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Solution to the exam in
TFY4275/FY8907 CLASSICAL TRANSPORT THEORY

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This solution consists of 7 pages.

Problem 1.

a) The diffusion equation in d-dimensions (for constant D) reads

$$\frac{\partial p(\mathbf{x},t|\mathbf{x}_0,t_0)}{\partial t} = D\nabla^2 p(\mathbf{x},t|\mathbf{x}_0,t_0). \tag{16}$$

Here $p(\mathbf{x},t|\mathbf{x}_0,t_0)$ denotes the probability density function for the particle being at position $\mathbf{x}$ at time t, given that it started at $\mathbf{x}_0$ at time t_0. The symbol D signifies the diffusion constant, and $\boldsymbol{\nabla}$ denotes the d-dimensional nabla-operator so that

$$\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \ldots + \frac{\partial^2}{\partial x_d^2}. \tag{17}$$

To show that Eq. (2) [on the problem set sheet] is a solution to Eq. (16) can be done in several ways. The first method we will mention, that is also the simplest, is to recognize that the diffusion in the various directions $\hat{\mathbf{x}}_i$ are all independent. Hence, the probability $p(\mathbf{x},t|\mathbf{x}_0,t_0)$ can be written as a product of the probabilities, $p_*(x_i,t|x_{0,i},t_0)$, for each direction, and thereby obtaining Eq. (3) from the problem set. The other, and more direct (and mathematical method) is to substitute Eq. (2) and (3) into the diffusion equation that you found. By noticing that

$$\frac{\partial^2}{\partial x_i^2} p(\mathbf{x},t|\mathbf{x}_0,t_0) = \frac{\partial^2}{\partial x_i^2} p_*(x_i,t|x_{0,i},t_0) \prod_{j\neq i}^{d} p_*(x_j,t|x_{0,j},t_0), \tag{18a}$$

so that

$$\nabla^2 p(\mathbf{x},t|\mathbf{x}_0,t_0) = \sum_{i=1}^{d} \frac{\partial^2}{\partial x_i^2} p_*(x_i,t|x_{0,i},t_0) \prod_{j\neq i}^{d} p_*(x_j,t|x_{0,j},t_0), \tag{18b}$$

and

$$\frac{\partial}{\partial t} p(\mathbf{x},t|\mathbf{x}_0,t_0) = \sum_{i=1}^{d} \frac{\partial}{\partial t} p_*(x_i,t|x_{0,i},t_0) \prod_{j\neq i}^{d} p_*(x_j,t|x_{0,j},t_0), \tag{18c}$$

it follows by substituting these expressions into the diffusion Eq. (16) that

$$\sum_{i=1}^{d}\left[\frac{\partial}{\partial t}p_*(x_i,t|x_{0,i},t_0) - D\frac{\partial^2}{\partial x_i^2}p_*(x_i,t|x_{0,i},t_0)\right]\prod_{j\neq i}^{d}p_*(x_j,t|x_{0,j},t_0) = 0. \tag{19}$$

Here (and below) the notation $\prod_{j\neq i}^{d}$ indicates a product-operator over the index j from 1 to d, but excluding $j = i$. The expression in the square brackets of Eq. (19) is identical zero for all i's since $p_*(x_i,t|x_{0,i},t_0)$ is the solution pf the one dimensional diffusion equation. Therefore, also the left-hand-side of Eq. (19) is zero showing that the expression in Eq. (2) is a solution to the diffusion equation.

