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

Home Work 14   *Solutions*

1. In one of the problems in another HW, you thought about fluorescence correlation spectroscopy. Here, you will have to use the results of real measurements, shown in figure 1, from the lab of Professor J. Mueller at the University of Minnesota. Data are presented in terms of the unitless quantity

$$g(\tau) \equiv \frac{\langle \delta I(t)\delta I(t+\tau)\rangle}{\langle I\rangle^2} \ , \tag{1}$$

where $I(t)$ is the intensity of fluorescence at time t, $\langle I\rangle$ is the time averaged fluorescence, and $\delta I(t) = I(t) - \langle I\rangle$. The optical system in this experiment provides illumination of the spot of the width $w = 0.22\,\mu$m.

Extract the raw data from the plot using, for instance, the online tool `WebPlotDigitizer`, and fit them to the theoretical expression for the correlation function that you found in the previous problem. Find the diffusion coefficient of the fluorescent molecules and the average number of fluorescent molecules in the illuminated spot. From the diffusion coefficient, find also the hydrodynamic radius of particles in question. Based on this, guess whether these particles could be proteins.

Solution

Following the solution of one of the problems in another HW, we find

$$\frac{\langle \delta I(t)\delta I(t+\tau)\rangle}{\langle I\rangle^2} = \frac{2/(\pi w^2 n)}{1+8D\tau/w^2} \ . \tag{2}$$

On the other hand, the number of particles in the spot, N, is $N = \pi w^2 n/4$, because w is the diameter. Thus, finally we get

$$\frac{\langle \delta I(t)\delta I(t+\tau)\rangle}{\langle I\rangle^2} = \frac{1/(2N)}{1+8D\tau/w^2} \ . \tag{3}$$

Least squares fit of the data using this formula yields $N \approx 4$ and $D \approx 269.3\,\mu$m^2/s.
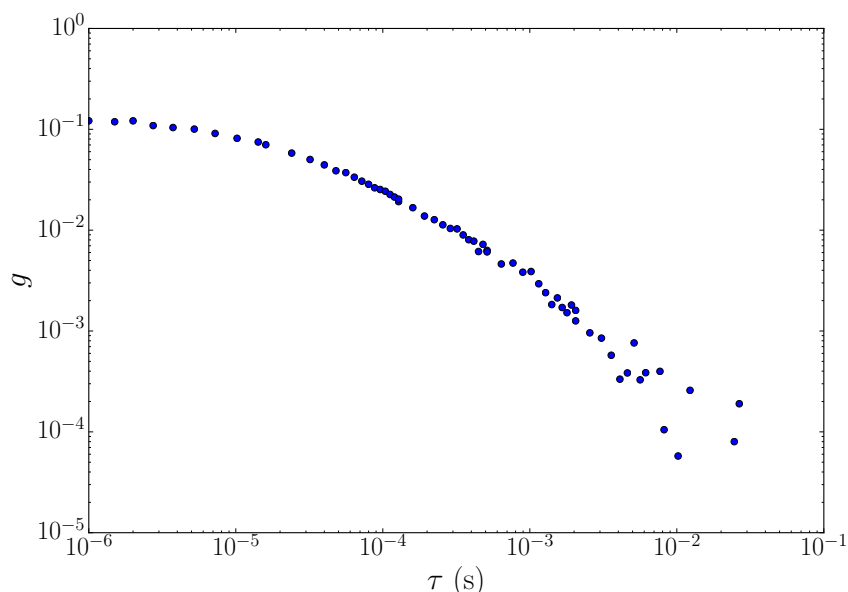

FIG. 1. For problem 1. Data is courtesy of J.Mueller, University of Minnesota.

The hydrodynamic radius of the molecules, R_H, can be found from the diffusion coefficient, D, using the Stokes-Einstein relation

$$6\pi\eta R_H = \frac{k_B T}{D} ,\tag{4}$$

where η is the viscosity of water. Using $\eta \approx 10^{-3}$ Js/m^3, and using our result for D, we get $R_H \approx 0.8$ nm. This is about an order of magnitude too small for a protein. We should conclude that the experiment was performed on some smaller molecules such as a low molecular weight dye.

