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A Molecular Ratchet Model without Feedback Control

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Abstract

Feedback controllers (which act like Maxwell's demon) can extract useful work by rectifying thermal fluctuations. However, feedback controllers consume energy, and the work extracted cannot compensate the energy consumed. In this paper, we propose a molecular ratchet model without any feedback controllers and report the simulation results to support its feasibility. In our model, we break the dynamic symmetry by using an electric field to create a concentration difference of solute ions between the two liquid surfaces of a solution. The simulation results show that our ratchet model can induce a continuous net solvent flux. In that sense, all the positive work extracted from the heat bath can be available energy because it doesn't need to compensate the energy cost of the feedback controller. Our work makes it possible to construct an entirely mechanical molecule-rectifying system as Szilárd expected.

1. Introduction.

To challenge the second law of thermodynamics, James Clerk Maxwell presented a thought experiment in 1867 of an intelligent being capable of accurately measuring the velocity of molecules¹. It would act between two separated reservoirs, permitting only fast molecules to enter one reservoir, while allowing only the slow ones to the other. Under such a process heat is transferred from cold to hot, apparently in violation of the second law. This idea, coined as "Maxwell's demon" by Lord Kelvin, has over a century spurred further research on the relation between information and energy establishing quantitative relations²⁻¹³. Classical Maxwell's demon experiments have been realized with cold atoms¹⁴, a molecular ratchet¹⁵, colloidal particles^{16,17}, single electrons¹⁸⁻²⁰, and photons²¹. It is well understood that the role of "Maxwell's demon" can be characterized as a feedback controller for thermodynamic systems^{22,23}. Szilárd thought that it should be possible to construct autonomous, maybe even mechanical, systems that act like Maxwell's demon yet fully obey the laws of physics. Is that possible to construct a mechanism that can rectify molecules without a feedback controller? In this paper we answer the question in the affirmative. Here we propose a molecular ratchet model and report the simulation results to support its feasibility. The most eye-catching feature of this model is that it doesn't need any feedback controllers and can extract positive work directly from a heat bath. We believe that this work takes a further step towards Szilard's goal of an entirely mechanical molecular ratchet.

2. Model setup and methods.

As shown in Fig. 1, there is some extremely dilute electrolyte solution (blue) in a sealed container with two liquid surfaces of A and B. The two liquid surfaces contact the same vapor phase above

them. A hydrophobic porous membrane (HPM) is set on liquid surface A. The membrane is hydrophobic so the liquid cannot wet it; and it is also made of electret material so that it can store a few quasi-permanent net charges²⁴. There is a pore in the middle of the membrane and there are 4 fixed charges (FC) around the pore. There are an equal number of free counter ions in the solution so the net charge of the system is zero. In this model, the electrostatic field of the fixed charges in HPM concentrates the free ions near liquid surface A, causing the concentration of liquid surface A always higher than that of liquid surface B. We will examine this model by molecular dynamic simulation and illustrate how the dynamic asymmetry between the two liquid surfaces functions as a ratchet and induces a continuous net flux of solvent as the arrows shown in Fig. 1.

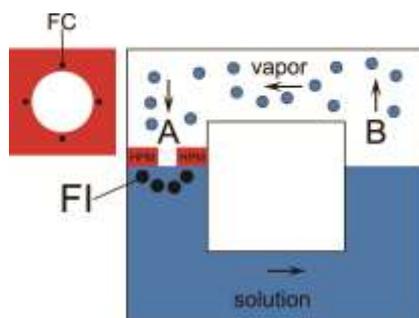


Fig. 1. Setup of molecular ratchet model. HPM denotes hydrophobic porous membrane; FC denotes the fixed charges around the pore; FI denotes the free ions in the solution. In the upper left corner is the top view of HPM.

The model shown in Fig. 1 can be modified to the model for simulation as shown in Fig. 2. The size of the simulation box is $l_x \times l_y \times l_z$ ($2.6 \times 2.6 \times 13$ nm). Periodic boundary conditions are applied to all the three directions. A 4 nm thick water slab, which is composed of 950 water molecules (blue circles), is located in the middle of the simulation box (approximately from 4.2 to 8.2 on z-axis). On the water slab is a 1 nm hydrophobic porous membrane (HPM) with a pore in the middle, its diameter is 1.6 nm. The HPM is located from 8.3 to 9.3 on z-axis and it is fixed so it cannot move during simulation. Four fixed ions embedded in the internal wall of the pore act as the quasi-permanent fixed charges (FC) of an electret, and they are located on the same xy-plane at 8.5 on z-axis (see the top view of HPM in Fig. 2). There are four free counter ions (FI) in the water slab, thus the net charge of the system is zero. There are two vapor-liquid interfaces of A and B, A is the upper vapor-liquid interface exposed at the pore of HPM, and B is the lower vapor-liquid interface. The system is connected to a heat bath at a temperature of 370K. See supplementary Sec. 1 for more about our simulation settings. The net flux induced by the model is determined by counting the net number of water molecules (NNWM) which have moved across the boundary of z-axis. If the value of NNWM at the end of simulation is positive, that means the model can induce a net vapor flux from liquid surface B to liquid surface A.