Writing out the full solution for the d-dimensional diffusion equation gives [with Eq. (3)]

$$p(\mathbf{x},t|\mathbf{x}_0,t_0) = \frac{1}{[4\pi D(t-t_0)]^{\frac{d}{2}}}\exp\left\{-\frac{(\mathbf{x}-\mathbf{x}_0)^2}{4D(t-t_0)}\right\}. \tag{20}$$

b) A straight forward calculation based on the definition of the average, using Eq. (20), $t_0 = 0$ and $\mathbf{x}_0 = \mathbf{x}(t_0) = 0$ gives

$$\begin{aligned}
\Delta(t) &= \left\langle [\mathbf{x}(t) - \mathbf{x}(0)]^2 \right\rangle \\
&= \int \mathrm{d}^d x\; \mathbf{x}^2 p(\mathbf{x},t|\mathbf{0},0) \\
&= \int \mathrm{d}^d x\; \left[\sum_{i=1}^{d} x_i^2\right]\prod_{j=1}^{d}p_*(x_j,t|0,0) \\
&= \sum_{i=1}^{d}\left[\int \mathrm{d}x_i\; x_i^2 p_*(x_i,t|0,0)\prod_{j\neq i}^{d}\int \mathrm{d}x_j\; p_*(x_j,t|0,0)\right].
\end{aligned} \tag{21}$$

Each of the integrals over x_j evaluates to one, since $p_*(x_j,t|0,0)$ is normalized. The integral over x_i is (shown by using formulas from the integration table or using partial integration twice)

$$\int \mathrm{d}x_i\; x_i^2 p_*(x_i,t|0,0) = 2Dt, \tag{22}$$

so that the expression in the square brackets simply is $2Dt$ independent of the value of the index i.

Hence, after performing the sum we arrive at

$$\Delta(t) = 2dDt, \tag{23}$$

where the factor d comes from the summation. This was the expression that should be derived. It should be noted that if $t_0 \neq 0$ then a one would get $\Delta(t) = 2dD(t-t_0)$ that scales like $\Delta(t) \simeq 2dDt$ in the long time limit. However, with $t_0 = 0$, this relation is satisfied for all times.

c) From the the definition

$$\Delta(t) = \left\langle [\mathbf{x}(t) - \mathbf{x}(0)]^2 \right\rangle, \tag{24}$$

we obtain by direct differentiation since ensemble averaging and time-differentiation are commuting operations

$$\begin{aligned} \frac{\mathrm{d}\Delta(t)}{\mathrm{d}t} &= \left\langle \frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t} \cdot 2\left[\mathbf{x}(t) - \mathbf{x}(0)\right] \right\rangle \\ &= 2\left\langle \mathbf{v}(t) \cdot \int_o^t \mathrm{d}t' \frac{\mathrm{d}\mathbf{x}(t')}{\mathrm{d}t'} \right\rangle \\ &= 2\int_0^t \mathrm{d}t' \left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle, \end{aligned} \tag{25}$$

which was what should be shown. In the last transition we have used the fundamental theorem of differentiation.

d) At equilibrium, the velocity, $\mathbf{v}(t)$, of the Brownian particle constitutes a stationary stochastic process. Then the two-point correlation function $\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \rangle$, can *only* depend on the time difference between t and t', and not explicitly on t and t'.

Since at equilibrium $\mathbf{v}(t)$ is a stationary stochastic process, it follows that

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle = \left\langle \mathbf{v}(t - t') \cdot \mathbf{v}(0) \right\rangle. \tag{26}$$

Thus, from the expression for $\mathrm{d}\Delta(t)/\mathrm{d}t$ derived in the previous sub-problem, Eq. (27), one gets

$$\begin{aligned} \frac{\mathrm{d}\Delta(t)}{\mathrm{d}t} &= 2\int_0^t \mathrm{d}t' \left\langle \mathbf{v}(t - t') \cdot \mathbf{v}(0) \right\rangle \\ &= 2\int_t^0 (-\mathrm{d}t'') \left\langle \mathbf{v}(t'') \cdot \mathbf{v}(0) \right\rangle \\ &= 2\int_0^t \mathrm{d}t'' \left\langle \mathbf{v}(t'') \cdot \mathbf{v}(0) \right\rangle, \end{aligned} \tag{27}$$

where we in the 2nd transition have introduced the new variable $t'' = t - t'$.