2. Jarzynski theorem, originally proven in the work [1], states

$$e^{-\beta\Delta F} = \left\langle e^{-\beta W} \right\rangle .\tag{5}$$

At the same time, as you know, second law of thermodynamics says that $\langle W \rangle \geq \Delta F$, where equality is achieved only in a quasi-static reversible process; that means $\delta W = \langle W \rangle - \Delta F$ represents the amount of dissipation.

Imagine that you run some experimental process pretty slowly, but not so slowly to neglect dissipation altogether. Since it is slow, the work fluctuates from one experimental run to another (with the same protocol) only by a very small amount, such that $W - \langle W \rangle = \delta W$ is small compared to T. Now, your task is two-fold:

(a) Show that in this case

$$\Delta F \simeq \langle W \rangle - \frac{\left\langle \delta W^2 \right\rangle}{2T} .\tag{6}$$

(b) Original paper [1] indicates that this small δW result was derived previously using Fluctuation-Dissipation theorem, and gives reference to this original derivation. Unfortunately, the reference contains an error. You have to do one of the two things:

- Derive formula (6) from FDT, or
- Locate the correct reference, read corresponding paper, and report how they derive (6) from FDT (in this context, "to report" means to provide enough details to show that you have repeated the calculations).

Solution

The first part is easy: You may re-write the Jarzynski formula as $\Delta F = -T \ln \left\langle e^{-\beta W} \right\rangle = -T \ln \left\langle e^{-\beta(\langle W \rangle + \delta W)} \right\rangle = -T \ln \left[e^{-\beta\langle W \rangle} \left\langle e^{-\beta\delta W} \right\rangle \right] = \langle W \rangle - T \ln \left\langle e^{-\beta\delta W} \right\rangle$, and in the last expression you resort to Taylor expansion, since $\beta\delta W$ is small.

For the second part, the correct reference is [2]. I am lazy to type it, but the complete solution to this problem must include the derivation itself, not only the reference.

3. Jarzynski theorem was discovered in 1997 [1]. Soon thereafter, this exciting new discovery was discussed at a special session in a large international conference. At the time, I did not understand the topic, and was eager to understand it. Unfortunately, speakers did not clarify the ideas, but rather concentrated on subtleties and generalizations. Then, I decided to think on my own, and to work out a simple – indeed, simplest possible – example. What is the simplest object of statistical mechanics? Of course, classical ideal gas. Thinking of ideal gas, I very soon came up with an argument which, I thought, disproved the whole Jarzynski theorem. So, I stood up and produced my argument on a transparency for everybody to see. My argument (see below) was wrong. Your task now is to find out what was wrong with it.

The argument went as follows. Consider an ideal gas in a cylinder with a piston. Suppose at the beginning volume inside the cylinder is V_{initial}. The system is equilibrated at this volume, and its pressure is $p = NT/V_{\text{initial}}$ in obvious notations. Now let us take piston and move it very fast outwards, to the point when volume inside becomes $V_{\text{final}} > V_{\text{initial}}$. Given that molecules inside move with velocities of the order of $\sqrt{T/m}$ on average, if we move our piston with the speed much larger than $\sqrt{T/m}$, then molecules will not be able to hit the piston while it moves (I assume there is complete vacuum outside), therefore, piston will feel no force, with the consequence that the work performed on the system will be zero $W = 0$. In that case, $\left\langle e^{-\beta W} \right\rangle = 1$ while $\Delta F \neq 0$ and $e^{-\beta\Delta F} \neq 1 \ldots$ What is wrong?

Solution

However fast we move the piston, there is still some probability that some molecules, from the tail of Maxwell distribution, will be fast enough to chase the piston, hit it, and thus lead to the work being not quite zero at least in some realizations of the experiment. Careful analysis of such events [3] is in complete agreement with the Jarzynski theorem.

4. We estimated the number of runs necessary to obtain a reasonably accurate estimate of average in the Jarzynski equation $\left\langle e^{-W/T} \right\rangle = e^{-\Delta F/T}$ in the following way:

