

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

Home Work 03

Solutions

1. Consider some chemical reaction $\nu_1 A_1 + \nu_2 A_2 + \dots \rightleftharpoons -\nu_3 A_3 - \nu_4 A_4 - \dots$. In Onsager framework, the rate of this reaction is written as $\dot{r} = -\gamma \Delta\mu$, where $\Delta\mu = \sum \nu_i \mu_i$ with μ_i chemical potentials. But if you open any chemical kinetics textbook, it says the rate of chemical reaction in a dilute solution is given by the mass action law, which reads $k_{\rightarrow}[A_1]^{\nu_1}[A_2]^{\nu_2} \dots - k_{\leftarrow}[A_3]^{-\nu_3}[A_4]^{-\nu_4} \dots$, where square brackets in $[A_i]$ mean concentration of the compound A_i , and where quantities k_{\rightarrow} and k_{\leftarrow} are called rate constants of the forward and backward reactions, respectively. The first question in this problem: how is one of these formulations related to the other?

Hint 1: Remember that Onsager theory is only valid at small deviations from equilibrium.

Hint 2 (reminder): You should know that chemical potential of a dilute system can be written as $\mu_i = T \ln[A_i] + T\chi_i$, where χ_i are constants independent of concentrations.

Solution

When $\Delta\mu$ is small, $\Delta\mu \ll T$, which is the only regime when Onsager method is applicable, both expressions for the reaction rate are the same. Indeed, let us see this.

Equilibrium condition for this reaction reads $\sum \nu_i \mu_i = 0$, where μ_i is chemical potential of component i . Chemical potential of component i in a dilute system can be written as $\frac{\mu_i}{T} = \ln[A_i] + \chi_i$. Therefore, equilibrium condition can be re-written as $\prod_i [A_i]^{\nu_i} = K$, where $K = k_{\leftarrow}/k_{\rightarrow}$ is called equilibrium constant, it is easily expressed in terms of χ_i . Let us denote equilibrium concentrations as $[A_i]_{\text{eq}}$; they satisfy

$$\prod_i [A_i]_{\text{eq}}^{\nu_i} = K. \quad (1)$$

This corresponds to the maximum of entropy. Now we imagine the system slightly away from equilibrium:

$$[A_i] = [A_i]_{\text{eq}} + r\nu_i; \quad (2)$$

this means, some r acts of chemical reaction (per unit volume) happened on the way from equilibrium; we assume r small.

An important note about signs: as it is defined above, increasing r in positive direction means acts of backward reactions; similarly, going into negative r means acts of forward reaction.

Then we find $\Delta\mu$ as follows:

$$\begin{aligned} \frac{1}{T} \Delta\mu &= \frac{1}{T} \sum_i \nu_i \mu_i = \ln \left[\frac{\prod_i [A_i]^{\nu_i}}{K} \right] = \ln \left[\frac{\prod_i [A_i]_{\text{eq}}^{\nu_i} \left[1 + \frac{r\nu_i}{[A_i]_{\text{eq}}} \right]^{\nu_i}}{K} \right] \\ &= \ln \left[\prod_i \left[1 + \frac{r\nu_i}{[A_i]_{\text{eq}}} \right]^{\nu_i} \right] \\ &\simeq \ln \left[\prod_i \left[1 + \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] \right] \\ &\simeq \ln \left[1 + \sum_i \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] \\ &\simeq r \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \end{aligned} \quad (3)$$

On every step, only linear terms in r were kept. Then, Onsager theory predicts reaction rate $\dot{r} = -\gamma \Delta\mu = -\gamma T r \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}}$.

