New York University
Physics Department
Class GA.2061 "Non-Equilibrium Statistical Physics", Fall 2021

Home Work 06 *Solutions*

1. We have seen already several derivations of the Einstein relation between friction coefficient and diffusion coefficient. Derive it directly from the Fluctuation-Dissipation theorem.

   Hint: If you encounter a response function that does not go to zero at long times, and thus is not welcoming for a Fourier transform, then you can insert there a factor $e^{-\epsilon t}$ and send $\epsilon \to 0$ at the very end.

   Solution

   For the overdamped system, velocity of a particle follows the applied force, $v(t) = f(t)/\zeta$. That means, particle position is given by $x(t) = \int_{-\infty}^{t} \frac{1}{\zeta} f(t')dt'$. That means, response function is $\chi(t) = 1/\zeta$ at $t > 0$ and $\chi(t) = 0$ at $t < 0$. To make integrals converging, it is convenient to write

   $$\chi(t) = \begin{cases} \frac{e^{-\epsilon t}}{\zeta} & \text{for } \ t > 0 \\ 0 & \text{for } \ t < 0 \end{cases} \tag{1}$$

   where ϵ will have to be sent to zero at the very end. From here, $\chi_\omega = \frac{1/\zeta}{\epsilon - \imath\omega}$ and $\chi''_\omega = \frac{\omega/\zeta}{\epsilon^2+\omega^2}$. Based on FDT, $\left(x^2\right)_\omega = (2T/\omega)\, \chi''_\omega$, we see that $\left(x^2\right)_\omega = \frac{2T/\zeta}{\epsilon^2+\omega^2}$. We can Fourier transform it back, according to Wiener-Khinchin theorem, this will be the autocorrelation function of $x(t)$: $\langle x(t)x(0)\rangle = -\frac{T}{\zeta}\frac{e^{-\epsilon|t|}}{\epsilon}$. This looks a bit scary, for it does not behave properly in the $\epsilon \to 0$ limit.

   But this correlation is not exactly what we need, we need mean square displacement as a function of time, $\left\langle (\Delta x)^2 \right\rangle \equiv \left\langle (x(t) - x(0))^2 \right\rangle = 2\left\langle (x(0))^2 \right\rangle - 2\left\langle x(t)x(0)\right\rangle$ (where we took into account that $\left\langle (x(0))^2 \right\rangle = \left\langle (x(t))^2 \right\rangle$). Using the above result (still with ϵ finite!), we arrive at

   $$\left\langle (\Delta x)^2 \right\rangle = 2\left\langle (x(0))^2 \right\rangle - 2\left\langle x(t)x(0)\right\rangle = -\frac{2T}{\zeta\epsilon} + \frac{2T}{\zeta\epsilon}e^{-\epsilon|t|} \ . \tag{2}$$

   And here finally we can safely send $\epsilon \to 0$, with the expected result $\left\langle (\Delta x)^2 \right\rangle = 2(T/\zeta)t$. First of all, mean squared displacement linear in time is the signature of simple diffusion. Second of all, we read out the diffusion coefficient, since $\left\langle (\Delta x)^2 \right\rangle = 2Dt$, so $D = T/\zeta$, which is exactly the requisite Einstein relation.

2. Considering nanopore, we have seen that applied voltage can drive not only electric current, but also flow of liquid. Similarly, applied pressure gradient can drive flow of liquid and also electric current. In general, off-diagonal Onsager coefficients describe the flux of x_i driven by "force" X_j, with $i \neq j$. There is the so-called Curie principle, you can read about it on the web, it is usually described as somewhat philosophical (Wikipedia says "the symmetries of the causes are to be found in the effects"). In the more specific context of Onsager theory, symmetry of the "force" (scalar, vector, tensor, etc) should be the same as symmetry of the flux. One example of purely scalar process would be chemical reaction, example of vector process would be an electric current in a bulk material. Give example of conjugate Onsager pair of scalar processes, and separate example conjugate pair of vector processes. How is it possible that molecular motor realizes conjugation of chemical reaction (scalar) with motion? Is not motion a vector? Would molecular motor be able to function without a "railroad" on which it moves?

   Solution

   Two conjugate chemical reactions would be the simplest example of two scalar processes. Diffusion driven by gradient of concentration and heat transfer driven by the gradient of temperature is an example of conjugate vector processes.

