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

Home Work 04 *Solutions*

1. Suppose x and f are conjugate variables such that they contribute an extra term in the system Hamiltonian $\delta\mathcal{H} = -xf$, and suppose you know the causal linear response function $\chi(t)$ that describes the response of x to the externally imposed protocol $f(t)$; assume $f(t)$ vanishes both far in the past and far in the future (i.e., force acts during a finite amount of time). Express in terms of χ the amount of energy dissipated into heat in the system due to the work of force f.

   Hint 1: You may want to start establishing Parseval relation[1] (also called identity, theorem, etc) for Fourier transforms: $\int_{-\infty}^{+\infty} A(t)B(t)dt = \int_{-\infty}^{+\infty} A_\omega B_{-\omega}\frac{d\omega}{2\pi}$.

   Hint 2: Since $f(t)$ is real, its Fourier transform (for real ω) has the property $f_\omega^* = f_{-\omega}$.

   Solution

   Since $A(t) = \int A_\omega e^{-i\omega t}\frac{d\omega}{2\pi}$ and similarly $B(t) = \int B_\omega e^{-i\omega t}\frac{d\omega}{2\pi}$, we plug this into the given expression, and re-arrange integrals:

   $$\int_{-\infty}^{+\infty} A(t)B(t)dt = \int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi} A_{\omega_1} B_{\omega_2} \underbrace{\int dt e^{-i\omega_1 t - i\omega_2 t}}_{2\pi\delta(\omega_1+\omega_2)} = \int_{-\infty}^{+\infty} A_\omega B_{-\omega}\frac{d\omega}{2\pi} \tag{1}$$

   This is Parseval identity.

   Now we go back to dissipation. Total dissipated energy during the entire time of experiment is $Q = -\int x(t)\frac{df}{dt}dt$. We use Parseval relation along with $\left(\dot{f}\right)_\omega = -i\omega f_\omega$ and write

   $$Q = -\int \underbrace{x_\omega}_{\chi_\omega f_\omega} \cdot \underbrace{\left(\dot{f}\right)_{-\omega}}_{i\omega f_{-\omega}} \frac{d\omega}{2\pi} = -\int \chi_\omega i\omega f_\omega f_{-\omega}\frac{d\omega}{2\pi} \tag{2}$$

   Here we separate integration over positive and negative frequencies to get

   $$Q = -\int_0^\infty \chi_\omega i\omega f_\omega f_{-\omega}\frac{d\omega}{2\pi} - \int_0^\infty \chi_{-\omega'} i(-\omega') f_{-\omega'} f_{\omega'}\frac{d\omega'}{2\pi} = \int_0^\infty \left[\chi_{-\omega} - \chi_\omega\right] i\omega f_\omega f_{-\omega}\frac{d\omega}{2\pi} \tag{3}$$

   Separating here real and imaginary parts of $\chi_\omega = \chi_\omega' + i\chi_\omega''$, we finally get

   $$Q = 2\int_0^\infty \omega\chi_\omega'' |f_\omega|^2 \frac{d\omega}{2\pi} \tag{4}$$

   This is the final answer. As expected, it is the sum of contributions from various frequencies; for every frequency, it is proportional to $|f_\omega|^2$; it is also proportional to $\omega\chi_\omega''$, such that integral can be extended to all positive and negative frequencies (by absorbing the 2 coefficient). Thus, dissipation is controlled by the imaginary part of the response function.

2. Response function of a harmonic oscillator in frequency representation is easy to find:

   $$\chi_\omega = \frac{1}{-m\omega^2 - i\omega\zeta + k} \ . \tag{5}$$

   Find $\chi(t)$. Does it satisfy causality? Find both real and imaginary part of response function, χ_ω' and χ_ω'' and plot them as a function of (real) frequency. *Note:* to make plots, do not assume arbitrary, out-of-nowhere, numerical values of parameters k, m, ζ, T, etc; instead, represent quantities of interest as unitless combinations. Indicate the unitless parameters that characterize the system.

   Suppose driving force is purely harmonic, $f_0\cos\Omega t$. Write down $x(t)$, as an explicitly real quantity, and explain why χ_ω' and χ_ω'' describe "in phase" and "out of phase" response.