On the other hand, we write down the Mass Action Law expression for the reaction rate, plug in there the expression (2) for perturbed concentrations, and linearize in r (see also a note about sign of r after formula (2)):

$$\begin{aligned}
 \dot{r} &= \underbrace{-k_{\rightarrow} \prod_{\nu_i > 0} [A_i]^{\nu_i}}_{\text{forward, all positive } \nu_i > 0} + \underbrace{k_{\leftarrow} \prod_{\nu_i < 0} [A_i]^{|\nu_i|}}_{\text{backward, all negative } \nu_i < 0} \\
 &= -k_{\rightarrow} \underbrace{\prod_{\nu_i > 0} [A_i]_{\text{eq}}^{\nu_i}}_q \left[1 + \frac{r\nu_i}{[A_i]_{\text{eq}}} \right]^{\nu_i} + k_{\leftarrow} \underbrace{\prod_{\nu_i < 0} [A_i]_{\text{eq}}^{-\nu_i}}_q \left[1 + \frac{r\nu_i}{[A_i]_{\text{eq}}} \right]^{-\nu_i} \\
 &= -q \prod_{\nu_i > 0} \left[1 + \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] + q \prod_{\nu_i < 0} \left[1 - \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] \\
 &= -q \left[1 + \sum_{\nu_i > 0} \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] + q \left[1 - \sum_{\nu_i < 0} \frac{r\nu_i^2}{[A_i]_{\text{eq}}} \right] \\
 &= -qr \left[\sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right].
 \end{aligned} \tag{4}$$

Thus, it is the same expression really! And we identify the phenomenological coefficient γ : $\gamma T = q$.

- Write down Langevin equation for the dynamics of a chemical reaction and find spectrum of corresponding “random force”, expressing it in terms of either rate constants k_{\rightarrow} and k_{\leftarrow} and equilibrium concentrations of all reagents $[A_i]_{\text{eq}}$, or in terms of q defined below.

Hint 3: In equilibrium, forward reaction and backward reaction, compensating each other, proceed with the same rate $q = k_{\rightarrow} \prod_{\nu_i > 0} [A_i]_{\text{eq}}^{\nu_i} = k_{\leftarrow} \prod_{\nu_i < 0} [A_i]_{\text{eq}}^{-\nu_i}$.

Solution

In Onsager’s framework, the rate of chemical reaction is written as $\dot{r} = -\gamma \Delta\mu$. Linearizing also $\Delta\mu$ close to equilibrium, we get $\dot{r} = -\lambda r(t)$ (valid on average). This is mathematically the same equation as, e.g., for coordinate of an overdamped Brownian particle on a spring in a viscous fluid, $\zeta \dot{x} = -kx$, accordingly, we can follow the same route. The next step is to introduce time-time correlation function $\phi(t) = \langle r(t)r(0) \rangle$. At $t > 0$, it satisfies the same equation $\dot{\phi} = -\lambda \phi(t)$, with the solution $\phi(t) = \phi(0)e^{-\lambda t}$ at $t > 0$. To continue it for negative t , we note that r does not change sign upon time reversal. We also note that $\phi(0) = \langle r^2 \rangle$ is the simultaneous average, an equilibrium property. Thus,

$$\phi(t) = \langle r^2 \rangle e^{-\lambda|t|}. \tag{5}$$

Now we want to write a more accurate equation, taking into account possible fluctuations, which is the Langevin equation

$$\dot{r} = -\lambda r(t) + \xi(t), \tag{6}$$

and we need to adjust random noise such as to reproduce the already known correlation function (5). We solve equation (6) $r(t) = \int_{-\infty}^t e^{\lambda(t'-t)} \xi(t') dt'$, and then construct

$$\langle r(0)r(t) \rangle = \int_{-\infty}^t \int_{-\infty}^0 e^{\lambda(t'+t''-t)} \langle \xi(t')\xi(t'') \rangle dt' dt''. \tag{7}$$

The result (5) is obtained if

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t)\xi(t') \rangle = 2\lambda \langle r^2 \rangle \delta(t - t'). \tag{8}$$

We need to find out what is $\langle r^2 \rangle$ and what is λ . The former is an equilibrium thermodynamic property, while the latter is a transport coefficient, so it should be related to rate constants. Let us look into this.