$$
\begin{aligned}
\frac{1}{\#\text{runs}} \sim \mathcal{P} &\approx \int_{\Gamma_{\text{ini}}^{\text{dominant}}} e^{(F_{\text{ini}} - \mathcal{H}_{\text{ini}})/T} d\Gamma_{\text{ini}} \approx \\
&\approx \int_{\Gamma_{\text{fin}}^{\text{typical}}} e^{(F_{\text{ini}} - \mathcal{H}_{\text{ini}})/T} d\Gamma_{\text{fin}} \approx \\
&\approx \int_{\Gamma_{\text{fin}}^{\text{typical}}} e^{(F_{\text{ini}} - \mathcal{H}_{\text{ini}})/T} e^{(-F_{\text{fin}} + \mathcal{H}_{\text{fin}} + F_{\text{fin}} - \mathcal{H}_{\text{fin}})/T} d\Gamma_{\text{fin}} \approx \\
&\approx \int_{\Gamma_{\text{fin}}^{\text{typical}}} e^{(F_{\text{fin}} - \mathcal{H}_{\text{fin}})/T} e^{\left(\underbrace{F_{\text{ini}} - F_{\text{fin}}}_{-\Delta F} + \underbrace{\mathcal{H}_{\text{fin}} - \mathcal{H}_{\text{ini}}}_{-W^{\text{reverse}}} \right)/T} d\Gamma_{\text{fin}} \approx \\
&\approx e^{(-\Delta F - \langle W^{\text{reverse}} \rangle)/T} \int_{\Gamma_{\text{fin}}^{\text{typical}}} e^{(F_{\text{fin}} - \mathcal{H}_{\text{fin}})/T} d\Gamma_{\text{fin}} \approx \\
&\approx e^{(-\Delta F - \langle W^{\text{reverse}} \rangle)/T} \approx e^{(-\text{Dissipation})/T}
\end{aligned}
\tag{7}
$$

Your task is to explain two features of this derivation:

(a) Why in the last transformation the integral is taken to be equal to unity?

(b) Why in the next to last transformation the work in the reversed process is replaced by its average?

Solution

I explained this in class on November 30. The integral is very nearly one, because it is taken over the region of typical states which give dominant contribution to the partition sum of the final state. The work is replaced by the average because the reverse protocol starts from the typical states, not the dominant ones.

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

5. Consider again experiment in which a colloidal (Brownian) particle is pulled through viscous fluid (e.g., water) by a moving optical trap. Specifically, consider the "switching" process in which steady velocity changes from some v_1 to v_2. It can of course be done in many different ways; time dependence of the driving velocity $v(t) \equiv \lambda(t)$ represents the "protocol". Consider in particular the following three protocols, each running from $t_{\text{ini}} = 0$ to $t_{\text{fin}} = \tau$:

(a) $v(t) = v_1 + (v_2 - v_1) \sin(\pi t/2\tau)$, with $\tau = 60\,\text{ms}$.
(b) $v(t) = v_1 + (v_1 - v_2) \sin(3\pi t/2\tau)$, with $\tau = 80\,\text{ms}$.
(c) $v(t) = v_1 + (v_1 - v_2) \sin(3\pi t/2\tau)$, with $\tau = 60\,\text{ms}$.

In which case do you expect the largest and the smallest difference between $\langle Y \rangle$ and $-\ln \left\langle e^{-Y} \right\rangle$, where Y is the quantity featuring in Hatano-Sasa theorem? What do you expect $-\ln \left\langle e^{-Y} \right\rangle$ to be?

Solution

This experiment was reported in the paper [4]. First of all, it was found that $-\ln \left\langle e^{-Y} \right\rangle = 0$, within experimental errors, in all cases, as it should be according to the Hatano-Sasa theorem. Protocol 6a involves the smallest amplitude of velocity change, because velocity is all the time within the interval between v_1 and v_2 (just one quarter of a sine wave); it is not surprising that this protocol gives the smallest value of $\langle Y \rangle$ (i.e., the smallest difference of this value and $-\ln \left\langle e^{-Y} \right\rangle = 0$). Of the other two protocols, 6b gives smaller $\langle Y \rangle$ than 6c because it has larger τ and, therefore, is softer.

6. Consider again experiment in which a colloidal (Brownian) particle is pulled through viscous fluid (e.g., water) by a moving optical trap. Specifically, consider the "switching" process in which steady velocity changes from some v_1 to v_2. It can of course be done in many different ways; time dependence of the driving velocity $v(t) \equiv \lambda(t)$ represents the "protocol". Consider in particular the following three protocols, each running from $t_{\text{ini}} = 0$ to $t_{\text{fin}} = \tau$:

(a) $v(t) = v_1 + (v_2 - v_1) \sin(\pi t/2\tau)$, with $\tau = 60\,\text{ms}$.