   Solution

To facilitate plotting, I write down the unitless quantity $k\chi$:

$$k\chi'_\omega = \frac{1 - \left(\frac{\omega}{\omega_0}\right)^2}{\left[1 - \left(\frac{\omega}{\omega_0}\right)^2\right]^2 + \left[\tau\omega_0\frac{\omega}{\omega_0}\right]^2} \quad ; \quad k\chi''_\omega = \frac{\tau\omega_0\frac{\omega}{\omega_0}}{\left[1 - \left(\frac{\omega}{\omega_0}\right)^2\right]^2 + \left[\tau\omega_0\frac{\omega}{\omega_0}\right]^2} \quad . \tag{6}$$

Here $\omega_0 = \sqrt{k/m}$ is the oscillator's own frequency, while $\tau = \zeta/k$ is the decay time. The plots are given in the figure 1.

To perform the inverse Fourier transform and find $\chi(t)$, the most convenient tool is complex plane integration. This requires viewing ω as a complex variable in the integral:

$$\chi(t) = \int_{-\infty}^{\infty} \chi_\omega e^{-\imath\omega t}\frac{d\omega}{2\pi} \quad . \tag{7}$$

Depending on the sign of t, we can close integration contour through upper or lower infinite arch, as follows:

$$\chi(t) = \begin{cases} 2\pi\imath\,[\text{Sum of residues in the upper half plane}] & \text{if } t < 0 \\[2mm] -2\pi\imath\,[\text{Sum of residues in the lower half plane}] & \text{if } t > 0 \end{cases} \tag{8}$$

Singularities of χ_ω occur where the denominator in formula (5) vanishes, which is at $\omega = \frac{-\imath\zeta\pm\sqrt{4km-\zeta^2}}{2m}$. It is more conveniently written as $\frac{\omega}{\omega_0} = -\imath\frac{\tau\omega_0}{2} \pm \sqrt{1 - \left(\frac{\tau\omega_0}{2}\right)^2}$. These two roots deliver two poles to χ_ω. Where are they on the complex plane ω? If $\tau\omega_0 < 2$ ($\zeta < 4km$), then they are located like red dots in figure 3, while in the opposite case of strong friction, when $\tau\omega_0 > 2$, the two poles are located like green dots. In either case, all poles are located in the lower half plane, as it must be to guarantee causal character of $\chi(t)$, i.e., that $\chi(t)|_{t<0} = 0$. Indeed, there are no singularities in the upper half plane. Computing residues, we arrive at

$$\chi(t) = \begin{cases} 0 & \text{if } t < 0 \\[3mm] \frac{1}{m}e^{-\frac{1}{2}\omega_0^2\tau t}\dfrac{\sin\left[\sqrt{1-\left(\frac{\omega_0\tau}{2}\right)^2}\,\omega_0 t\right]}{\sqrt{1-\left(\frac{\omega_0\tau}{2}\right)^2}} & \text{if } t > 0 \end{cases} \tag{9}$$

3. Consider Rouse model of a polymer chain. That is a chain of $N \gg 1$ beads, each moving in an immobile solvent with friction coefficient ζ, and each connected to its two neighbors by Hookean springs. If position vectors of
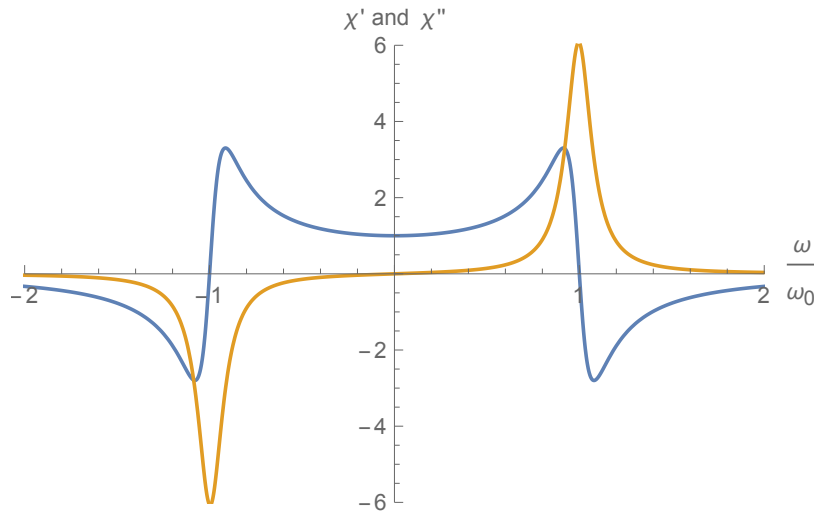