First we look at equilibrium fluctuation $\langle r^2 \rangle$. Thus, entropy (per unit volume), s , which is a function of all concentrations, can be expanded in powers of r . Since $T \frac{\partial s}{\partial [A_i]} = -\mu_i$, the first term, linear in r , vanishes, and

quadratic term in entropy is related to the linear term in $\Delta\mu$: $s \simeq -\frac{1}{2}r^2 \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}}$. Probability distribution of r over volume V reads $\mathcal{P}(r) \propto \exp\left[-\frac{1}{2}r^2 V \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}}\right]$ and thus

$$\langle r^2 \rangle = \frac{1}{\left[V \sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}}\right]} \quad (9)$$

Note that this is proportional to $1/V$, which is a manifestation of “square-root-of- n -law”. Indeed, r is the number of reactions per unit volume, total number of reaction in the system is rV , and so what we see is fluctuation of total number of reaction $\sqrt{\langle (rV)^2 \rangle}$ is proportional to \sqrt{V} .

Now let us go for the transport coefficient λ . From the results above, $\lambda = q \left[\sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right]$.

Collecting things together, we now arrive at the Langevin equation

$$\dot{r} = -\lambda r + \xi(t) \text{ , where } \lambda = q \left[\sum_i \frac{\nu_i^2}{[A_i]_{\text{eq}}} \right] \text{ , } \langle \xi(t) \rangle = 0 \text{ and } \langle \xi(t)\xi(t') \rangle = 2\frac{q}{V}\delta(t-t') \text{ .} \quad (10)$$

A useful check, as always, is to look at units: one can see that all terms in Langevin equation have dimension $1/Vt$. It is interesting that “chemical noise” here is controlled by q , the rate at which compensated forward and backward reactions occur in equilibrium.

3. We considered Langevin equation for a particle moving in a liquid

$$m\dot{v} = -\zeta v + \xi(t) \text{ ,} \quad (11)$$

with white noise random force $\xi(t)$:

$$\langle \xi(t) \rangle = 0 \text{ , } \langle \xi(t)\xi(t') \rangle = 2\zeta T\delta(t-t') \text{ .} \quad (12)$$

For a typical colloidal particle in a usual liquid like water, inertia is usually unimportant, the system is overdamped. One is then tempted to neglect the $m\dot{v}$ term, write $v = \dot{x}$, and view Langevin equation as equation for $x(t)$. You can solve it and then find mean squared displacement over time t . Follow this path, compare your result with that obtained by integrating velocity, and explain physically what is similar and what is different.

Solution

If we neglect inertia, we get equation

$$\zeta \dot{x} = \xi(t) \text{ ,} \quad (13)$$

which is easy to solve: $x(t) - x(0) = \frac{1}{\zeta} \int_0^t \xi(t') dt'$. Squaring this, we get

$$\langle [x(t) - x(0)]^2 \rangle = \frac{1}{\zeta^2} \int_0^t \int_0^t \underbrace{\langle \xi(t')\xi(t'') \rangle}_{2\zeta T\delta(t'-t'')} dt' dt'' = 2\frac{T}{\zeta} t \text{ .} \quad (14)$$

This is exactly the same answer that we got before analyzing velocity – in the long time limit, when $t \gg \tau$. Thus, inertia is indeed negligible beyond velocity correlation time τ . But inertia is important at short times, for ballistic regime.