   Vector process, such as mechanical overdamped motion under the action of a force, $\dot{\mathbf{x}} = \frac{1}{\zeta}\mathbf{f}$, cannot be conjugate to a scalar process, such as $\dot{r} = -\lambda\Delta\mu$. This is mathematically obvious, you cannot add to the equation $\dot{\mathbf{x}} = \frac{1}{\zeta}\mathbf{f}$ a new term proportional to $\Delta\mu$ in the right hand side, because $\Delta\mu$ is a scalar and you cannot in any way combine it with vector – unless, there is a "railroad" and your vector equation is reduced to the projection to 1D,

   Molecular motor needs constraints that allows it to move only along one-dimensional line, effectively making its motion scalar, otherwise it cannot be conjugate to chemical reaction.

3. For a harmonic oscillator placed in a viscous thermostat, use Fluctuation-Dissipation Theorem to find
   (a) the time-dependent position-position correlation function;
   (b) the time dependent velocity-coordinate correlation function.

Solution

From FDT, we know that $(x^2)_\omega = \frac{2T}{\omega}\chi''_\omega$, and we also know χ''_ω; therefore

$$\langle x(t)x(0)\rangle = 2T\xi \int_{-\infty}^{\infty} \frac{e^{\imath\omega t}}{(-m\omega^2+k)^2+\xi^2\omega^2}\frac{d\omega}{2\pi} . \tag{3}$$

This integral is evaluated using complex plane of ω. The poles of the integrand were investigated before, upon doing algebra we arrive at the result. For weakly dumped oscillator $\xi^2 < 4km$ we have

$$\langle x(t)x(0)\rangle = \frac{T}{k}e^{-\frac{\xi}{2m}t}\left[\frac{\xi}{\sqrt{4km-\xi^2}}\sin\left(\frac{\sqrt{4km-\xi^2}}{2m}t\right)+\cos\left(\frac{\sqrt{4km-\xi^2}}{2m}t\right)\right] . \tag{4}$$

For strongly dumped oscillator with $\xi^2 > 4km$ the result reads

$$\langle x(t)x(0)\rangle = \frac{T}{k}e^{-\frac{\xi}{2m}t}\left[\frac{\xi}{\sqrt{\xi^2-4km}}\sinh\left(\frac{\sqrt{\xi^2-4km}}{2m}t\right)+\cosh\left(\frac{\sqrt{\xi^2-4km}}{2m}t\right)\right] . \tag{5}$$

As a sanity check, in both cases $\langle x(0)x(0)\rangle = T/k$.

In the velocity case, $A = v$ and $B = x$, so we have to find the new susceptibility $\chi(t)$ or χ_ω which describes the response of velocity of the force conjugate to coordinate, which is the regular force. Simple analysis indicates that $\chi^{new}_\omega = -\imath\omega\chi_\omega$. Therefore,

$$\langle v(t)x(0)\rangle = -2\imath T\int_{-\infty}^{\infty}\frac{\Re\chi^{new}_\omega}{\omega}e^{\imath\omega t}\frac{d\omega}{2\pi} = -2\imath T\xi\int_{-\infty}^{\infty}\frac{\omega e^{\imath\omega t}}{(-m\omega^2+k)^2+\xi^2\omega^2}\frac{d\omega}{2\pi} . \tag{6}$$

Analytical structure of this integral in complex plane was investigated before. The result reads

$$\langle v(t)x(0)\rangle = -2Te^{-\frac{\xi}{2m}t}\frac{\sin\left(\frac{\sqrt{4km-\xi^2}}{2m}t\right)}{\sqrt{4km-\xi^2}} \tag{7}$$

for weakly damped case $\xi^2 < 4km$ and

$$\langle v(t)x(0)\rangle = -2Te^{-\frac{\xi}{2m}t}\frac{\sinh\left(\frac{\sqrt{\xi^2-4km}}{2m}t\right)}{\sqrt{\xi^2-4km}} \tag{8}$$

for strongly damped case $\xi^2 > 4km$.