FIG. 1. Real and imaginary parts of the response function for a harmonic oscillator. Abscissa is ω/ω_0, with $\omega_0 = \sqrt{k/m}$, vertical axis is χ in units of $1/k$. Dissipation parameter ζ is chosen such that $\tau\omega_0 = 0.165$, where $\tau = \zeta/k$.

bead i are $\{\mathbf{r}_i\}$, then (neglecting inertia) equations of motion read (for every i, $1 < i < N$)

$$0 = -\zeta\dot{\mathbf{r}}_i + k\left(\mathbf{r}_{i+1} - \mathbf{r}_i\right) + k\left(\mathbf{r}_{i-1} - \mathbf{r}_i\right) + \vec{\xi}_i(t) \ , \tag{10}$$

where $\vec{\xi}_i(t)$ is Langevin random force. Random forces for different beads are not correlated to one another; therefore, random force satisfies

$$\langle\xi_{i\alpha}(t)\xi_{j\beta}(t')\rangle = 2\zeta T\delta_{ij}\delta_{\alpha\beta}\delta(t-t') \ . \tag{11}$$

The $2\zeta T$ coefficient we studied in the single particle case.

(a) Transform equation of motion (10) into a differential equation, by replacing $\mathbf{r}_{i+1} - \mathbf{r}_i \simeq \partial\mathbf{r}_i/\partial i$ etc. This equation operates with time dependent monomer position $\mathbf{r}(t,i)$.

(b) Each monomer in the Rouse model experiences forces from two neighbors, but end monomers 1 and N do not. To account for that, let us formally introduce fictitious monomers 0 and $N+1$, with the convention $\mathbf{r}_0 \equiv \mathbf{r}_1$ and $\mathbf{r}_{N+1} \equiv \mathbf{r}_N$; then equation (10) is valid for all monomers from 1 to N. Based on that, show that boundary conditions for differential version of equation (10) read $\frac{\partial\mathbf{r}}{\partial i}\big|_{i=0} = \frac{\partial\mathbf{r}}{\partial i}\big|_{i=N} = 0$.

(c) Show that $\mathbf{r}(t,i)$ can be decomposed into modes consistent with boundary conditions as

$$\mathbf{r}(t,i) = \mathbf{y}_0(t) + 2\sum_{p=1}^{\infty}\mathbf{y}_p(t)\cos\frac{\pi pi}{N} \ . \tag{12}$$

(d) Find Langevin equations for all modes $\mathbf{y}_p(t)$ and find correlators for the corresponding random forces.

(e) Show that all motion of Rouse polymer decomposes into independent relaxation of modes. Find relaxation times for all modes.

Solution

Viewing link number along the chain, i, as a continuous variable, equation of motion (10) becomes

$$0 = -\zeta\frac{\partial\mathbf{r}_i}{\partial t} + k\frac{\partial^2\mathbf{r}_i}{\partial i} + \vec{\xi}_i(t) \ , \tag{13}$$

with boundary conditions stated in the problem, $\frac{\partial\mathbf{r}}{\partial i}\big|_{i=0} = \frac{\partial\mathbf{r}}{\partial i}\big|_{i=N} = 0$, these boundary conditions express the simple physical fact that while each non-end monomer in the chain experiences two elastic forces from two neighbors, each of the two end monomers experiences only force from the side and no force from the absent neighbor. These boundary conditions imply that expanding $\mathbf{r}_i$ as a function of i into a Fourier series should use only cosines, not sines, as suggested in formula (12). Plugging this expansion in the equation (13) yields

$$0 = -\zeta\frac{\partial\mathbf{y}_0}{\partial t} + \sum_{p=1}^{\infty}\left[-2\zeta\frac{\partial\mathbf{y}_p}{\partial t} - 2k\left(\frac{\pi p}{N}\right)^2\mathbf{y}_p\right]\cos\frac{\pi pi}{N} + \vec{\xi}_i(t) \ , \tag{14}$$

