Non-equilibrium physics WS 20/21 – Exercise Sheet 2:

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1 Discussion:

i) What are *Markovian* out-of equilibrium processes? What is the general form of *linear constitutive relations* and what are *direct and indirect* transport phenomena? What symmetry principles and constraints apply to the linear kinetic coefficients?

- *Markovian* out-of equilibrium processes are assumed to be memory-less system where the flux at a given point in space and time only depends on the intensive parameters and affinities at that point

$$J_i(\vec{r},t) = J_i(\{F_i(\vec{r},t)\},\{Y(\vec{r},t)\}) \ , \tag{1}$$

- *Linear constitutive relations* are written as the Taylor expanssion

$$J_i(\vec{r},t) = J_i^{\mathrm{eq}}(\vec{r},t) + \sum_j L_{ij}F_j \ , \qquad L_{ij} = \left.\frac{\partial J_i(\vec{r},t)}{\partial F_j}\right|_{F_j=F_j^{\mathrm{eq}}=0} \tag{2}$$

- *Direct* transport correponds to the diagonal terms of L_{ij}, i.e. where the flux of a quantity is driven by its own affinity.

- While *indrect* transport corresponds to the off-diagonal terms of L_{ij}, i.e. where the flux of one quantity is driven by the affinity of a different quantity.

- Symmetries:

  + Curie symmetry principle: "Physical effects have the same symmetries as their causes"
    In an isotropic system: flux and affinities with different parity rank cannot be coupled. Transport of scalar quantities with vector fluxes and affinites is coupled with a tensor proptional to identity $\mathbb{L}_{ij} = L_{ij}\mathbb{I}$.
  + Onsager reciprocal relations: When i and j behave the same under time reversal

$$L_{ij} = L_{ji} \ . \tag{3}$$

2 In-class problems:

2.1 Constitutive relations for heat and particle transfer between containers

Consider again the heat and particle transfer between two containers A and B (c.f. problem 3.1 sheet 1). We found that the net energy and particle fluxes were determined by

$$J^N = J_N^{B\to A} - J_N^{A\to B} \ , \qquad J^E = J_E^{B\to A} - J_E^{A\to B} \ ,$$

with

$$J_N^{A\to B} = \frac{1}{\sqrt{2\pi m k_B T_A}}\, S\, p_A\,, \qquad J_E^{A\to B} = \sqrt{\frac{2k_B T_A}{\pi m}}\, S\, p_A$$

and similarly for $J_{N/E}^{B\to A}$.

i) Express the fluxes J^N and J^E in terms of the affinities

$$F_N = \Delta\left(-\frac{\mu}{T}\right) = -\frac{\mu_A}{T_A} + \frac{\mu_B}{T_B} \qquad F_E = \Delta\left(\frac{1}{T}\right) = \frac{1}{T_A} - \frac{1}{T_B}\,.$$

to linear order for small F_N and F_E. If necessary, you can use that the following identity for the pressure of an ideal gas $\frac{p_A}{p_B} = \left(\frac{T_A}{T_B}\right)^{5/2} e^{\frac{\mu_A}{k_B T_A} - \frac{\mu_B}{k_B T_B}}$.

- Let us define

$$T_A = T + \frac{\delta T}{2}\,, \qquad T_B = T - \frac{\delta T}{2}\,, \tag{4}$$

The affinity at first order of δT becomes

$$F_E = \frac{\delta T}{T^2}\,, \Rightarrow \delta T = T^2 F_E\,. \tag{5}$$

The fluxes can be written as an expanssion of the affinities

$$J^N = J_N^{B\to A} - J_N^{A\to B}\,, \tag{6}$$

$$= \frac{1}{\sqrt{2\pi m k_B}}\, S\, p_B \frac{1}{\sqrt{T_B}}\left[1 - \frac{p_A}{p_B}\sqrt{\frac{T_B}{T_A}}\right]\,, \tag{7}$$

$$= \frac{1}{\sqrt{2\pi m k_B}}\, S\, p_B \frac{1}{\sqrt{T - T^2 F_E/2}}\left[1 - \left(\frac{T + T^2F_E/2}{T - T^2F_E/2}\right)^2 e^{\frac{-F_N}{k_B}}\right]\,, \tag{8}$$

