaluation of the Bromwich integral (10.380).

To begin, there are two poles at [see §Code below]

$$z_\pm = \frac{1}{2\,m'^2}\left(-2\,m'\,\zeta + \Delta^2\,\zeta^2 \pm \sqrt{-4\,m'\,\Delta^2\,\zeta^3 + \Delta^4\,\zeta^4}\,\right) \qquad (10.381b)$$

Next, we need to know where $z_\pm$ are located. Using (10.375d), we have

$$-2\,m'\,\zeta + \Delta^2\,\zeta^2 = \left(-2\,m' + \frac{9}{2}\,M\right)\zeta = \left(-2\,m + \frac{7}{2}\,M\right)\zeta$$

$$\sqrt{-4\,m'\,\Delta^2\,\zeta^3 + \Delta^4\,\zeta^4} = \Delta\,\zeta^{3/2}\,\sqrt{-4\,m' + \Delta^2\,\zeta}$$

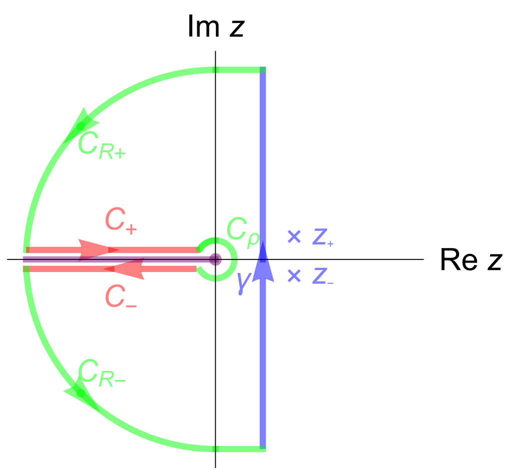
$$= \Delta\,\zeta^{3/2}\,\sqrt{-4\,m' + \frac{9}{2}\,M} \qquad \text{[(10.375d) used.]}$$

$$= \Delta\,\zeta^{3/2}\,\sqrt{-4\,m + \frac{5}{2}\,M} \qquad \text{[(10.375e) used.]}$$

Since a typical Brownian particle is slightly lighter than the fluid it displaces, we can assume

$$\frac{5}{8}\,M < m < M$$

so that $z_\pm$ is in the $\begin{matrix}1^{st}\\4^{th}\end{matrix}$ quadrant of the z-plane, or $\mathrm{Re}\,z_\pm > 0$. Hence, they cannot be enclosed by the contour because they lead to residues that are proportional to a $e^{z\,|t|}$ factor that explodes as $|\,t\,| \to \infty$.



Because a branch cut cannot be crossed by the contour, we place it on the negative $\mathrm{Re}\,z$ axis and replace (10.380) with

$$C_{u\,u}(t) = \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{d\,z}{2\,\pi\,i}\,e^{z\,|t|}\,\frac{k_B\,T}{m'\,z + \zeta + \zeta\,\Delta\,\sqrt{z}}$$

(10.381c)

where $\mathrm{Re}\,z_\pm > \gamma > 0$ so that the path of the Bromwich integral lies to the right of the branch cut [see

Figure above].

Since $|t| \geq 0$, the contour must be closed on the LHS of the z-plane, giving

$$C_{uu}(t) + \mathcal{I}_{R+} + \mathcal{I}_{+} + \mathcal{I}_{\rho} + \mathcal{I}_{-} + \mathcal{I}_{R-} = 0 \qquad (10.381d)$$

As usual,

$$\mathcal{I}_{R\pm} = \mathcal{I}_{\rho\pm} = 0$$

Using

$$\sqrt{z}\,\Big|_{\pm} = \sqrt{x\,e^{\pm i\pi}} = \pm i\sqrt{x}$$

we have

$$\mathcal{I}_{\pm} = \pm\int_{\infty}^{0} \frac{d(-x)}{2\pi i} e^{-x|t|} \frac{k_B T}{m'\,(-x) + \zeta + \zeta\Delta\left(\pm i\sqrt{x}\right)}$$

$$= \pm\int_{0}^{\infty} \frac{dx}{2\pi i} e^{-x|t|} \frac{k_B T}{-m'\,x + \zeta \pm i\zeta\Delta\sqrt{x}}$$