As always with Fourier transforms and other expansions over eigenfunctions, we use the fact that $\cos\pi pi/N$ and $\cos\pi qi/N$ are orthogonal , i.e., $\int_0^N\cos(\pi pi/N)\cos(\pi qi/N)di = (N/2)\delta_{pq}$. We multiply the above equation by $\cos(\pi qi/N)$ and integrate over i. The resulting equations are easily massaged to the following form:

$$
\begin{aligned}
\zeta N\frac{\partial\mathbf{y}_0}{\partial t} &= \underbrace{\int_0^N\vec{\xi}_i(t)di}_{\vec{\Xi}_0(t)} \ , & q = 0 \\[2mm]
2\zeta N\frac{\partial\mathbf{y}_q}{\partial t} &= -\frac{\pi^2 kq^2}{N}\mathbf{y}_q + \underbrace{2\int_0^N\vec{\xi}_i(t)\cos\frac{\pi qi}{N}di}_{\vec{\Xi}_q(t)} \ , & q \neq 0
\end{aligned}
\tag{15}
$$

Thus, all modes $\mathbf{y}_p(t)$ are decoupled, and each is driven by the new noise. First of all, it is immediately seen that on average each new noize is zero, $\left\langle\vec{\Xi}_q(t)\right\rangle = 0$. And for the second moment we get

$$
\begin{aligned}
\langle\Xi_{\alpha,0}(t)\Xi_{\beta,0}(t')\rangle &= \int_0^N di\int_0^N dj\ \underbrace{\langle\xi_{\alpha,i}(t)\xi_{\beta,j}(t')\rangle}_{2\zeta T\delta_{\alpha\beta}\delta(i-j)\delta(t-t')} = 2\zeta NT\delta_{\alpha\beta}\delta(t-t') \\[2mm]
\langle\Xi_{\alpha,p}(t)\Xi_{\beta,q}(t')\rangle &= 4\int_0^N di\int_0^N dj\ \underbrace{\langle\xi_{\alpha,i}(t)\xi_{\beta,j}(t')\rangle}_{2\zeta T\delta_{\alpha\beta}\delta(i-j)\delta(t-t')}\cos\frac{\pi pi}{N}\cos\frac{\pi qj}{N} = 4\zeta NT\delta_{\alpha\beta}\delta(t-t')\delta_{pq}
\end{aligned}
\tag{16}
$$

Noises for different modes are thus independent, which means modes are truly decoupled. As it should be, the amplitude of noise for each mode is consistent with friction coefficient, which is ζN for mode $\mathbf{y}_0$ and $2\zeta N$ for all other modes.

To understand the meaning of the mode $\mathbf{y}_0$, we can integrate equation (12) over i (or use inverse Fourier transform) to see $\mathbf{y}_0 = \frac{1}{N}\sum_{i=1}^{N}\mathbf{r}_i$; thus, $\mathbf{y}_0$ is nothing else, but the center of mass of the entire system. As we see, it undergoes the regular diffusion with friction coefficient ζN (N beads experience friction, ζ each) and diffusion coefficient $D = T/\zeta N$.

All other modes describe internal motions in the chain, and they all relax with relaxation times which are read out of the equation $\tau_p = 2\zeta N^2/\pi^2 k p^2$.

For further details, and also for physics applications, see, e.g., in my book [2, Sec. 31] or the book [3].

4. Consider a large volume of a liquid. Although in equilibrium the liquid does not move, its velocity is zero everywhere ($\mathbf{v}(\mathbf{r}) = 0$ in every point $\mathbf{r}$), there are fluctuations. You will have to characterize these fluctuations in space in time. In preparation for the task, in this problem you will have to analyze fluctuations of velocity in equilibrium. Clearly, averaged velocity is zero $\langle v_\alpha(\mathbf{r}, t)\rangle$, for any Cartesian component α and for any point $\mathbf{r}$. Therefore, to describe equilibrium fluctuations you have to find $\langle v_\alpha(\mathbf{r}, t)v_\beta(\mathbf{r}', t)\rangle$, where time moment t is the same in both terms (we can take $t = 0$). For simplicity, assume liquid incompressible and consider hydrodynamic limit in which all distances in question, including the size of liquid element which is used to define velocity $\mathbf{v}$, or the distance between $\mathbf{r}$ and $\mathbf{r}'$, are much larger than molecular sizes. Show that velocity field for an incompressible fluid is purely transverse, meaning that any Fourier component of velocity field $\mathbf{v_k}$ is perpendicular to wave vector, $\mathbf{k}\cdot\mathbf{v_k} = 0$. Find one time (equilibrium) correlation function of transverse velocities in Fourier representation.

