Molecular ratchets - verification of the principle of detailed balance and driving them in one direction

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We argue that the recent experiments of Kelly et. al. (Angew. Chem. Int. Ed. Engl. 36, 1866 (1997)) on molecular ratchets, in addition to being in agreement with the second law of thermodynamics, is a test of the principle of detailed balance for the ratchet. We suggest new experiments, using an asymmetric ratchet, to further test the principle. We also point out methods involving a time variation of the temperature to give it a directional motion.

It was pointed out long ago by Feynman [1] that a microscopic ratchet, in equilibrium with an isothermal heat bath cannot have a net rotation in any direction - otherwise, the ratchet can be used to extract work from an isothermal system, which is a violation of the second law of thermodynamics. Recently, in a very interesting paper, Kelly et. al. [2] reported the synthesis and the study of the rotational motion of a molecular ratchet. They found the rotation of the ratchet to occur with equal likelihood in either direction, and they conclude that this is in agreement with the second law of thermodynamics (see also comment on this paper by Davis [3]).

In the following, we argue that the experiment not only verifies the second law of thermodynamics, but it also provides a direct test of the principle of detailed balance. Our argument is based upon the fact that the experiment is equivalent to putting a label on the Hydrogens which are opposite the pawl and then probing their dynamics under the rotation of the ratchet. By putting such a label, we are preparing the system in a rather special, but non-equilibrium state (see below). As time passes, the probability distribution evolves and eventually would reach equilibrium. Hence the fact that results of the experiment show no net rotation is surprising! We argue that this results from detailed balance and hence in this experiment, one is verifying more than the second law - actually the principle of detailed balance. We suggest new experiments involving an asymmetric ratchet which would further prove this conclusion. We also suggest a way to cause the symmetric ratchet to undergo a net directional motion, which should be possible to experimentally observe.

In the experiment, first the spin of the atom $H_a$ in the molecule is selectively polarized. This means that a population inversion of the spin states of these atoms has been caused. Then, as the internal rotation proceeds, $H_a$ gets converted into $H_0$ or $H_c$ depending on the direction in which the rotation happens, resulting in a transfer of the polarization and the amount of this transfer is measured.

We denote the population difference between the up and down states of $H_a$ at the time $t$ by $\Delta N_a(t)$. Its equilibrium value is $\Delta N_{a,e} = -N_0 \frac{1}{e^\beta - 1}$, where $N_0$ is the total number of molecules and $\mu = e^{-\Delta E/(k_B T)}$, $\Delta E$ being the energy difference between the up and the down spin states. Let $n_A(t) = \Delta N_a(t) - \Delta N_{a,e}$ denote the deviation of $\Delta N_a(t)$ from its equilibrium value. Its initial value is $n_A(0) = 2N_0 \frac{1-\mu}{1+\mu}$.

The molecular ratchet can undergo internal rotation and the corresponding angle coordinate is denoted by $\phi$. It varies in the range $(-\pi, \pi)$. We divide this range into three regions $A \equiv (-\pi/3, \pi/3)$, $B \equiv (\pi/3, \pi)$ and $C \equiv (-\pi, -\pi/3)$ (see the figure 1). The equilibrium probability distribution $P_e(\phi)$ (see below) is shown in the figure 2(a). At equilibrium, all the three regions are equally likely. When $H_a$ is selectively spin polarized, one is effectively putting a label on a population $n_A(0)$ of the molecules, which have $\phi$ in the range $A$. The experiment studies the dynamics of internal rotation of these molecules by measuring the amounts $n_B(t)$ and $n_C(t)$ crossing over to the other regions $B$ and $C$. The rotational motion may be taken to obey the diffusion equation

$$\frac{\partial P(\phi, t)}{\partial t} = \left\{ \frac{\partial}{\partial \phi} V'(\phi) + k_B T \frac{\partial^2}{\partial \phi^2} \right\} P(\phi, t)$$

(1)

We have absorbed the (unnecessary) constants into our definitions of variables because of which the "time" $t$ has now dimensions of $1/\text{energy}$. $V(\phi)$ is the potential energy for the (internal) rotation. It has an asymmetric form making the molecule a ratchet [4]. We shall neglect spin relaxation in our analysis. The above equation has an equilibrium state with $P_e(\phi) = N e^{-\beta V(\phi)}$, where $N = 1/\int_{\pi}^{-\pi} d\phi e^{-\beta V(\phi)}$ with $\beta = 1/(k_B T)$. As $V(\phi)$ is periodic with period $2\pi/3$, the equilibrium probability distribution too is periodic with the same period.
The spin polarization of $H_a$ is due to an initial distribution with the excess population spread only over the region $A$ with a probability distribution $P_e(\varphi)$. That is, $P(\varphi, 0) = 3P_e(\varphi)$ if $-\pi/3 < \varphi < \pi/3$ and $P(\varphi, 0) = 0$ otherwise (The numerical factor 3 is put to ensure normalization. The number density of molecules in the population, having an angle $\varphi$ is $n_A(0)P(\varphi, 0)$). To calculate the values of $n_A(t)$, $n_B(t)$ and $n_C(t)$, we need to look at the dynamics of this population. For this, we have to solve the equation (4) subject to this initial condition and then calculate $n_B(t) = \int d\varphi P(\varphi, t)$, for $I = A, B, C$. This initial probability distribution function is shown by the full line in figure 2(b).