(10.381d) then gives

$$C_{uu}(t) = -\mathcal{I}_{+} - \mathcal{I}_{-}$$

$$= k_B T\int_{0}^{\infty} \frac{dx}{2\pi i} e^{-x|t|}\left(\frac{-1}{-m'\,x + \zeta + i\zeta\Delta\sqrt{x}} - \frac{-1}{-m'\,x + \zeta - i\zeta\Delta\sqrt{x}}\right)$$

$$= \frac{k_B T}{\pi}\int_{0}^{\infty} dx\, e^{-x|t|} \frac{\zeta\Delta\sqrt{x}}{(-m'\,x + \zeta)^2 + \zeta^2\Delta^2 x} \qquad (10.382)$$

Since the integrand in (10.382) is always non-negative,

$$C_{uu}(t) \geq 0 \qquad \forall\ t$$

(10.382a)

Therefore, the region where $C_{uu}(t) < 0$ in Rahman's stimulation [see Reichl's Fig.10.10] cannot be explained by our model. However, as discussed in Reichl's text, pretty good agreement can be achieved if one uses the slippery boundary condition so that the torque on the Brownian particle vanishes.

For large $|t|$, the factor $e^{-x|t|}$ vanishes quickly for large x. The main contribution to the integral (10.382) therefore comes from the region of small x. Hence,

$$C_{uu}(t) = \frac{k_B T}{\pi}\int_{0}^{\infty} dx\, e^{-x|t|}\left(\frac{\Delta}{\zeta}\sqrt{x} + \ldots\right)$$

$$= \frac{k_B T}{\pi}\frac{\Delta}{\zeta}\frac{\sqrt{\pi}}{2\,|t|^{3/2}} + \ldots \qquad \text{[see §Code.]}$$

$$= \frac{D\Delta}{2\sqrt{\pi}\,|t|^{3/2}} + \ldots$$

(10.383)

which, in contrast to the conventional exponential decay, is called the long-time tail.

In order not to confuse with the complex variable z, we shall denote the displacement of the Brownian particle by

$$x(t) = x(0) + \int_0^t d\,s\,u(s) \qquad (10.383a)$$

The displacement variance is therefore

$$\begin{aligned}\left\langle \Delta x^2(t) \right\rangle &\equiv \left\langle [\,x(t) - x(0)\,]^2 \right\rangle \\ &= \left\langle \int_0^t d\,s\,u(s) \int_0^t d\,s'\,u(s') \right\rangle \qquad [\,(10.383a) \text{ used. }] \\ &= \int_0^t d\,s \int_0^t d\,s' \,\langle u(s)\,u(s') \rangle \\ &= \int_0^t d\,s \int_0^t d\,s' \,\langle u(\,|\,s - s'\,|\,)\,u(0) \rangle \\ &= \int_0^t d\,s \int_0^t d\,s' \; C_{u\,u}(s - s')\end{aligned}$$

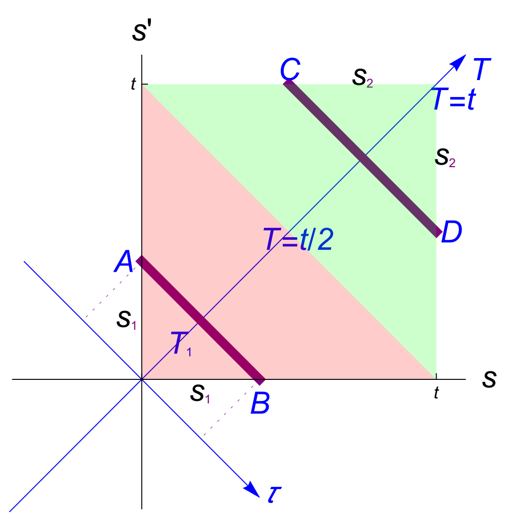
(10.383b)