e) We have already shown that for long times $\Delta(t) = 2dDt$, so it readily follows that

$$\frac{\mathrm{d}\Delta(t)}{\mathrm{d}t} = 2dD. \tag{28}$$

Combining this result with the expression found in Eq. (27) for $\mathrm{d}\Delta(t)/\mathrm{d}t$, one gets

$$2dD \simeq 2\int_0^t \mathrm{d}t'' \left\langle \mathbf{v}(t'') \cdot \mathbf{v}(0) \right\rangle. \tag{29}$$

Rearranging this expression, and taking the limit $t \to \infty$, gives

$$D = \frac{1}{d}\int_0^\infty \mathrm{d}t'' \left\langle \mathbf{v}(t'') \cdot \mathbf{v}(0) \right\rangle. \tag{30}$$

Now, denoting the integration variable t (instead of t'') one gets the Einstein-Green-Kubo relation that we intended to derive

$$D = \frac{1}{d}\int_0^\infty \mathrm{d}t \left\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\right\rangle . \tag{31}$$

Problem 2.

a) Let $\mathbf{x}(t)$ be the position vector of the Brownian particle of mass m in d-dimensional space. The friction that the particle feels from the surrounding liquid is characterized by the friction coefficient γ. The random impact due to the bath we denote by $\mathbf{R}(t)$, and the standard assumption (that we will follow as well) is that this force is uncorrelated. With these quantities, the Langevin equation for the particle that follows from Newtons 2nd law reads

$$m\ddot{\mathbf{x}}(t) = -\,\gamma m\dot{\mathbf{x}}(t) + \mathbf{R}(t). \tag{32}$$

We have assumed when writing this equation that there is no external potential. Using that the velocity of the particle is defined as

$$\mathbf{v}(t) = \dot{\mathbf{x}}(t), \tag{33}$$

it follows that

$$\dot{\mathbf{v}}(t) = -\,\gamma\mathbf{v}(t) + \boldsymbol{\xi}(t), \tag{34}$$

where we have introduced a "mass normalized" stochastic force

$$\boldsymbol{\xi}(t) = \frac{\mathbf{R}(t)}{m}. \tag{35}$$

b) The solution of the stochastic differential equation (34) follows by direct integration:

$$\mathbf{v}(t) = \mathbf{v}_0\mathrm{e}^{-\gamma t} + \int_0^t \mathrm{d}t'\mathrm{e}^{-\gamma(t-t')}\boldsymbol{\xi}(t'); \qquad \mathbf{v}_0 = \mathbf{v}(0). \tag{36}$$

To see this, let us multiply the stochastic ordinary differential equation by the integrating factor $\exp(\gamma t)$, so that Eq. (34 can be written in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\mathrm{e}^{\gamma t}\mathbf{v}(t)\right] = \mathrm{e}^{\gamma t}\boldsymbol{\xi}(t). \tag{37}$$

By integrating this equation over time from 0 (there the initial condition is specified) to some time t, one gets

$$\int_0^t \mathrm{d}t'\frac{\mathrm{d}}{\mathrm{d}t'}\left[\mathrm{e}^{\gamma t'}\mathbf{v}(t')\right] = \mathrm{e}^{\gamma t}\mathbf{v}(t) - \mathbf{v}(0) = \int_0^t \mathrm{d}t'\mathrm{e}^{\gamma t'}\boldsymbol{\xi}(t'),$$

or after some minor manipulations ($\mathbf{v}_0 = \mathbf{v}(0)$)

$$\mathbf{v}(t) = \mathbf{v}_0\mathrm{e}^{-\gamma t} + \int_0^t \mathrm{d}t'\mathrm{e}^{-\gamma(t-t')}\boldsymbol{\xi}(t'). \tag{38}$$

Here the first term on the right-hand-side is the homogeneous solution while the second is the particular solution.