4. If a small particle moves in a liquid, then its velocity $\mathbf{v}(t)$ changes very rapidly and chaotically, due to the random kicks from surrounding molecules. Apart from a very short interval of ballistic motion, the particle undergoes a random walk, and its mean-squared displacement over time t is linear in t , it is usually written in the form $\langle \mathbf{R}^2(t) \rangle = 6Dt$ (in $d=3$), where D is called the diffusion coefficient. Based on this, prove the following Green-Kubo relation between velocity-velocity correlation function and the diffusion coefficient:

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(t')\mathbf{v}(0) \rangle dt' \text{ .} \quad (15)$$

Hint: While studying random walks, we presented end-to-end vector as the sum of vector steps. Generalizing this, you may want to present the vector of particle displacement as an integral of fluctuating velocity. Then,

the first step is to average this integral. Since this does not yield anything interesting, the next step is to square the integral, and then to average. This will lead to double integral similar to the double sum $\sum_{\alpha\beta} \langle \mathbf{y}_\alpha \cdot \mathbf{y}_\beta \rangle$ which we encountered in the theory of random walk. Remember that different Cartesian components of velocity are not correlated.

Solution

Particle displacement over time t reads

$$\mathbf{R}(t) = \int_0^t \mathbf{v}(t') dt' . \quad (16)$$

Because of spherical symmetry, average velocity vanishes, leading to zero average displacement: $\langle \mathbf{R} \rangle = 0$, as in an unbiased random walk. Squaring $\mathbf{R}(t)$ yields the expression of the type that we studied already several times:

$$\mathbf{R}^2(t) = \int_0^t dt' \int_0^t dt'' \mathbf{v}(t') \cdot \mathbf{v}(t'') . \quad (17)$$

Averaging now reveals the presence of velocity-velocity correlation function:

$$\langle \mathbf{R}^2(t) \rangle = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle . \quad (18)$$

The left hand side, as we know, increases like t with time for diffusing particle, while right hand side may seem to increase as t^2 , because it involves two integrations. This suggests that velocity-velocity correlation function must rapidly decrease with $t' - t''$, such that the integration is effectively restricted to only the diagonal of the square in the (t', t'') plane. To formalize this idea, we can introduce new integration variables, $\tau = t' - t''$ and another notation for half-sum $(t' + t'')/2$. The latter variable is mute (integrand does not depend on it), so integration over it yields factor of t . Jacobian of the coordinate transformation is unity. Thus, collecting things together, we arrive at

$$6Dt = t \int_{-\infty}^{\infty} d\tau \langle \mathbf{v}(0) \mathbf{v}(\tau) \rangle , \quad (19)$$

where integration can be pulled to infinity because it rapidly converges anyway. This is exactly the requisite Green-Kubo relation.

5. Consider an *LRC*-circuit (with no battery) maintained at temperature T . Find the power spectrum of voltage developed by the resistor due to fluctuations.

Hint: The result you are supposed to obtain is known to electrical engineers as Nyquist formula. (Do not forget that while ω in mathematics runs from $-\infty$ to $+\infty$, the frequency f for engineers is always positive.)

Solution

For the *LRC* circuit we have

$$L\ddot{q} + R\dot{q} + \frac{q}{C} = V^r , \quad (20)$$

where the random voltage V^r is the source of fluctuations. Given the dictionary

$$q \leftrightarrow x , \quad L \leftrightarrow m , \quad R \leftrightarrow \zeta , \quad 1/C \leftrightarrow k , \quad V^r \leftrightarrow f^r , \quad (21)$$

we directly borrow the answer from our previous deliberations: $(V^2)_\omega = 2RT$. Since frequencies ω and $-\omega$ are physically equivalent, we combine them together to obtain the power of fluctuations within the frequency band Δf :

$$\langle V^2 \rangle_{\Delta f} = 4RT \Delta f , \quad (22)$$

which is exactly the Nyquist theorem.

The underlying physics of this solution is that capacitor plays no role in noise (just like random kicks in mechanics are not affected by the presence of a spring), and we can consider a simpler equation $L\dot{I} + RI = V^r$ for the

current. This implies correlations function for the current $\langle I(t)I(0) \rangle = \langle I^2 \rangle_{\text{eq}} e^{-(R/L)|t|}$, where $\langle I^2 \rangle_{\text{eq}} = T/L$ by equipartition. The rest of the argument is exactly the same as in the mechanical case.