$$\overset{F_N,F_E\ll 1}{\simeq} \frac{1}{\sqrt{2\pi m k_B}}\, S\, p_B \frac{4 - F_E T}{4\sqrt{T}}\left[1 - (1 - 2F_E T)\left(1 - \frac{F_N}{k_B}\right)\right]\,, \tag{9}$$

$$= \frac{1}{\sqrt{2\pi m k_B T}}\, S\, p_B \left[2TF_E + \frac{F_N}{k_B}\right]\,, \tag{10}$$

$$\tag{11}$$

We replace $T_A \to \frac{T_B}{1+T_B F_E} \simeq T_B - T_B^2 F_E$ and only take the first order of F_E/F_N

$$J^N \simeq \frac{1}{\sqrt{2\pi m k_B T}}\, S\, p_B \left[\frac{F_N}{k_B} + 2TF_E\right]\,. \tag{12}$$

$$\begin{aligned}
J^E &= J_N^{B\to A} - J_N^{A\to B} \,, &(13)\\
&= \sqrt{\frac{2k_BT_B}{\pi m}}\; S\; p_B \left[1 - \frac{p_A}{p_B}\sqrt{\frac{T_A}{T_B}}\right] \,, &(14)\\
&= \sqrt{\frac{2k_BT_B}{\pi m}}\; S\; p_B \left[1 - \left(\frac{T_A}{T_B}\right)^3 e^{\frac{-F_N}{k_B}}\right] \,, &(15)\\
&= \sqrt{\frac{2k_B(T-T^2F/2)}{\pi m}}\; S\; p_B \left[1 - \left(\frac{T+T^2F/2}{T-T^2F/2}\right)^3 e^{\frac{-F_N}{k_B}}\right] \,, &(16)\\
&\overset{F_N,F_E\ll 1}{\simeq} \sqrt{\frac{2k_BT}{\pi m}}\; S\; p_B(1+TF_E/8) \left[1 - \left(1-\frac{3}{2}TF_E\right)\left(1-\frac{F_N}{k_B}\right)\right] \,, &(17)\\
&\simeq \sqrt{\frac{2k_BT}{\pi m}}\; S\; p_B \left[\frac{F_N}{k_B} + 3TF_E\right] \,. &(18)\\
& &(19)
\end{aligned}$$

ii) Determine the kinetic coefficients $L_{EE}, L_{EN}, L_{NE}, L_{NN}$. What symmetries do you recognize?

- In linear theory the flux is written

$$J_i = \sum_j L_{ij} F_j \,. \qquad (20)$$

Using this expression we obtain from the previous question

$$L_{NN} = \frac{1}{\sqrt{2\pi m k_B T}}\; S\; p_B \frac{1}{k_B} \,, \qquad L_{NE} = \frac{2T}{\sqrt{2\pi m k_B T}}\; S\; p_B \,, \qquad (21)$$

$$L_{EE} = 3T\sqrt{\frac{2k_BT}{\pi m}}\; S\; p_B \,, \qquad L_{EN} = \sqrt{\frac{2T}{\pi m k_B}}\; S\; p_B \,. \qquad (22)$$

We can see clearly that $L_{NE} = L_{EN}$

iii) Calculate the entropy production rate dS/dt in the linear transport regime and show that $dS/dt \geq 0$.

- The entropy production rate is written

$$\begin{aligned}
dS/dt &= \sum_{ij} L_{ij} F_i F_j \,, &(23)\\
&= L_{NN}F_N^2 + 2L_{NE}F_NF_E + L_{EE}F_E^2 \,, &(24)
\end{aligned}$$

Consider the matrix $(\mathbb{L})_{ij}$, its eigenvalues are positive iif $\mathrm{Tr}(\mathbb{L}) \geq 0$ and $\det(\mathbb{L}) \geq 0$. Clearly $\mathrm{Tr}(\mathbb{L}) \geq 0$ is satisfied. Let us check the second condition

$$\begin{aligned}
\det(\mathbb{L}) &= L_{NN}L_{EE} - L_{NE}^2 \,, &(25)\\
&= \left(\frac{1}{\sqrt{2\pi m k_B T}}\; S\; p_B \frac{1}{k_B}\right)\left(3T_B\sqrt{\frac{2k_BT}{\pi m}}\; S\; p_B\right) - \left(\frac{2T}{\sqrt{2\pi m k_B T}}\; S\; p_B\right)^2 \,, &(26)\\
&= 3\frac{S^2\, p_B^2 T}{\pi m k_B} - \frac{2S^2\, p_B^2 T}{\pi m k_B} = \frac{S^2\, p_B^2 T}{\pi m k_B} \geq 0 \,, &(27)
\end{aligned}$$