Alternatively, and instead of deriving this solution, you can also show that Eq. (11) is a solution to the stochastic ordinary differential equation (9) by substituting it into the differential equation.this solution into the into For the derivative of the velocity one obtains

$$\dot{\mathbf{v}}(t) = -\gamma\mathbf{v}_0 \mathrm{e}^{-\gamma t} - \gamma\int_0^t \mathrm{d}t' \mathrm{e}^{-\gamma(t-t')}\boldsymbol{\xi}(t') + \boldsymbol{\xi}(t), \tag{39}$$

where we have used the fundamental theorem of calculus. From Eq. (39) it readily follows that indeed velocity as given by Eq. (36) satisfies the stochastic ODE for $\mathbf{v}(t)$.

Note that if you have trouble to arrive at expression (39), it might be illuminating to realize that the particular solution can be rewritten as

$$\int_0^t \mathrm{d}t' \mathrm{e}^{-\gamma(t-t')}\boldsymbol{\xi}(t') = \mathrm{e}^{-\gamma t}\int_0^t \mathrm{d}t' \mathrm{e}^{\gamma t'}\boldsymbol{\xi}(t'), \tag{40}$$

where the derivative with respect to time of the right-hand-side of this equation can be performed by the product rule.

c) The velocity-velocity correlation function of the particle is defined by $\langle \mathbf{v}(t)\cdot\mathbf{v}(t')\rangle$. Using the solution (36) one gets

$$\begin{aligned}
\left\langle \mathbf{v}(t)\cdot\mathbf{v}(t')\right\rangle &= \left\langle \left[\mathbf{v}_0 \mathrm{e}^{-\gamma t} + \int_0^t \mathrm{d}\tau \mathrm{e}^{-\gamma(t-\tau)}\boldsymbol{\xi}(\tau)\right]\cdot\left[\mathbf{v}_0 \mathrm{e}^{-\gamma t'} + \int_0^{t'} \mathrm{d}\tau' \mathrm{e}^{-\gamma(t'-\tau')}\boldsymbol{\xi}(\tau')\right]\right\rangle \\
&= v_0^2 \mathrm{e}^{-\gamma(t+t')} + \left\langle \int_0^t \mathrm{d}\tau \int_0^{t'} \mathrm{d}\tau'\; \mathrm{e}^{-\gamma(t-\tau)} \mathrm{e}^{-\gamma(t'-\tau')}\boldsymbol{\xi}(\tau)\cdot\boldsymbol{\xi}(\tau')\right\rangle \\
&= v_0^2 \mathrm{e}^{-\gamma(t+t')} + \int_0^t \mathrm{d}\tau \int_0^{t'} \mathrm{d}\tau'\; \mathrm{e}^{-\gamma(t-\tau)} \mathrm{e}^{-\gamma(t'-\tau')}\underbrace{\left\langle\boldsymbol{\xi}(\tau)\cdot\boldsymbol{\xi}(\tau')\right\rangle}_{=C\delta(\tau-\tau')} \\
&= v_0^2 \mathrm{e}^{-\gamma(t+t')} + C\int_0^t \mathrm{d}\tau \int_0^{t'} \mathrm{d}\tau'\; \mathrm{e}^{-\gamma(t-\tau)} \mathrm{e}^{-\gamma(t'-\tau')}\delta(\tau-\tau')
\end{aligned} \tag{41}$$

where we have neglected terms linear in $\langle\boldsymbol{\xi}\rangle$ since such terms are zero, used that integration and ensemble averages commute, and the properties of the correlation $\langle\boldsymbol{\xi}(\tau)\cdot\boldsymbol{\xi}(\tau')\rangle$. In proceeding, one has to take care since one does not know a priory if $t\leq t'$ or $t'\leq t$.