Let

$$T = \frac{1}{2}(s + s') \qquad \tau = s - s'$$

$$\rightarrow \quad s = T + \frac{1}{2}\tau \qquad s' = T - \frac{1}{2}\tau$$

$$d\,\tau\,d\,T = \left| \begin{matrix} 1 & -1 \\ \frac{1}{2} & \frac{1}{2} \end{matrix} \right| d\,s\,d\,s' = d\,s\,d\,s'$$



As shown in the figure above, the area integral in (10.383b) splits up into two regions:

$$\int_0^t d\,s \int_0^t d\,s' = \int_0^{t/2} d\,T \int_{\tau_A}^{\tau_B} d\,\tau + \int_{t/2}^t d\,T \int_{\tau_C}^{\tau_D} d\,\tau$$

The $(s,\ s')$-coordinates of the points are

$$A = (0,\ s_1)_{s\,s'} \qquad B = (s_1,\ 0)_{s\,s'} \qquad C = (t - s_2,\ t)_{s\,s'}\ D = (t,\ t - s_2)_{s\,s'}$$

In the $(\tau,\ T)$-coordinates

$$A = \left(-s_1,\ \frac{s_1}{2}\right)_{\tau\,T} \quad \rightarrow \quad T_1 = \frac{s_1}{2} \rightarrow \quad A = (-2\,T_1,\ T_1)_{\tau\,T}$$

$$B = \left(s_1, \frac{s_1}{2}\right)_{\tau T} \to \quad T_1 = \frac{s_1}{2} \to \quad B = (2\,T_1,\, T_1)_{\tau T}$$
$$C = \left(-s_2, t - \frac{s_2}{2}\right)_{\tau T} \to \quad T_2 = t - \frac{s_2}{2} \quad \to \quad C = (2\,T_2 - 2\,t,\, T_2)_{\tau T}$$
$$D = \left(s_2, t - \frac{s_2}{2}\right)_{\tau T} \to \quad T_2 = t - \frac{s_2}{2} \quad \to \quad D = (2\,t - 2\,T_2,\, T_2)_{\tau T}$$

(10.383b) then becomes

$$\left\langle \Delta x^2(t) \right\rangle = \left[\int_0^{t/2} d\,T \int_{-2\,T}^{2\,T} d\,\tau + \int_{t/2}^{t} d\,T \int_{-2\,(t-T)}^{2\,(t-T)} d\,\tau\right] C_{u\,u}(\tau)$$

Since $C_{u\,u}(\tau) = C_{u\,u}(\,|\,\tau\,|\,)$,

$$\left\langle \Delta x^2(t) \right\rangle = 2\left[\int_0^{t/2} d\,T \int_0^{2\,T} d\,\tau + \int_{t/2}^{t} d\,T \int_0^{2\,(t-T)} d\,\tau\right] C_{u\,u}(\tau) \qquad (10.383c)$$

Using

$$(t, 0)_{s\,s'} = \left(t, \frac{t}{2}\right)_{\tau T} \qquad (s, 0)_{s\,s'} = \left(s, \frac{s}{2}\right)_{\tau T} = \left(\tau, \frac{\tau}{2}\right)_{\tau T}$$

we can change the order of the integration and get

$$\int_0^{t/2} d\,T \int_0^{2\,T} d\,\tau = \int_0^{t} d\,\tau \int_0^{\tau/2} d\,T$$

(10.383d)

$$= \frac{1}{4} t^2 \qquad \text{(As expected.)}$$

Similarly, using

$$(t, s')_{s\,s'} = \left(t - s', \frac{t + s'}{2}\right)_{\tau T} = \left(\tau, t - \frac{\tau}{2}\right)_{\tau T}$$

we have

$$\int_{t/2}^{t} d\,T \int_0^{2\,(t-T)} d\,\tau = \int_0^{t} d\,\tau \int_{t/2}^{t-\tau/2} d\,T$$

(10.383e)

$$= \frac{1}{4} t^2 \qquad \text{(As expected.)}$$

Combing (10.383d-e) turns (10.383c) into

$$\left\langle \Delta x^2(t) \right\rangle = 2 \int_0^{t} d\,\tau \left[\int_0^{\tau/2} + \int_{t/2}^{t-\tau/2}\right] d\,T\, C_{u\,u}(\tau)$$
$$= t \int_0^{t} d\,\tau\, C_{u\,u}(\tau)$$