The conclusion: because of fluctuations, a resistor of resistance R develops a voltage whose mean squared average is given by the above formula. To explore this a little further, consider “our” resistor R connected in a circuit with another resistor R' – a “load”. Suppose first the other resistor is supported at zero temperature, so it does not create any noise. Then the current in the system will be $I = V/(R + R')$ and the power delivered by “our” resistor to the load due to fluctuations will be $I^2 R'$ or $V^2 R'/(R + R')^2$. Suppose now both resistors are at temperature T and the load is matched, i.e., $R = R'$. The matching condition implies that anything coming from one resistor gets absorbed in the other, and vice versa; and thermodynamic equilibrium condition means that each resistor produces as much energy as it absorbs back. Then we must have $V^2 R'/(R + R')^2|_{R=R'} = V^2/4R$ must be equal to $T\Delta f$ – which is the Nyquist result.

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. This problem is particularly useful for those who have taken the Soft Matter class. For a worm-like polymer chain, correlation between tangent vectors of the chain in two points contour distance s apart decays exponentially with s , $\langle \mathbf{t}(s)\mathbf{t}(s') \rangle = e^{-|s-s'|/\ell_p}$, where ℓ_p is persistence length. Derive from here the expression for mean squared average end-to-end distance, and compare the result with mean squared average of displacement for a Brownian particle whose velocity-velocity correlation function.

Solution

In both cases we have essentially the same formula:

$$\langle \mathbf{r}^2 \rangle = 6 \langle v^2 \rangle \tau^2 \left[\frac{t}{\tau} + e^{-t/\tau} - 1 \right], \quad (23)$$

in one case, and

$$\langle \mathbf{r}^2 \rangle = 2\ell_p^2 \left[\frac{L}{\ell_p} + e^{-L/\ell_p} - 1 \right], \quad (24)$$

in the other case. The analogy is completely apparent.

7. 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 $\mathbf{v}_{\mathbf{k}}$ is perpendicular to wave vector, $\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}} = 0$. 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 $\sim \exp[-W_{\min}/k_B T]$, 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 , $R_{\min} = \delta V \rho \bar{v}^2/2$. With such probability distribution, the simultaneous (one time) average reads

$$\langle v_\alpha v_\beta \rangle = \frac{\int \exp \left[-\frac{\delta V \rho \bar{v}^2}{2T} \right] v_\alpha v_\beta d^3 \bar{v}}{\int \exp \left[-\frac{\delta V \rho \bar{v}^2}{2T} \right] d^3 \bar{v}} = \delta_{\alpha\beta} \frac{T}{\rho \delta V}. \quad (25)$$

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

$$\langle v_\alpha(\vec{r}) v_\beta(\vec{r}') \rangle = \delta_{\alpha\beta} \delta(\vec{r} - \vec{r}') \frac{T}{\rho}. \quad (26)$$

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

$$\langle v_{\alpha \vec{k}} v_{\beta \vec{l}} \rangle = (2\pi)^3 \delta_{\alpha\beta} \delta(\vec{k} + \vec{l}) \frac{T}{\rho} \implies (v_\alpha v_\beta)_{\vec{k}} = \delta_{\alpha\beta} \frac{T}{\rho}. \quad (27)$$

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 $\vec{v}^\parallel = (\vec{v} \cdot \vec{k}) \vec{k}/k^2$ (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

$$(v_\alpha^\perp v_\beta^\perp)_{\vec{k}} = \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \frac{T}{\rho}. \quad (28)$$

For example, if \mathbf{k} is oriented along x , then

$$(v_\alpha^\perp v_\beta^\perp)_{\vec{k}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & T/\rho & 0 \\ 0 & 0 & T/\rho \end{pmatrix}. \quad (29)$$

This simultaneous correlation is what equilibrium statistical mechanics tells us.