leading to conclude that the eigenvalues are positive, making the symmetric matrix $\mathbb{L}$ positive definite. The scalar product $(\mathbb{F}^T\mathbb{L}\mathbb{F})$ of a positive definite matrix with arbitrary vectors leads to a positive quantity when the eigenvalues of $\mathbb{L}$ are positive, which proves that $dS/dt \geq 0$ for arbitrary $(\mathbb{F} = F_N, F_E)$ vector.

3 Homework problems:

3.1 Stokes-Einstein relation

Consider a rare species of heavy particles of mass m suspended in a fluid in thermal equilibrium at a const. temperature T and subject to the gravitational force $\vec{F}_g(\vec{x}) = -\vec{\nabla}V(\vec{x})$, where $V(\vec{x}) = mgz$ denotes the gravitational potential.

i) Determine the form of the linear constitutive relation for the current $\vec{J}_n$ in the presence of the gravitational potential. Express the result in terms of a diffusion and drift contribution $\vec{J}_n = \vec{J}_n^{Diffusion} + \vec{J}_n^{Drift}$ analogous to the discussion of a charged particle in an electric field.

- In the presence of the gravity field the energy density changes to $e_{\mathrm{tot}} = e + nV(\vec{x})$ and the entropy density can be written

$$s(e, n, V) = s(e - nV(\vec{x}), n, 0) \ , \tag{28}$$

leading the to the gravito-chemical potential

$$\frac{\partial s}{\partial n} = -\frac{\mu + V(\vec{x})}{T} = -\frac{\mu_g}{T} \ . \tag{29}$$

The linear constitutive relation for the current

$$\vec{J}_n = L_{nn}\vec{\nabla}\left(-\frac{\mu_g}{T}\right) = L_{nn}\vec{\nabla}\left(-\frac{\mu + V(\vec{x})}{T}\right) \ . \tag{30}$$

using $\vec{\nabla}\mu = \left(\frac{\partial \mu}{\partial n}\right)_T \vec{\nabla}n$, we have

$$\vec{J}_n = \underbrace{-\frac{L_{nn}}{T}\left(\frac{\partial \mu}{\partial n}\right)_T \vec{\nabla}n}_{\text{Diffusion}} \underbrace{- \frac{L_{nn}}{T}\vec{\nabla}V(\vec{x})}_{\text{Drift}} \ . \tag{31}$$

For a classical gaz one has $\left(\frac{\partial \mu}{\partial n}\right)_T = \frac{k_B T}{n}$, leading to

$$\vec{J}_n = -\frac{k_B L_{nn}}{n}\vec{\nabla}n - \frac{L_{nn}}{T}\vec{\nabla}V(\vec{x}) \ . \tag{32}$$

ii) Show that the general form of the equilibrium density distribution $n(z)$ (as a function of the height z) is of the form $n(z) = n_0 e^{-\lambda z}$ and determine λ as a function of m, g, k_B, T.

- In equilibrium the flux vanishes and we have

$$\vec{J}_n^{Diffusion} = -\vec{J}_n^{Drift} \ , \tag{33}$$

$$\frac{1}{n}\vec{\nabla}n = -\frac{1}{k_B T}\vec{\nabla}V(\vec{x}) \ , \tag{34}$$

$$\frac{1}{n}\begin{pmatrix} \frac{\partial n}{\partial x} \\ \frac{\partial n}{\partial y} \\ \frac{\partial n}{\partial z} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -\frac{mg}{k_B T} \end{pmatrix} \ , \tag{35}$$

$$\tag{36}$$

The equilibrium distribution is then

$$n(z) \;=\; n_0 e^{-\frac{mgz}{k_B T}} \tag{37}$$

We will now consider a microscopic description of the particles inside the fluid, which in addition to the gravitational force $\vec{F}_g$ are subject to a damping force $\vec{F}_s = -6\pi R\eta\dot{\vec{x}}$, where R and $\dot{\vec{x}}$ denote the radius and velocity of the particle and η is the shear viscosity.

iii) Determine the terminal drift velocity v_{Drift} of particles in the gravitational field and calculate the associated drift current $\vec{J}_n^{Drift}$ in terms of n, m, g, R, η. By comparing your result of the microscopic calculation of $\vec{J}_n^{Drift}$, with the corresponding expression obtained from the linear constitutive relation obtained in (i), determine the kinetic coefficient L_{nn} as a function of m, g, k_B, T, η, R.