Hint: The probability of a fluctuation in equilibrium statistical physics is written as $\sim \exp\left[-W_{\min}/k_B T\right]$, where $W_{\min}$ is the minimal amount of work required to create the fluctuation in question. In this case, if we consider the probability that some volume δV of liquid moves with velocity $\mathbf{v}$, then minimal work is simply the kinetic energy.

Solution

Probability of fluctuation $\exp(-W_{\min}/T)$. In a liquid, minimal work is simply kinetic energy. For volume δV, $W_{\min} = \delta V \rho \vec{v}^2/2$. With such probability distribution, the simultaneous (one time) average reads

$$\langle v_\alpha v_\beta \rangle = \frac{\int \exp\left[-\frac{\delta V \rho \vec{v}^2}{2T}\right] v_\alpha v_\beta d^3\vec{v}}{\int \exp\left[-\frac{\delta V \rho \vec{v}^2}{2T}\right] d^3\vec{v}} = \delta_{\alpha\beta}\frac{T}{\rho\delta V} \ . \tag{17}$$

This is true if both $\mathbf{r}$ and $\mathbf{r}'$ points in $\langle v_\alpha(\mathbf{r}, t)v_\beta(\mathbf{r}', t)\rangle$ are within volume δV. If they are not in the same volume δV, then these velocities, within hydrodynamic approximation, are independent: $\langle v_\alpha(\mathbf{r}, t)v_\beta(\mathbf{r}', t)\rangle = \langle v_\alpha(\mathbf{r}, t)\rangle \langle v_\beta(\mathbf{r}', t)\rangle = 0$. This means

$$\langle v_\alpha(\vec{r}) v_\beta(\vec{r}')\rangle = \delta_{\alpha\beta}\delta(\vec{r} - \vec{r}')\frac{T}{\rho} \ . \tag{18}$$

An equivalent more formal argument would be this. Minimal work to create velocity field $\mathbf{v}(\mathbf{r})$ is $W_{\min} = \int \frac{\rho}{2}\mathbf{v}^2(\mathbf{r})d^3\mathbf{r}$. Therefore, probability distribution of the velocity field can be written as

$$\propto \exp\left[-\int \frac{\rho}{2T}\mathbf{v}_\alpha(\mathbf{r}_1)\mathbf{v}_\beta(\mathbf{r}_2)\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2\right] \tag{19}$$

It is now a matter of dealing with the Gaussian ("path") integral

$$\frac{\int \mathbf{v}_\alpha(\mathbf{r})\mathbf{v}_\beta(\mathbf{r}')\exp\left[-\int \frac{\rho}{2T}\mathbf{v}_\alpha(\mathbf{r}_1)\mathbf{v}_\beta(\mathbf{r}_2)\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2\right] D\mathbf{v}(\mathbf{r})}{\int \exp\left[-\int \frac{\rho}{2T}\mathbf{v}_\alpha(\mathbf{r}_1)\mathbf{v}_\beta(\mathbf{r}_2)\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2\right] D\mathbf{v}(\mathbf{r})} = \delta_{\alpha\beta}\delta(\vec{r} - \vec{r}')\frac{T}{\rho} \ . \tag{20}$$

to see the above result for the correlation function.

In Fourie components, $v_{\alpha\,\vec{k}} = \int v_\alpha(\vec{r})e^{i\vec{k}\cdot\vec{r}}d^3\vec{r}$ this reads

$$\left\langle v_{\alpha\,\vec{k}}\, v_{\beta\,\vec{l}}\right\rangle = (2\pi)^3\delta_{\alpha\beta}\delta\left(\vec{k} + \vec{l}\right)\frac{T}{\rho} \implies (v_\alpha v_\beta)_{\vec{k}} = \delta_{\alpha\beta}\frac{T}{\rho} \ . \tag{21}$$