4. Consider some particles diffusing in the medium, and denote $c(\mathbf{r}, t)$ the time- and space-dependent field of their concentration. This field evolves according to the diffusion equation

$$\frac{\partial c}{\partial t} = D\nabla^2 c ; \tag{9}$$

we will study the diffusion equation in greater details later, but for now let us take it for granted. Decompose the field $c(\mathbf{r}, t)$ in spatial Fourier modes

$$c_{\vec{q}}(t) = \int_V c(\vec{r}, t)e^{-\imath\vec{q}\cdot\vec{r}}d\vec{r} \tag{10a}$$

$$c(\vec{r}, t) = \frac{1}{\Delta V}\sum_{\vec{q}} c_{\vec{q}}(\omega)e^{\imath\vec{q}\cdot\vec{r}} \tag{10b}$$

and show how each mode $c_{\vec{q}}(t)$ represents a quantity similar to x_i and evolves according to $\dot{x}_i = -\lambda x_i$. Find relaxation time of every mode. Which modes relax faster? Why? Is there a mode which does not relax at all? Why? Find also correlation function of fluctuations for each mode, at both positive and negative t.

Note: Concentration $c(\vec{r}, t)$ is, of course, real, but modes $c_{\vec{q}}(t)$ are not; accordingly, reasonable correlation for a mode is $\left\langle c_{\vec{q}}(t) c^{\star}_{\vec{q}}(0) \right\rangle$.

Solution

Each mode satisfies $\dot{c}_{\vec{q}}(t) = -Dq^2 c_{\vec{q}}(t)$, therefore, its relaxation time is $\tau_q = 1/Dq^2$. Short wave length (large q) relax faster, because it does not require particles to diffuse very far: with wave length $\sim 1/q$, the time to diffuse this distance is $\sim \lambda^2/D \sim 1/Dq^2$.

The $q = 0$ mode does not relax. This is because $c_{q=0}$ is simply the total number of particles in the system, which is conserved.

Correlation function is even in time, because c has positive time reversal signature: $\left\langle c_{\vec{q}}(t) c^{\star}_{\vec{q}}(0) \right\rangle = \left\langle \left| c_{\vec{q}} \right|^2 \right\rangle e^{-Dq^2 |t|}$.

As regards the equilibrium average $\left\langle \left| c_{\vec{q}} \right|^2 \right\rangle$, if the diffusing particles do not interact to one another (i.e., form an ideal gas), then their spatial correlation function is $\langle \delta c(\mathbf{r}) \delta c(\mathbf{r}') \rangle = c\delta(\mathbf{r} - \mathbf{r}')$ (assuming fluctuating density is $c(\mathbf{r}) = c + \delta c(\mathbf{r})$), which means spatial power spectrum is flat, $\left\langle \left| c_{\vec{q}} \right|^2 \right\rangle = c/V$ does not depend on q, with V system volume.

5. We have analyzed relaxation of transverse velocity in the incompressible fluid governed by the equation:

$$\frac{\partial \mathbf{v}^{\perp}}{\partial t} = \frac{\eta}{\rho} \nabla^2 \mathbf{v}^{\perp} \ . \tag{11}$$

As any quantity, transverse velocity never relaxes to complete zero, because of the thermal motion. Write down the corresponding Langevin equation that describes fluctuations of transverse velocity.

Hint 1: You may find it more convenient to work in the space of wave vectors instead of the real space.

Hint 2: As in all other cases studied before, you may want to use prior results on the equilibrium fluctuations of transverse velocity.

Solution

Relaxation equation of transverse velocity in $\mathbf{k}$ space

$$\frac{\partial \mathbf{v}^{\perp}_{\mathbf{k}}}{\partial t} = -\frac{\eta k^2}{\rho} \mathbf{v}^{\perp}_{\mathbf{k}} \tag{12}$$

is of the same type as familiar $\dot{x} = -\lambda x$. For the latter, we know that the correct noise spectrum is such that $\langle \xi(t) \xi(t') \rangle = 2\lambda \left\langle x^2 \right\rangle_{\text{eq}} \delta(t - t')$. By analogy, and knowing the equilibrium (simultaneous) correlations from the previous assignment, we can conclude for the noise driving transverse velocity fluctuations

$$\langle \xi_{\alpha,\mathbf{k}}(t) \xi_{\alpha',\mathbf{k}'}(t') \rangle = \frac{2k^2 \eta T}{\rho^2} \delta(t - t') \delta(\mathbf{k} + \mathbf{k}') \left(\delta_{\alpha\alpha'} - \frac{k_\alpha k_{\alpha'}}{k^2} \right) \tag{13}$$