- Newton's equation for each particle leads to

$$m\dot{v}_{Drift} = \vec{F}_g + \vec{F}_s \,, \quad (38)$$
$$= -mg - 6\pi R\eta\dot{\vec{x}} \,, \quad (39)$$
$$(40)$$

The terminal $(t \to infty)$ drift velocity is constant

$$0 = -mg - 6\pi R\eta v_{Drift} \,, \quad (41)$$
$$v_{Drift} = -\frac{mg}{6\pi R\eta} \,. \quad (42)$$

The associated drift current is written

$$\vec{J}_n^{Drift} = nv_{Drift} = -n\frac{mg}{6\pi R\eta} \,. \quad (43)$$

We found earlier

$$\vec{J}_n^{Drift} = \frac{L_{nn}}{T}\vec{\nabla}V(\vec{x}) \,, \quad (44)$$

The kinetic coefficient is given by

$$L_{nn} = \frac{nT}{6\pi R\eta} \,. \quad (45)$$

iv) Establish the Stokes-Einstein relation between the diffusion constant D and the shear viscosity η.

- The diffusion constant is read from Eq. (32), leading to the following Stokes-Einstein relation

$$D = \frac{k_B L_{nn}}{n} = \frac{k_B T}{6\pi R\eta} \,. \quad (46)$$

3.2 Causal diffusion

Consider a modification of the diffusion equation, where instead of the usual constitutive relation $\vec{J}_n = -D\vec{\nabla}n$ the continuity equation

$$\frac{\partial}{\partial t}n + \vec{\nabla}\vec{J}_n = 0 \,,$$

is supplemented by an additional relaxation type equation

$$\frac{\partial}{\partial t}\vec{J}_n + \frac{1}{\tau}\left(\vec{J}_n + D\vec{\nabla}n\right) = 0 \,,$$

for the particle flux density $\vec{J}_n$.

i) Decouple the evolution equations for $\vec{J}_n$ and n to derive the Cattaneo equation for the evolution particle number density $n(t,\vec{x})$, assuming a constant relaxation time τ and diffusion coefficient D.

- We introduce a time derivate to the first equation

$$\frac{\partial^2}{\partial t^2} n + \vec{\nabla} \frac{\partial}{\partial t} \vec{J}_n = 0 \;, \tag{47}$$

$$\frac{\partial^2}{\partial t^2} n - \vec{\nabla} \frac{1}{\tau} \left(\vec{J}_n + D \vec{\nabla} n \right) = 0 \;, \tag{48}$$

$$\left[\tau \frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} - D \triangle \right] n(t,\vec{x}) = 0 \;, \tag{49}$$

where we used the second equation in the second step to express the time derivative of the flux and in the last step the first equation to express $\vec{\nabla}\vec{J}_n$.

ii) Expressing the solution of the d-dimensional Cattaneo equation

$$\left[\tau \frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} - D \triangle \right] n(t,\vec{x}) = 0$$

in the form $n(t,\vec{x}) = \int \frac{d^d k}{(2\pi)^d} \frac{d\omega}{(2\pi)} \int \tilde{n}(\omega,k) e^{-i\omega t} e^{+i\vec{k}\vec{x}}$, determine the dispersion relation $\omega(k)$.