Let us first assume that $t\leq t'$. Then we first perform the integral over τ' to make sure that the delta-function will give a contribution when $\tau=\tau'$. One gets

$$\begin{aligned}
\left\langle \mathbf{v}(t)\cdot\mathbf{v}(t')\right\rangle &= v_0^2 \mathrm{e}^{-\gamma(t+t')} + C\int_0^t \mathrm{d}\tau\; \mathrm{e}^{-\gamma(t+t'-2\tau)} \\
&= v_0^2 \mathrm{e}^{-\gamma(t+t')} + C\mathrm{e}^{-\gamma(t+t')}\int_0^t \mathrm{d}\tau\; \mathrm{e}^{2\gamma\tau} \\
&= v_0^2 \mathrm{e}^{-\gamma(t+t')} + \frac{C}{2\gamma}\mathrm{e}^{-\gamma(-t+t')} - \frac{C}{2\gamma}\mathrm{e}^{-\gamma(t+t')}, \qquad t\leq t'.
\end{aligned} \tag{42}$$

Instead if $t' \leq t$, we perform the τ integral first. The calculation is completely similar to the one presented above, and the result reads

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle = v_0^2 \mathrm{e}^{-\gamma(t+t')} + \frac{C}{2\gamma}\mathrm{e}^{-\gamma(t-t')} - \frac{C}{2\gamma}\mathrm{e}^{-\gamma(t+t')}, \qquad t' \leq t. \tag{43}$$

Hence, we observe that independent of $t \leq t'$ or $t' \leq t$ we may write write

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle = v_0^2 \mathrm{e}^{-\gamma(t+t')} + \frac{C}{2\gamma}\mathrm{e}^{-\gamma|t-t'|} - \frac{C}{2\gamma}\mathrm{e}^{-\gamma(t+t')}, \tag{44}$$

which is the final result for the velocity-velocity correlation function.

d) For long times, $t + t' \gg 1/\gamma$, the first and last term of the correlation function (44) can be neglected and one obtains the *stationary* or *equilibrium* correlation function given by

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle_{\text{eq}} = \frac{C}{2\gamma}\mathrm{e}^{-\gamma|t-t'|}, \tag{45}$$

that only depending on the time difference $|t - t'|$ as it should.

e) From Eq. (45) it follows that at equilibrium the velocity-velocity correlations are exponential. Then according to Doobs theorem the process, since it is non-trivial, should be an Ornstein-Uhlenbeck process.

To determine the constant C we start by taking the equal time ($t = t'$) equilibrium correlation

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t) \right\rangle_{\text{eq}} = \left\langle \mathbf{v}^2 \right\rangle_{\text{eq}} = \frac{C}{2\gamma}. \tag{46}$$

According to the equipartition theorem one has at equilibrium at absolute temperature T that

$$\frac{1}{2} m \left\langle \mathbf{v}^2 \right\rangle_{\text{eq}} = d\frac{1}{2}k_B T, \tag{47}$$

where k_B is Boltzmann's constant.

Combining these two result gives

$$C = d\frac{2\gamma k_B T}{m}. \tag{48}$$

The final expression for the equilibrium velocity-velocity correlation function therefore becomes:

$$\left\langle \mathbf{v}(t) \cdot \mathbf{v}(t') \right\rangle_{\text{eq}} = d\frac{k_B T}{m}\mathrm{e}^{-\gamma|t-t'|}, \tag{49}$$

f) Since we have available the equilibrium velocity-velocity correlation function (49) we can directly calculate the diffusion constant from the Einstein-Green-Kubo relation.

One gets

$$
\begin{aligned}
D &= \frac{1}{d}\int_0^\infty \mathrm{d}t\, \langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle_{\mathrm{eq}} \\
&= \frac{k_B T}{m}\int_0^\infty \mathrm{d}t \mathrm{e}^{-\gamma t} \\
&= \frac{k_B T}{m\gamma}.
\end{aligned}
\tag{50}
$$

This is the famous Einstein relation that we derived by another method in the lectures. Notice that this relation is independent of the dimension of space.