(b) $v(t) = v_1 + (v_1 - v_2)\sin(3\pi t/2\tau)$, with $\tau = 80$ ms.

(c) $v(t) = v_1 + (v_1 - v_2)\sin(3\pi t/2\tau)$, with $\tau = 60$ ms.

In which case do you expect the largest and the smallest difference between $\langle Y \rangle$ and $-\ln\langle e^{-Y} \rangle$, where Y is the quantity featuring in Hatano-Sasa theorem? What do you expect $-\ln\langle e^{-Y} \rangle$ to be?

Solution

This experiment was reported in the paper [4]. First of all, it was found that $-\ln\langle e^{-Y} \rangle = 0$, within experimental errors, in all cases, as it should be according to the Hatano-Sasa theorem. Protocol 6a involves the smallest amplitude of velocity change, because velocity is all the time within the interval between v_1 and v_2 (just one quarter of a sine wave); it is not surprising that this protocol gives the smallest value of $\langle Y \rangle$ (i.e., the smallest difference of this value and $-\ln\langle e^{-Y} \rangle = 0$). Of the other two protocols, 6b gives smaller $\langle Y \rangle$ than 6c because it has larger τ and, therefore, is softer.

7. Consider a membrane which is submerged in a liquid and fluctuates at temperature T. Suppose, for simplicity, stress-free state of the membrane is flat. According to Helfrich [5], energy of deformation can be written in the following form:

$$\mathcal{H} = \frac{1}{2}\int\left[\kappa\left(\nabla^2 h\right)^2 + \sigma\left(\vec{\nabla}h\right)^2\right] dx\,dy \tag{8}$$

Here x and y are the coordinates in the plane of un-deformed membrane, while $h(x,y)$ gives the z-coordinate of the membrane when it is deformed (this is called Monge gauge, see details in any differential geometry textbook). κ and σ are moduli which describe membrane elasticity; σ is an area modulus, it describes the reaction of the membrane to stretching, while κ is bending modulus. The goal is to find power spectrum density of membrane fluctuations in one particular point. You may want to follow these steps.

Step 1.: Expand $h(x,y)$ in terms of Fourier modes h_q and find equilibrium average $\left\langle |h_q|^2 \right\rangle$.

Step 2.: For each mode, find its relaxation time $\tau(q)$. This is the most difficult step. Physically, relaxation is controlled by the friction, and friction in this case is provided by the surrounding viscous fluid.

Step 3.: Write down the time-dependent correlation function $\langle h_q(t)h_q(0) \rangle$ for every mode q.

Step 4.: Use Wiener-Khinchim theorem to find power spectrum density, as a function of frequency ω.

Your result will be diverging at $q \to 0$; why?

Hint: If you find it too hard to solve the step 2, you can look in the paper [6]. This paper treats a significantly more general and more difficult problem, but does contain the answer to this step 2 question.

Solution

This problem is solved in the paper [7].

8. Consider paper [8]

9. Crooks identity is widely used in the context of computational modelling [9, 10]. What is the "shadow Hamiltonian"?

Solution

When people use molecular dynamics simulation, they essentially integrate the Newton's dynamic equations of motion. In Brownian dynamics, langevin equations are numerically integrated. This is inevitably done by discretizing time. But this discretizing leads to an unwanted result that finite difference equations of motion do not conserve energy. Energy of the system changes up and down because finite difference equations of motion are an inaccurate approximation of the continuous time Newton's equations. To understand it, turns out useful to imagine that finite difference dynamics of the real system is actually a continuous time dynamics of another system, whose Hamiltonian parameters change in some step-like fashion. That Hamiltonian is called shadow Hamiltonian. The work [10] describes how Crooks relation can be used to understand the fluctuations arising from switching from shadow hamiltonian to the real one and back.