- We introduce the Fourier transform to the equation leading to

$$\left[\tau \frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} - D \triangle \right] \int \frac{d^d k}{(2\pi)^d} \frac{d\omega}{(2\pi)} \, \tilde{n}(\omega,k) e^{-i\omega t} e^{+i\vec{k}\vec{x}} = 0 \;, \tag{50}$$

$$\int \frac{d^d k}{(2\pi)^d} \frac{d\omega}{(2\pi)} \, \tilde{n}(\omega,k) \left[-\tau\omega^2 - i\omega + D\vec{k}^2 \right] e^{-i\omega t} e^{+i\vec{k}\vec{x}} = 0 \;. \tag{51}$$

The dispersion relation is the solution to $\left[-\tau\omega^2 - i\omega + D\vec{k}^2 \right] = 0$

$$\omega(k) = \frac{-i \pm \sqrt{4D\vec{k}^2\tau - 1}}{2\tau} \;. \tag{52}$$

iii) Determine the group velocity $v_g(k) = Re\frac{\partial\omega(k)}{\partial k}$ and the phase velocity $v_{ph}(k) = Re\frac{\omega(k)}{k}$

- The group velocity is given by

$$v_g(k) \;=\; Re\frac{\partial \omega(k)}{\partial k} = \begin{cases} 0 \;, & \text{for} \quad 0 \le k \le 1/\sqrt{4\tau D} \\ \pm\frac{2Dk}{\sqrt{4D\vec{k}^2\tau - 1}} \;, & \text{for} \quad k > 1/\sqrt{4\tau D} \end{cases} \tag{53}$$

- The phase velocity is given by

$$v_p(k) \;=\; Re\frac{\partial \omega(k)}{\partial k} = \begin{cases} 0 \;, & \text{for} \quad 0 \le k \le 1/\sqrt{4\tau D} \\ \pm\frac{\sqrt{4D\vec{k}^2\tau - 1}}{2k\tau} \;, & \text{for} \quad k > 1/\sqrt{4\tau D} \end{cases} \tag{54}$$

iv) Show that the retarded Greens function

$$G_R(t,\vec{k}) = \frac{i}{2\pi\tau}\frac{e^{-i\omega_+(k)t} - e^{-i\omega_-(k)t}}{\omega_+(k)-\omega_-(k)}\theta(t)$$

with $\omega_\pm(k) = \frac{-i}{2\tau} \pm \frac{1}{2\tau}\sqrt{4Dk^2\tau - 1}$, is the solution to the equation

$$\left[\tau\frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} + Dk^2\right] G_R(t,\vec{k}) = \frac{1}{(2\pi)}\delta(t) ,$$

which describes the time evolution of a density perturbation localized at the point $\vec{x} = 0$ and initial time $t = 0$

- Plugging the reatrded Greens function to the evolution equation

$$\left[\tau\frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} + Dk^2\right] G_R(t,\vec{k}) = \left[\tau\frac{\partial^2}{\partial t^2} + \frac{\partial}{\partial t} + Dk^2\right] \frac{i}{2\pi\tau}\frac{e^{-i\omega_+(k)t} - e^{-i\omega_-(k)t}}{\omega_+(k)-\omega_-(k)}\theta(t) , \quad (55)$$

$$= \frac{1}{2\pi}\delta(t) . \quad (56)$$

v) Now we will focus on the case of one-dimensional diffusion ($d = 1$). Determine the retarded propagator $G_R(t,x)$ in coordinate space, using that

$$\int_{-\infty}^{\infty} dk \frac{e^{-i\omega_+(k)t} - e^{-i\omega_-(k)t}}{\omega_+(k)-\omega_-(k)} e^{ikx} = \frac{-i\pi}{\sqrt{D/\tau}} e^{-t/2\tau} I_0(\xi)\theta(\sqrt{D/\tau}\ t - |x|) .$$

where I_0 is the modified Bessel function and $\xi = \frac{1}{2}\sqrt{\frac{t^2}{\tau^2} - \frac{x^2}{D\tau}}$. Visualize the propagation of the wave-package. Which properties do the coefficients D, τ have to satisfy for the evolution to be causal?

- The retarted propagator in coordinate space is given by

$$G_R(t,x) = \int_{-\infty}^{\infty} dk\ G_R(t,k) e^{ikx} , \quad (57)$$

$$= \int_{-\infty}^{\infty} dk\ \frac{i}{2\pi\tau}\frac{e^{-i\omega_+(k)t} - e^{-i\omega_-(k)t}}{\omega_+(k)-\omega_-(k)}\theta(t) e^{ikx} , \quad (58)$$

$$= \frac{i}{2\pi\tau}\frac{-i\pi}{\sqrt{D/\tau}} e^{-t/2\tau} I_0(\xi)\theta(\sqrt{D/\tau}\ t - |x|) , \quad (59)$$

$$= \frac{1}{2\sqrt{D/\tau}} e^{-t/2\tau} I_0(\xi)\theta(\sqrt{D/\tau}\ t - |x|) , \quad (60)$$