The initial probability distribution $P(\varphi, 0)$ is a truncated equilibrium probability function, truncated to zero outside the region $A$. The second law and the symmetry of the ratchet requires that the amounts that pass over to $B$ and $C$ would be the same initially - that is, at $t = 0$, $\frac{dn_B(t)}{dt} = \frac{dn_C(t)}{dt}$ . However, as time passes, one expects $P(\varphi, t)$ to become a truly non-equilibrium probability distribution (a typical one is shown by the dotted curve of figure 2(b)), and hence one would expect that $n_B(t) \neq n_C(t)$, in general, even though, experiment shows the two are equal. We now ask why is this so.

The solution of the equation (4) may be written as

$$P(\varphi, t) = \int_{-\pi}^\pi d\varphi G(\varphi, t; \varphi_1, 0)P(\varphi_1, 0)$$

where $G(\varphi, t; \varphi_1, 0)$ is the Green’s function for the differential equation in (4). The principle of detailed balance implies (5)

$$G(\varphi, t; \varphi_1, 0)P_e(\varphi_1) = G(\varphi_1, t; \varphi, 0)P_e(\varphi)$$

It is easy to derive this equation starting from the equation (4). The equation (5) can be written as

$$P(\varphi, t) = 3\int_A d\varphi G(\varphi, t; \varphi_1, 0)P_e(\varphi_1)$$

Now, $n_B(t) = \int_B d\varphi P(\varphi, t) = 3\int_B d\varphi \int_A d\varphi G(\varphi, t; \varphi_1, 0)P_e(\varphi_1)$. Using the detailed balance condition of equation (5) we get

$$n_B(t) = 3\int_A d\varphi \int_B d\varphi G(\varphi, t; \varphi_1, 0)P_e(\varphi_1).$$

As the potential is a periodic function, with period $2\pi/3$, the propagator and the equilibrium probability distribution too are periodic functions with the same period of $2\pi/3$. Hence we can write

$$n_B(t) = 3\int_C d\varphi \int_A d\varphi G(\varphi, t; \varphi_1, 0)P_e(\varphi_1)$$

$$= \int_C d\varphi P(\varphi, t)$$

$$= n_C(t)$$

Thus, though the probability distribution would develop in to a non-equilibrium one as in figure 2(b), the distribution is rather special and $n_B(t) = n_C(t)$ at all times! Further, it is also clear that one can arrive at the same conclusion for any problem for which the equations (4) and (5) are valid. Having proved the general result, we ask: how can one overcome this, and cause $n_B(t) \neq n_C(t)$? Noticing that our arguments made use of the periodicity of the potential $V(\varphi)$, we conclude that if one had an asymmetric ratchet, like the one in the figure 3, the step from equation (4) to (5) would not go through.

Hence $n_B(t)$ cannot be equal to $n_C(t)$, and this should be seen if an experiment similar to that of Kelly et. al is performed. Making the ratchet asymmetric is not difficult - one would have to use a molecule like the one in the figure 4. It is also possible to use such a molecule for a more stringent test of the principle of detailed balance. One first polarizes $H_b$ and measures $n_B(t)$ and then polarizes $H_b$ and then measures $n_A(t)$ - detailed balance implies that the two have to be equal. A similar test can be done with the molecule of Kelly too (though it has not been done), but an experiment with an asymmetric ratchet would be more
interesting. An easy experiment to make the molecule have a net transient motion in one direction is to have a sudden temperature jump in the experiments of Kelly et. al. immediately after spin polarizing $H_a$. This should lead to $n_B(t) \neq n_C(t)$ which can then be experimentally observed. Finally, it is possible to vary the temperature periodically in time - this would correspond to a Carnot cycle for the molecular ratchet. This will cause the system to settle into a steady state with net rotation in one direction. We have performed model calculations and computer simulations and verified these possibilities [5]. In principle, when ultrasonic waves pass through a liquid containing the molecular ratchet, transfer of energy to the rotational motion of the ratchet, from the translational motion of the surrounding liquid molecules can set the ratchet in a steady state with net rotation in one direction.

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Figure Captions

1. Figure 1: The ratchet and the regions $A$, $B$ and $C$

2. Figure 2: (a) The equilibrium probability distribution against the angle co-ordinate. (b) The full line shows the initial probability distribution. It develops into a non-equilibrium distribution of the type shown by the dotted line.

3. Figure 3: The asymmetric ratchet. Notice that the teeth are of different sizes.

4. Figure 4: An asymmetric molecular ratchet.
