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

Home Work 02 *Solutions*

1. Molecular motors are nanometer scale objects which "burn" chemical fuel (called ATP) to perform mechanical work. For instance, some of them (e.g. kinesin) pick up some molecules which are synthesized in a neuron body in your back and transport them through the axon of this neuron to the tip of your toe.

   Consider a single-molecule experiment on a molecular motor, such as RNA polymerase (whose normal function involves moving along DNA by burning ATP). The fuel supply is characterized by $\Delta\mu = \mu_{\mathrm{ATP}} - \mu_{\mathrm{ADP}} - \mu_{\mathrm{P}}$, the difference in chemical potentials between ATP and the products of its hydrolysis, ADP and inorganic phosphate; the experimenter pulls on the enzyme with some force f using e.g. optical tweezers, in either forward or backward direction. Assuming that both chemical drive $\Delta\mu$ and force f are weak enough, develop a linear response model and identify all possible regimes.

   Comment 1: The assumption of weak forces seldom holds for real motors, which usually operate in a non-linear regime.

   Comment 2: Make sure to begin by analyzing the conditions on kinetic coefficients γ imposed by the Second Law.

   Solution

   In the linear response range, the speed of the motion, v, and the rate of burning fuel, r, are both linear in the applied external force f and chemical imbalance $\Delta\mu$. The entropy production (dissipation) rate is given by

$$W = fv + r\Delta\mu \ . \qquad (1)$$

   This indicates that v and r are the speeds conjugate to forces f and $\Delta\mu$, so

$$v = \gamma_{11} f + \gamma_{12}\Delta\mu \qquad (2)$$
$$r = \gamma_{21} f + \gamma_{22}\Delta\mu \qquad (3)$$

   From the Onsager reciprocal relation, we know that $\gamma_{12} = \gamma_{21}$. We also know from the Second Law that W must be non-negative.

   - If $\Delta\mu = 0$, then the condition $W > 0$ means $fv > 0$, or $\gamma_{11} f^2 > 0$, or $\gamma_{11} > 0$. This condition means that without any fuel the particle moves in the direction determined by the applied force.
   - If $f = 0$, then the condition $W > 0$ means $r\Delta\mu > 0$, or $\gamma_2(\Delta\mu)^2 > 0$, or $\gamma_{22} > 0$. In the absence of forcing, the enzyme burns fuel, rather than creating it.
   - If both $f \neq 0$ and $\Delta\mu \neq 0$, then the condition $W > 0$ requires $\gamma_{11}\gamma_{22} > \gamma_{12}^2$.
   - And the value of γ_{12} may have either sign: for instance, $\gamma_{12} > 0$ means that burning fuel contributes to the motion in the same direction which experimented designated as $f > 0$, and vice versa. Thus, the sign of γ_{12} has to do only with the convention as to what direction of force is called positive.

   All possible regimes are shown in figure 1, where the mutual positions of the two dividing lines are fixed by the conditions $\gamma_{11} > 0$, $\gamma_{22} > 0$, and $\gamma_{12}^2 < \gamma_{11}\gamma_{22}$. The regimes are as follows (let us take $\gamma_{12} > 0$):

   (a) The most boring situation: $v > 0$, $r > 0$ – the chemical and mechanical forces are aligned, so we move in that direction.

   (b) Still $v > 0$ and $r > 0$, but since $f < 0$, we move against the external force at the expense of burning fuel. This is a motor!

   (c) Now $v < 0$, but $r > 0$: we do burn fuel, but it is not enough to resist the forcing, so we move down the force direction, albeit slower than without burning the fuel. The system behaves as a stubborn animal which spends effort to resist your pulling.

   (d) Since $v < 0$ and $f < 0$, so we follow the force, but now $r < 0$, so we produce fuel on the expense of the external force.

   (e) We still have $v < 0$ and $r < 0$. But since $\Delta\mu < 0$ and $f < 0$, it is as boring as case (1).

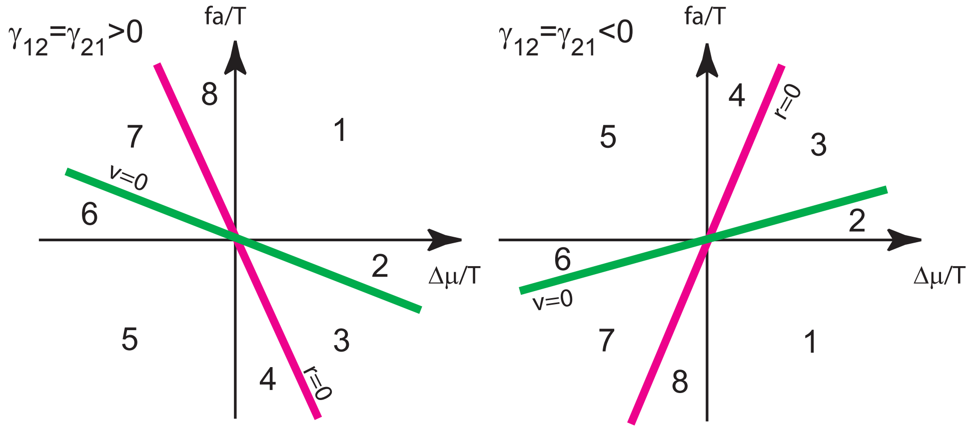

FIG. 1: The diagram of regimes for the motor within linear response range, assuming $\gamma_{12} = \gamma_{21} > 0$ (left figure) or $\gamma_{12} = \gamma_{21} < 0$ (right figure). In complete solution, each regime should be identified, for instance: regime 3 in the left figure is where motor works against the external force on the expense of burning fuel; regime 7 is where it synthesizes ATP on the expense of external source of force, etc.