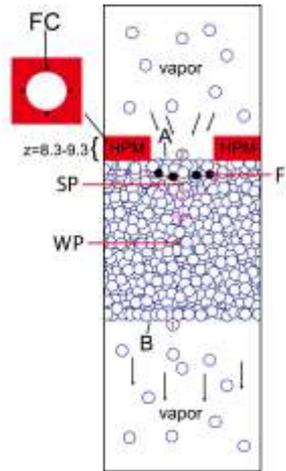


Fig. 2. Side view of model for simulation. SP denotes solution phase; PWP denotes pure water phase. (Note: in order to clearly show each part, the scale of the figure is not consistent with the simulation model.)

3. Results and discussion.

We have tried different types of ions as free ions in the water slab to examine whether the model could induce a net flux. Each of the simulation examples has a specific ID, such as B1, B2, and so on. The results of all examples show that the free ions were concentrated near the liquid surface A, resulting in a concentration difference between the two surfaces of A and B. Table 1 lists the results of each simulation example. We can see that the *nnwm* value of each simulation example is positive and reasonably large, indicating that the model can induce a net water flux as the arrows shown in Fig. 2--liquid surface B keeps evaporating, and the vapor molecules move downward across the bottom boundary of the simulation box and then condense on liquid surface A. The results of examples of B1~B6 also show that the model can induce a net flux whether the free ions are positive or negative. We believe that ions of small inorganic salts are applicable to our model. It was experimentally observed that ions of inorganic solutes can lower the evaporation rate of water²⁵ because the librational modes of the water molecules is hindered due to the strong interaction between the ions and their surrounding water molecules²⁵⁻²⁷. When an ion is close to the vapor-liquid interface, the liquid surface layer cannot completely screen its electric field²⁸, causing an additive potential to the local liquid surface (i.e. the surface barrier becomes higher), where water molecules need greater kinetic energy to escape, so the evaporation rate will decrease accordingly²⁹. The concentration difference between the two liquid surface of A and B results in a difference of barrier height and a difference of evaporation rate between the two liquid surfaces. The key to the ratchet model is that the vapor phase cannot reach equilibrium with both liquid surfaces of A and B at the same time.

Exam-ID	Type-FI	Temp (K)	Time-sim (ns)	V-NNWM	F-rate (/ns)
B1	Na ⁺	370	400	399	0.9975
B1-1	Na ⁺	370	4,000	4,352	1.088
B2	K ⁺	370	400	422	1.055
B3	Li ⁺	370	400	434	1.085
B4	Cl ⁻	370	400	522	1.305
B5	F ⁻	370	400	360	0.9
B6	Br ⁻	370	400	571	1.43
B7	Na ⁺	400	400	794	1.985
B8	Na ⁺	430	400	1,049	2.6225

Table 1. Statistical results of each simulation example. Exam-ID denotes example ID; Type-FI denotes the type of the free ions in the water slab; Temp denotes temperature of the heat bath; Time-sim denotes the simulation time; V-NNWM denotes the NNWM value at the end of simulation; F-rate denotes the average flow rate (water molecules/ns).

We believe that the net flux should increase with the increase of vapor density. The results of examples of B1, B7 and B8 show that the net flux increases with the increase of temperature of the heat bath, which is in line with our expectation. Considering the limited computing resources, we examine the continuity of the net flux by only extending example B1 to 4,000 ns (example B1-1). See the line chart in Fig. 3, it is very clear that the trend has converged to a stable flow rate and shows no signs of weakening over time, indicating that the model can continuously induce a net flux without any external biased forces (for more details of other simulation examples, see supplementary Sec. 2). Also, all of condensed water molecules entered the bulk and the water slab remained almost the same as its initial state, showing the robustness of the system.

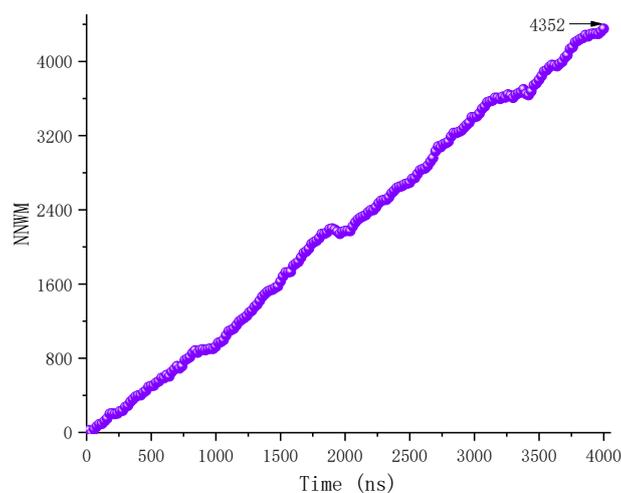


Fig. 3. Variation of NNWM value as a function of time in example B1-1.