And here, for the incompressible fluid, we have to take only the transverse component of the velocity field, as explained before. We can extract transverse component in the following way. Start with parallel component $\vec{v}^{\parallel} = \left(\vec{v} \cdot \vec{k}\right) \vec{k}/k^2$ (this is also called a projection operator); therefore, perpendicular component is $\vec{v}^{\perp} = \vec{v} - \vec{v}^{\parallel}$; in Cartesian components, this means $v_{\alpha}^{\perp} = \left(\delta_{\alpha\beta} - \frac{k_{\alpha}k_{\beta}}{k^2}\right) v_{\beta}$. With this in mind, simple algebra leads to

$$\left(v_{\alpha}^{\perp} v_{\beta}^{\perp}\right)_{\vec{k}} = \left(\delta_{\alpha\beta} - \frac{k_{\alpha}k_{\beta}}{k^2}\right) \frac{T}{\rho} \; . \tag{22}$$

For example, if **k** is oriented along x, then

$$\left(v_{\alpha}^{\perp} v_{\beta}^{\perp}\right)_{\vec{k}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & T/\rho & 0 \\ 0 & 0 & T/\rho \end{pmatrix} \; . \tag{23}$$

This simultaneous correlation is what equilibrium statistical mechanics tells us.

5. Using semi-conductor technology, people can make very tiny holes (called "nanopores") in solid-membrane-like materials. For instance, it could be a solid silicon membrane of thickness in the range of 100 nm and a hole of diameter 10 to 20 nm, as shown in Figure 2. This membrane can be submerged in a water solution with salt, and ionic electric current can pass through the nanopore. Bulk solution has positive and negative mobile ions in the exact same amount, it is neutral. Rim of the pore usually has some ionized, i.e., charged groups, of some sign x. As a result, liquid in the pore is charged, it has excess of ions of the sign $-x$. Therefore, when voltage ΔU is applied, liquid starts moving through the pore in the appropriate direction (phenomenon called electroosmosis). But liquid can also be pushed through the pore by applying hydrostatic pressure Δp. Does applying Δp generate an electric (ionic) current? Present phenomenological description of this system. Identify electric resistance of the pore that can be measured if only voltage is applied. Identify hydraulic resistance of the pore that can be measured if only Δp is applied. Plot a diagram in variables ΔU and Δp and identify and explain all possible regimes. Can you say physically what determines the sign of the off-diagonal coefficients? Separately, determine what happens if the entire container is closed, filled with water, and water is incompressible – water has nowhere to go; write down phenomenological equations describing this situation. Does closing container increase or decrease electric resistance?

Hint: Start by writing entropy production and identifying conjugate "forces" and "currents". Knowing that experimenter can apply any ΔU and Δp to their system, and dissipation power must remain positive, find what you can say about phenomenological coefficients characterizing the pore.

Solution

To understand this quantitatively, we consider general situation: there are currents of electric charge J_Q and mass J_M driven by the voltage drop ΔU and pressure drop Δp across the gel pore, respectively. We should start writing down the dissipation (entropy production) rate. The important point is that conjugate to pressure is volume, not mass; therefore, we should write

$$T\dot{S} = J_Q \Delta U + \frac{J_M}{\rho} \Delta p \; , \tag{24}$$

where ρ is the density of liquid, and, therefore, J_M/ρ is the "current of volume". From here we should "read out" the pairs of conjugate currents and thermodynamic forces. Thus, we see that $\Delta p/\rho$ is the thermodynamic force conjugated to the current J_M, while of course ΔU is conjugated to J_Q. Therefore, the phenomenological linear relations between currents and forces have to be written as follows:

$$J_Q = \frac{1}{R}\Delta U + \Gamma\frac{\Delta p}{\rho} \tag{25}$$

$$J_M = \Gamma\Delta U + \frac{1}{\Xi}\Delta p \; , \tag{26}$$

where R, Ξ, and Γ are transport coefficients; Γ is the same in both equations because of Onsager reciprocity relations.

The sign of Γ is controlled by the sign of mobile charges in the pore, opposite to the sign of immobile charges in the rim of the pore.

Second law of thermodynamics dictates that dissipation (24) must be positive-definite for every choice of forces. This means that kinetic coefficients must satisfy

$$R > 0 \ , \quad \Xi > 0 \ , \quad \text{and} \quad \frac{\Gamma^2 R\Xi}{\rho} < 1 \ . \tag{27}$$

Note that in the absence of hydraulic driving, at $\Delta p = 0$, equation (25) represents nothing more than Ohm's law, while in the absence of electric driving, at $\Delta U = 0$ formula (26) represents Darcy's law.