10. Consider an electric circuit presented in figure 2, with resistance R and capacitance C. Imagine that it exists in a medium (e.g., in the lab air) at temperature T. For simplicity, neglect internal resistance of the battery, as well as inductance in the circuit. Suppose that battery EMF was maintained at the level $\mathcal{E}_1$ for a while and then was changed to $\mathcal{E}_2$ over some period of time τ, following the prescribed protocol $\mathcal{E}(t)$. Joule heat power changes from $\mathcal{E}_1^2/R$ to $\mathcal{E}_2^2/R$. How much extra dissipation to you incur while switching?
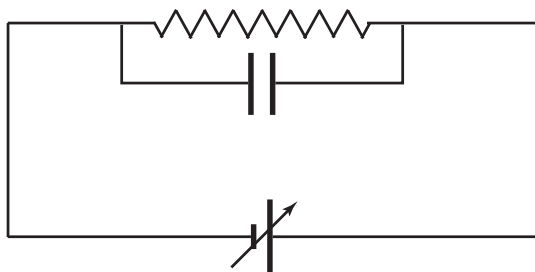
Solution

FIG. 2. While voltage is fixed, and in a macroscopic circuit, there is a constant current and constant charge on the capacitor. If the circuit is small, you can observe thermal fluctuations. If you change voltage, then you shift from one steady state to the other. How much dissipation do you incur while switching?

11. (a) Consider two parallel resistors R_1 and R_2. If total current flowing through is I, the charge conservation implies that currents in both branches satisfy $I = I_1 + I_2$. Show that I_1 and I_2 are such that total Joule heat is minimal.

   (b) Consider a non-unform sample, with electrical conductivity $\sigma(\mathbf{x})$ dependent on place. Charge conservation implies that electric current satisfies $\nabla \cdot \mathbf{j} = 0$ (or in other notation div$\mathbf{j} = 0$). Show that the distribution of current in the medium satisfies the minimal Joule heat principle.

   (c) Consider the paper [11] published in Europhysics Letters some time ago. What is the physical principle that leads the authors to conclude that mechanism (C) becomes dominant instead of (A) at large frequencies? Please be specific.

   Solution

   The authors make their conclusion based on the principle of minimal entropy production.

12. Consider paper [12]. Authors claim to have verified Crooks theorem for the particular system under study. For this system, can you estimate how many experiments would be needed to recover equilibrium free energy difference based on Jarzynski identity?

   Solution

13. In class, we discussed Continuous Time Random Walks. We used physics arguments to derive proper relations of exponents. You may want to see a more formal mathematical exposition. I found nice the presentation in lecture 23 on the web site:

   `https://ocw.mit.edu/courses/mathematics/18-366-random-walks-and-diffusion-fall-2006/lecture-notes`

[1] C. Jarzynski, Nonequilibrium equality for free energy differences, Phys. Rev. Lett. **78**, 2690 (1997).
[2] J. Hermans, Simple analysis of noise and hysteresis in (slow-growth) free energy simulations, J. Phys. Chem. **95**, 9029 (1991).
[3] R. C. Lua and A. Y. Grosberg, Practical applicability of the jarzynski relation in statistical mechanics: A pedagogical example, J. Phys. Chem. B **109**, 6805 (2005).
[4] E. H. Trepagnier, C. Jarzynski, F. Ritort, G. E. Crooks, C. J. Bustamante, and J. Liphardt, Experimental test of Hatano and Sasa's nonequilibrium steady-state equality, Proc. Nat. Ac. Sci. **101**, 15038 (2004).
[5] W. Helfrich, Elastic properties of lipid bilayers: theory and possible experiments, Zeitschrift für Naturforschung C **28**, 693 (1973).
[6] J. Prost, J.-B. Manneville, and R. Bruinsma, Fluctuation-magnification of non-equilibrium membranes near a wall, Eur. Phys. J. B **1**, 465 (1998).
[7] T. Betz and C. Sykes, Time resolved membrane fluctuation spectroscopy, Soft Matter **8**, 5317 (2012).
[8] V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger, Thermodynamics of a colloidal particle in a time-dependent nonharmonic potential, Phys. Rev. Lett. **96**, 070603 (2006).
[9] M. R. Shirts, E. Bair, G. Hooker, and V. S. Pande, Equilibrium free energies from nonequilibrium measurements using maximum-likelihood methods, Phys. Rev. Lett. **91**, 140601 (2003).
[10] D. A. Sivak, J. D. Chodera, and G. E. Crooks, Using nonequilibrium fluctuation theorems to understand and correct errors in equilibrium and nonequilibrium simulations of discrete langevin dynamics, Phys. Rev. X **3**, 011007 (2013).

[11] H. Wada and R. R. Netz, Plectoneme creation reduces the rotational friction of a polymer, EPL (Europhysics Letters) **87**, 38001 (2009).

[12] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies, Nature **437**, 231 (2005).