(f) Still $v < 0$ and $r < 0$, but since $f > 0$, we move against the force. This is interesting, because $\Delta\mu < 0$, so you might think there is no fuel. In fact, there is such an excess of ADP and phosphate that making ATP from them becomes favorable to the extent that our motor can perform work on the expense of this transformation.

(g) Now $v > 0$, so molecule moves in the direction of force, but $r < 0$, so the chemical reaction develops in the direction of the chemical potential.

(h) Now $v > 0$ along the force, and $r > 0$ against chemical potential: we produce ATP at the expense of the external force.

2. Consider some chemical reaction $\nu_1 A_1 + \nu_2 A_2 + \ldots \leftrightharpoons -\nu_3 A_3 - \nu_3 A_4 - \ldots$. 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 is given by the mass action law, which reads $k_{\rightarrow}[A_1]^{\nu_1}[A_2]^{\nu_2}\ldots - k_{\leftarrow}[A_3]^{\nu_3}[A_4]^{\nu_4}\ldots$. How is one related to the other? Square brackets in $[A_i]$ mean concentration of the compound A_i.

Solution

In a dilute system, chemical potentials are $\mu_i = T\ln[A_i] + \chi_i$ which means $\Delta\mu = T\ln\left(\frac{[A_1]^{\nu_1}[A_2]^{\nu_2}}{[A_3]^{\nu_3}[A_4]^{\nu_4}\ldots} e^{\sum \nu_i \chi_i}\right)$. When $\Delta\mu$ is small, $\Delta\mu \ll T$, which is the only regime when Onsager method is applicable, both expression for the reaction rate are the same.

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

3. If time reversal signature of x_i and x_j is $+1$, then $\langle x_i(t) x_j(0)\rangle = \langle x_i(0) x_j(t)\rangle$ and then Onsager reciprocal relation follows: $\gamma_{ij} = \gamma_{ji}$. Consider now x_l and x_m whose time reversal signature is -1. What can you say about their correlation function? And about γ_{lm} versus γ_{ml}? And how about γ_{im} versus γ_{mi}?

Solution

In the expression for correlation function, $\langle x_a(t) x_b(0)\rangle$, average can be understood over equilibrium ensemble of coordinates and momenta of the microstate at $t = 0$. In that distribution, $\{q, p\}$ comes with the same probability as $\{q, -p\}$ (assuming there is no magnetic field and we are not in the rotating reference frame). Accordingly, flipping momentum in the intial distribution leads to

(a) Both a and b are coordinate-like, time reversal signature $+1$: $x_i(t) \to x_i(-t)$, $x_j(0) \to x_j(0)$;

(b) One variable is coordinate-like, the other is velocity-like, time reversal signatures are $+1$ and -1: $x_i(t) \to x_i(-t)$, $x_j(0) \to -x_j(0)$;

(c) Both a and b are velocity-like, time reversal signature -1: $x_i(t) \to -x_i(-t)$, $x_j(0) \to -x_j(0)$;

The end result reads now

$\gamma_{ij} = \gamma_{ji}$ and $\gamma_{lm} = \gamma_{ml}$ and $\gamma_{im} = -\gamma_{mi}$

4. Consider a leaking capacitor – an isolated system consisting of two pieces of metal connected by a very thin wire. Capacitance, resistance of the wire, and its inductance are all known to you. Suppose that initially the capacitor is charged to voltage V_0. Derive, from Onsager theory, the phenomenological equation which describes the time evolution of voltage. That means, you have to identify the variables x_i and proceed from there.

Solution

The variables x_i which fully describe the dynamics of the system is charge $x_1 = Q$ and current $x_2 = \dot{Q}$. The "mechanical" energy of the system is $Q^2/2C + L\dot{Q}^2/2$. If the total energy of the system is E_0, then internal energy of the material in the system has energy $E = E_0 - Q^2/2C - L\dot{Q}^2/2$ and its entropy is $S(E_0 - Q^2/2C - L\dot{Q}^2/2)$. Now we use $X_i = -\partial S/\partial x_i$ and get $X_1 = Q/CT$ (T being absolute temperature) and $X_2 = L\dot{Q}/T$. Linear "equations of motion" read

$$\dot{Q} = -\gamma_{11} Q/CT - \gamma_{12} L\dot{Q}/T \ , \tag{4}$$

$$\ddot{Q} = -\gamma_{21} Q/CT - \gamma_{22} L\dot{Q}/T \ . \tag{5}$$

The first of these equations must just simply yield $\dot{Q} = \dot{Q}$, which means $\gamma_{11} = 0$ and $\gamma_{12} = -L/T$. Onsager reciprocity gives $\gamma_{21} = -\gamma_{12}$, because Q has time reversal signature $+1$ while $\dot{Q}$ has -1; therefore, $\gamma_{21} = T/L$. Thus, our final "equation of motion" reads

$$\ddot{Q} = -\frac{1}{LC} Q - \frac{\gamma_{22} L}{T} \dot{Q} \ . \tag{6}$$

This is exactly the result which is familiar from the study of electric circuits, and you can identify $\gamma_{22} = TR/L^2$, with R resistance.