(10.384)

Now, for a Brownian particle in equilibrium (i.e., long-times) with the fluid [see (5.85) of §5.E],

$$\left\langle \Delta x^2(t) \right\rangle = 2\,D\left[t - \frac{m'}{\zeta}\left(1 - e^{-\zeta\,t/m'}\right)\right]$$

(10.385)

The time-dependent diffusion coefficient is defined as

$$D(t) \equiv \frac{1}{2}\frac{d}{d\,t}\left\langle \Delta x^2(t) \right\rangle$$

(10.386)

Using (10.385) we have

$$D(t) = D - D\,e^{-\zeta\,t/m'} \xrightarrow[t\to\infty]{} D$$

(10.386a)

Using (10.384) on (10.386) gives

$$\begin{aligned} D(t) &= \frac{1}{2}\left[t\,C_{u\,u}(t) + \int_0^t d\,\tau\,C_{u\,u}(\tau)\right] \\ &= \frac{1}{2}\int_0^t d\,\tau\,C_{u\,u}(\tau) + \frac{D\,\Delta}{4\sqrt{\pi}\,t^{1/2}} + \ldots \end{aligned}$$

(10.386b)

where (10.383) was used.

Comparing (10.386b) with (10.386a) at $t = \infty$ gives

$$D = \frac{1}{2}\int_0^\infty d\,\tau\,C_{u\,u}(\tau)$$

(10.386c)

so that (10.386b) becomes

$$\begin{aligned} D(t) &= D - \frac{1}{2}\int_t^\infty d\,\tau\,C_{u\,u}(\tau) + \frac{D\,\Delta}{4\sqrt{\pi}\,t^{1/2}} + \ldots \\ &= D - \frac{1}{2}\int_t^\infty d\,\tau\,\frac{D\,\Delta}{2\sqrt{\pi}\,\tau^{3/2}} + \frac{D\,\Delta}{4\sqrt{\pi}\,t^{1/2}} + \ldots \qquad \text{[(10.383) used.]} \\ &= D - \frac{D\,\Delta}{2\sqrt{\pi}\,\tau^{1/2}} + \frac{D\,\Delta}{4\sqrt{\pi}\,t^{1/2}} + \ldots \\ &= D - \frac{D\,\Delta}{4\sqrt{\pi}\,\tau^{1/2}} + \ldots \end{aligned}$$

(10.387)

Read Reichl’s discussion on experimental results that concludes the section.

Code

```
Solve[m z + ζ + ζ Δ √z == 0, z]
```

$$\left\{\left\{z \to \frac{-2\,m\,\zeta + \Delta^2\,\zeta^2 - \sqrt{-4\,m\,\Delta^2\,\zeta^3 + \Delta^4\,\zeta^4}}{2\,m^2}\right\}, \left\{z \to \frac{-2\,m\,\zeta + \Delta^2\,\zeta^2 + \sqrt{-4\,m\,\Delta^2\,\zeta^3 + \Delta^4\,\zeta^4}}{2\,m^2}\right\}\right\}$$

$$\text{Assuming}\left[t > 0, \int_0^\infty e^{-x t} \sqrt{x}\, dx\right]$$

$$\frac{\sqrt{\pi}}{2\, t^{3/2}}$$

$$\text{Series}\left[\frac{\zeta\, \Delta \sqrt{x}}{(-m'\, x + \zeta)^2 + \zeta^2\, \Delta^2\, x}, \{x, 0, 3\}\right]$$

$$\frac{\Delta \sqrt{x}}{\zeta} + \frac{\left(-\Delta^3\, \zeta + 2\, \Delta\, m'\right)\, x^{3/2}}{\zeta^2} + \frac{\left(\Delta^5\, \zeta^2 - 4\, \Delta^3\, \zeta\, m' + 3\, \Delta\, (m')^2\right)\, x^{5/2}}{\zeta^3} + O[x]^{7/2}$$

$$\text{Assuming}\left[t > 0, \int_0^\infty e^{-x t}\, x^{3/2}\, dx\right]$$

$$\frac{3\sqrt{\pi}}{4\, t^{5/2}}$$