

Molecular ratchets: Verification of the principle of detailed balance and the second law of dynamics

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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 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.

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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 the comment on this paper by Davis [4]).

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 hydrogen atoms 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 nonequilibrium state (see below). As time passes, the probability distribution evolves and eventually would reach equilibrium. Hence the fact that the 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 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 observe experimentally.

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_b 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.

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population difference between the up and down states of H_a at the time t by $\Delta N_a(t)$, and its equilibrium value by $\Delta N_{a,e}$. Let $n_A(t) = \Delta N_a(t) - \Delta N_{a,e}$ denote the deviation of $\Delta N_a(t)$ from its equilibrium value.

The molecular ratchet can undergo internal rotation and the corresponding angle coordinate is denoted by φ . It varies in the range $(-\pi, \pi)$. We divide this range in to three regions $\mathcal{A} \equiv (-\pi/3, \pi/3)$, $\mathcal{B} \equiv (\pi/3, \pi)$ and $\mathcal{C} \equiv (-\pi, -\pi/3)$ (see Fig. 1). The equilibrium probability distribution $P_e(\varphi)$ (see below) is shown in Fig. 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 φ in the range \mathcal{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 \mathcal{B} and \mathcal{C} . We shall neglect spin relaxation in our analysis. We denote by $V(\varphi)$, the potential energy for the (internal) rotation. It has an asymmetric form making the molecule a ratchet [2]. The probability distribution at equilibrium for the angle φ is denoted as $P_e(\varphi)$ and is given by $P_e(\varphi) = \mathcal{N}e^{-\beta V(\varphi)}$, where $\mathcal{N} = 1/\int_{-\pi}^{\pi} d\varphi e^{-\beta V(\varphi)}$ with $\beta = 1/(k_B T)$. As $V(\varphi)$ 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 \mathcal{A} with a probability distribution $P_e(\varphi)$. Using $P(\varphi, t)$ to denote the probability distribution function at time t , we have $P(\varphi, 0) = 3P_e(\varphi)$ if $-\pi/3 < \varphi < \pi/3$ and $P(\varphi, 0) = 0$ other-

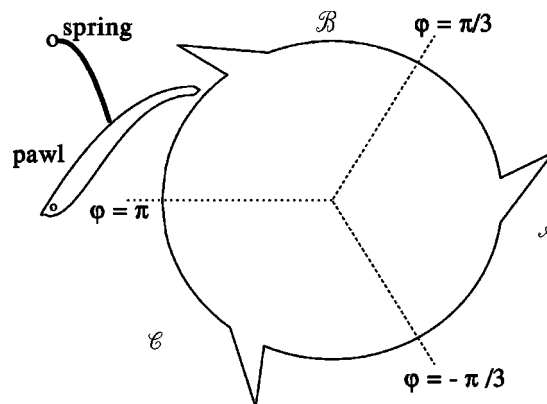


FIG. 1. The ratchet and the regions \mathcal{A} , \mathcal{B} , and \mathcal{C} .

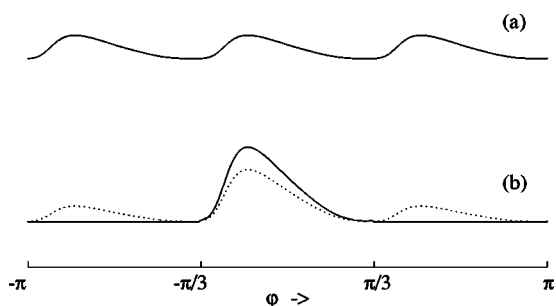


FIG. 2. (a) The equilibrium probability distribution against the angle coordinate. (b) The full line shows the initial probability distribution. It develops into a nonequilibrium distribution of the type shown by the dotted line.

wise (the numerical factor 3 is used to ensure normalization). The number density of molecules in the population, having an angle φ is $n_A(0)P(\varphi, 0)$. The values of $n_A(t)$, $n_B(t)$, and $n_C(t)$, may be obtained from the probability distribution function at the time t , $P(\varphi, t)$ using $n_{\mathcal{I}}(t) = n_A(0) \int_{\mathcal{I}} d\varphi P(\varphi, t)$, for $\mathcal{I} = A, B, C$. The initial probability distribution function is shown by the full line in Fig. 2(b).

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

The probability distribution function $P(\varphi, t)$ may be written as

$$P(\varphi, t) = \int_{-\pi}^{\pi} d\varphi_1 G(\varphi, t; \varphi_1, 0) P(\varphi_1, 0), \quad (1)$$

where $G(\varphi, t; \varphi_1, 0)$ is the transition probability from φ_1 at the time 0 to φ at the time t . The principle of detailed balance implies [3]

$$G(\varphi, t; \varphi_1, 0) P_e(\varphi_1) = G(\varphi_1, t; \varphi, 0) P_e(\varphi). \quad (2)$$

Using $P(\varphi_1, 0)$, Eq. (1) can be written as

$$P(\varphi, t) = 3 \int_{\mathcal{A}} d\varphi_1 G(\varphi, t; \varphi_1, 0) P_e(\varphi_1).$$

Now,

$$\begin{aligned} n_B(t) &= n_A(0) \int_B d\varphi P(\varphi, t) \\ &= 3n_A(0) \int_B d\varphi \int_{\mathcal{A}} d\varphi_1 G(\varphi, t; \varphi_1, 0) P_e(\varphi_1). \end{aligned}$$

Using the detailed balance condition of Eq. (2) we get

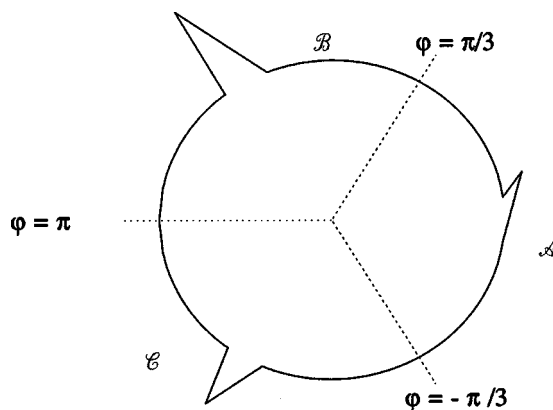


FIG. 3. The asymmetric ratchet. Notice that the teeth are of different sizes.

$$n_B(t) = 3n_A(0) \int_{\mathcal{A}} d\varphi \int_B d\varphi_1 G(\varphi, t; \varphi_1, 0) P_e(\varphi_1). \quad (3)$$

As the potential $V(\varphi)$ 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

$$n_B(t) = 3n_A(0) \int_C d\varphi \int_{\mathcal{A}} d\varphi_1 G(\varphi, t; \varphi_1, 0) P_e(\varphi_1) \quad (4)$$

$$= n_A(0) \int_C d\varphi P(\varphi, t) = n_C(t). \quad (5)$$

Thus, though the probability distribution would develop into a nonequilibrium one as in Fig. 2(b), the distribution is rather special and $n_B(t) = n_C(t)$ at all times. Having proved the general result, we ask the following: 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 Fig. 3, the step from Eq. (3) to Eq. (4) 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 Fig. 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_a 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

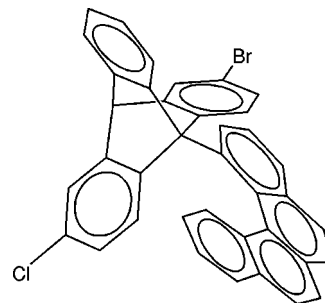


FIG. 4. An asymmetric molecular ratchet.

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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