In the system in a closed reservoir we must assume $J_M = 0$: mass does not flow anywhere. Then, formula (26) gives pressure buildup

$$\Delta p = -\Gamma\Xi\Delta U \ ; \tag{28}$$

plugged in (25), this yields

$$J_Q = \frac{\Delta U}{R_{\text{eff}}} \ , \tag{29}$$

with the effective resistance

$$R_{\text{eff}} = \frac{R}{1 - \frac{\Gamma^2 R\Xi}{\rho}} \geq R \ . \tag{30}$$

According to formula (27), the effective resistance is certainly positive and larger than the resistance itself. That means, the effect of coupling between electric and hydraulic currents can, in principle, reduce the electric current, but cannot enhance and cannot reverse it.

I do not show here the diagram of regimes in terms of ΔU and Δp, it is similar to the case of molecular motors.

The problems below are not required and will not be graded, but recommended to those students who want to improve their knowledge and performance.

6. We know that imaginary part of response function describes dissipation power, which is proportional to $\omega\chi''_\omega$. However, if we flip the roles of force f and displacement x, then imaginary part of $1/\chi_\omega$ is equal to $(1/\chi_\omega)'' = -\chi''_\omega/|\chi_\omega|^2$. Does this minus sign signals violation of the Second Law?

Solution

No, there is no violation. The key to understand this is to consider energy of an agent which creates force f.

7. We had a couple of problems about chemical reactions. To make it a bit more specific, make estimates. Consider water inside the volume of a cell nucleus (roughly $10\,\mu$m in size). How many H_2O are there? Assuming the solution is neither basic nor acidic (which is not a good approximation for real cell!), how many HO^- ions are there on average? What is the root-mean-squared average fluctuation of the number of HO^- ions? What is the relaxation time of these fluctuations?
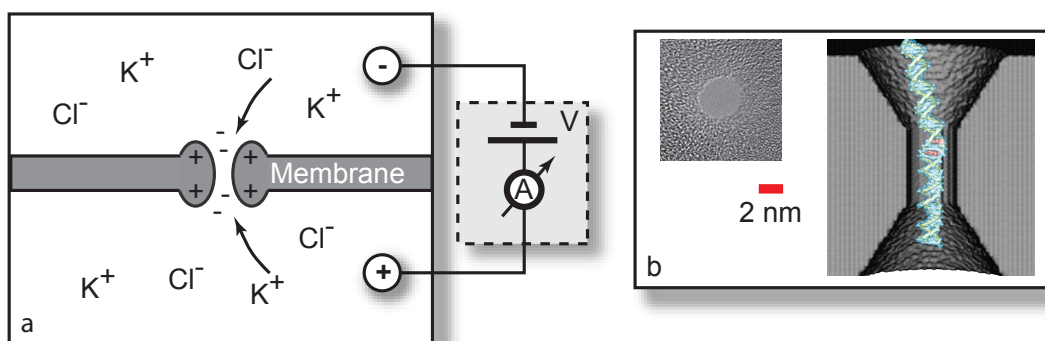

FIG. 2. For problem 5. Panel b represents electron micrograph of a real solid state nanopore and an artist impression of DNA passing through. We in this problem do not think of DNA.

Comment: You may or may not know necessary numbers, such as the relevant equilibrium constant and relevant rate constant. If you do not know them, you should find them. But, of course, you can also find all the answers to all my questions. Therefore, your work will be graded not on just giving the right numbers, but rather on explaining their origin and on making connection to the problems in previous HWs. For theoretical treatment of this reaction, I recommend work [4].

Solution

Pure water density is close to 55 M, where M means moles per liter. That is $55 \times \frac{6 \cdot 10^{23}}{10^{24} \, \text{nm}^3} = 33 \, \text{nm}^{-3}$. Here, density is measured in the number of molecules per unit volume. The number of water molecules in the specified volume is $33 \, \text{nm}^{-3} \times 10^{12} \, \text{nm}^3 = 3.3 \cdot 10^{13}$.