All the above simulation examples were done with a pore diameter of 1.6nm. Here we just briefly

introduce a little about the relation between the net flux and pore size. We also tried enlarging the model to examine whether the net flux increases when the pore diameter is 2.8 nm. Unfortunately, the net flux decreased by nearly 50%. On the one hand, when the number of free ions is given, a larger pore size will result in a lower ion concentration near liquid surface A; On the other hand, the electric field of the ions can mainly affect the first hydration shell^{27,30}. When the pore is larger, there will be a smaller proportion of liquid surface A affected by the free ions. Therefore, we cannot increase the net flux only by enlarging the pore size. We will discuss the relation between pore size and the net flux in another paper.

4. What energy drives the net flux.

The electric field of the fixed charges in HPM breaks the uniform distribution of the free ions in the water slab, so that the slab is no longer a homogeneous phase. We can simply divide it into two phases with a curved dotted line according to the concentration (Fig. 2). The part where the free ion always appears is the solution phase (SP), and the other part where the free ion hardly appears can be considered a pure water phase (WP). Including the vapor phase, it is a three-phase system. The relation between chemical potential μ For species in solution and its concentration X can be given by:

$$\mu = \mu_{\theta} + R T \ln X$$

Where μ_{θ} is the chemical potential in a given standard state, R is the gas constant, T is the temperature. Therefore, the water's chemical potential in WP is sure higher than that in SP,

$\mu_b > \mu_a$; this chemical potential gradient drives water molecules from liquid surface B to liquid surface A, resulting in a net vapor flux. The following processes illustrate how kinetic energy of molecules is converted into work.

Molecule 1 is a water molecule escaping from liquid surface B (Fig. 2). During escape, it loses most of its kinetic energy to overcome intermolecular interactions and enlarge its surface area. Note that, the escape is a surface-energy-increasing process. When it becomes a free vapor molecule, its surface energy reaches its maximum.

Molecule 2 is a vapor molecule that is falling onto liquid surface A. When it contacts the liquid surface, the area of liquid surface A becomes larger. Because of intermolecular interactions, the liquid surface will contract spontaneously to minimize its surface energy. Interestingly, the surface contraction can perform work and it includes the following two parts. On one hand, the contraction force pushes molecule 2 into the bulk of the liquid, so W_1 is the work which directly drives the liquid to move downwards; On the other hand, the contraction force also drives another water molecule (molecule 3) to move from SP into WP, so W_2 is the work which makes the chemical potential of molecule 3 increase from μ_a to μ_b (i.e. $W_2 = \mu_b - \mu_a$). In fact, W_2

drives the vapor flux indirectly because the chemical potential difference between μ_b and μ_a drives the vapor flux. Since W_1 drives the liquid flux and W_2 drives the vapor flux, all the

work is actually done by the contraction of liquid surface A. W_2 is the main part of the extracted work, but our calculation shows that it accounts for only about 0.29% of the intermolecular interaction energy of the vapor molecules condensed on liquid surface A (see our calculation in supplementary Sec. 3). Fundamentally speaking, the energy released during vapor condensation on liquid surface A comes from the kinetic energy the molecules lose when they escape from liquid surface B. Net evaporation will lower the temperature of liquid surface A, while net condensation will release condensation heat on liquid surface B, so the temperature of liquid surface A is slightly higher than that of liquid surface B. Because the system is quite small, the temperature difference will be limited to a very small range, and its impact can be ignored. We can see that surface contraction during net vapor condensation plays a key role in breaking the symmetry of periodic potential, because it generates a directed driving force. This is how the model extracts positive work by capturing the surface energy on a cycle (see supplementary animation 1 for the dynamic process).

Feynman-Smoluchowski ratchet is an entirely mechanical system without any feedback controllers, first analyzed in 1912 as a thought experiment by Polish physicist Marian Smoluchowski³¹. It's an apparent perpetual motion machine of the second kind. Feynman demonstrated that if the entire system is at the same temperature, the model will not produce any useful work³². Our model is not driven by temperature difference and it can extract useful work from a single heat bath. The role of "Maxwell's demon" can be characterized as a feedback controller. Feedback controllers consume energy and each feedback controller usually can handle only a single particle¹⁵⁻²⁰. It's extremely difficult to induce a large net flux because it will require a large number of feedback controllers working together. Our model doesn't need any feedback controllers to detect the velocity, position or state of molecules; in that sense, our model can be expanded simply by increasing the number of the single-pore units, and all the work extracted can be available energy because it doesn't need to compensate the energy cost of the feedback controller.

5. Conclusion.

In conclusion, the simulation results support the feasibility of our molecular ratchet model--it is possible for an entirely mechanical model with broken spatial symmetry to convert heat (kinetic energy of molecules) from isothermal environment into useful energy. Combined with a micro transducer, it will become a micro generator and shows a promising application prospect. Our work is a step towards the realization of an entirely mechanical molecule-rectifying system which we have been exploring for more than a century.

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