- For the evolution to be causal, $ct - |x| \geq 0$ should hold, leading to

$$\sqrt{D/\tau} \leq c \quad (61)$$

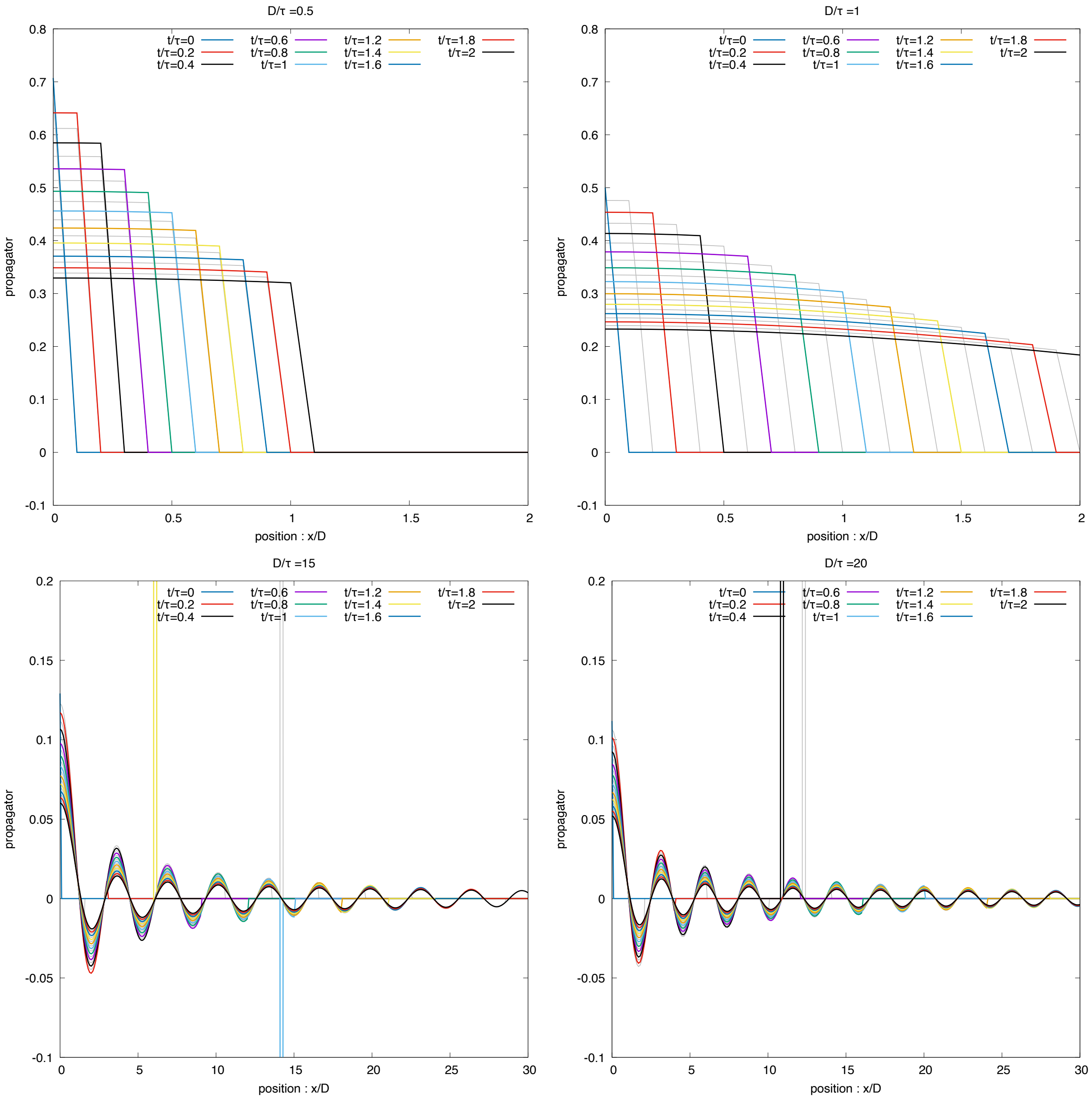

Fig. 1: Evolution of the propagator for different D/τ.