In water, there is a dissociation reaction $H_2O \leftrightharpoons OH^- + H^+$, or, as more sophisticated chemistry textbooks say,

$$2H_2O \leftrightharpoons OH^- + OH_3^+ \ . \tag{31}$$

Stoichiometric coefficients here are $\nu_1 = 2$, $\nu_2 = \nu_3 = -1$. Equilibrium constant of this reaction is a unitless number $K = \frac{[OH^-][OH_3^+]}{[H_2O]^2}$, it is close to 10^{-14}. If the solution is neither basic nor acidic, $[OH^-] = [OH_3^+]$, meaning each of them is $10^{-7}[H_2O]$. In the specified volume, it means about $3 \cdot 10^6$ ions of either kind. This is an equilibrium, averaged number.

About fluctuations, we saw that

$$\langle r^2 \rangle = \frac{1}{\left[V \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right]} \tag{32}$$

That means, root-mean-squared fluctuation of particle number within volume V is

$$\delta N = V \sqrt{\langle r^2 \rangle} = \sqrt{\frac{V}{\left[\sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right]}} = \sqrt{\frac{V}{\frac{4}{[H_2O]} + \frac{1}{[OH^-]} + \frac{1}{[OH_3^-]}}} \ . \tag{33}$$

The term with neutral water here is completely negligible, as its concentration is 7 orders of magnitude larger. In the end, the numbers specified above, we get $\delta N \approx 10^3$; roughly, the number of ions is about three million, fluctuating up and down by about a thousand.

Now about time dependence. We saw that

$$\dot{r} = -\lambda r + \xi(t) \ , \quad \text{where} \quad \lambda = q \left[\sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right] \ , \quad \langle \xi(t) \rangle = 0 \quad \text{and} \quad \langle \xi(t)\xi(t') \rangle = 2\frac{q}{V}\delta(t - t') \ . \tag{34}$$

where $q = k_{\to}[H_2O]^2$. For the rate constant, the best estimate I have found is $k_{\to} = 10^{-6} \, \text{nm}^3/\text{s}$. This gives $q = 1 \, \text{nm}^{-3}\text{s}^{-1}$ and $\lambda = 3 \cdot 10^5 \, \text{s}^{-1}$, or characteristic relaxation time is about one day. That means, if you look at one particular water molecule, you have to wait for tens of hours to see it dissociating.

8. Consider a causal response function $\chi(t)$ and its Fourier transform χ_ω. Show that in general causality condition means that χ_ω has no singularities in the upper half of ω-complex plane [5]. Show that $1/\chi_\omega$ also has these properties, and explain why.

Solution

Viewing ω as a complex variable and representing $\chi(t) = \int^{-\imath\omega t} \chi_\omega \frac{d\omega}{2\pi}$, one see that at $t < 0$, the integration contour can be closed through the upper half-plane. For the result to be zero, there should be no singularities.

Since $1/\chi_\omega$ must also satisfy the same property, it follows that χ_ω has no zeros in the upper half plane.

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[1] I find it amusing that Parseval, after whom this result is called, never proved it (at least never published any proof), but referred to it, in his memoir of 1805, as self-evident!

[2] A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP, 1994) p. 350.

[3] M. Rubinstein and R. Colby, *Polymer Physics* (Oxford University Press, 2005) p. 442.

[4] P. L. Geissler, C. Dellago, D. Chandler, J. Hutter, and M. Parrinello, Autoionization in liquid water, Science **291**, 2121 (2001).

[5] Assuming the following sign convention for Fourier transforms: $x_\omega = \int_{-\infty}^{\infty} x(t)e^{\imath\omega t}dt$.
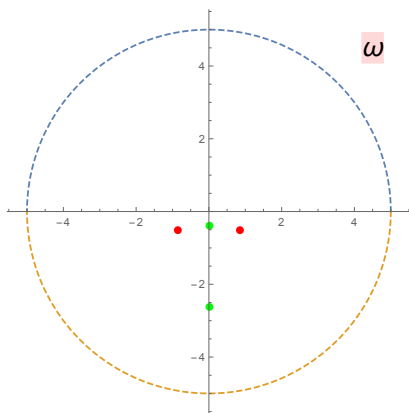
FIG. 3. Complex plane of frequencies ω. Integration contour, which runs along the real axis, must be closed along upper arch (counter-clockwise) in case $t < 0$ and along lower arch (clockwise) if $t > 0$. Green and red pais of poles correspond to the cases when $4km$ is larger or smaller than ζ^2; in other words, whether $\tau\omega_0$ is larger or smaller than 2