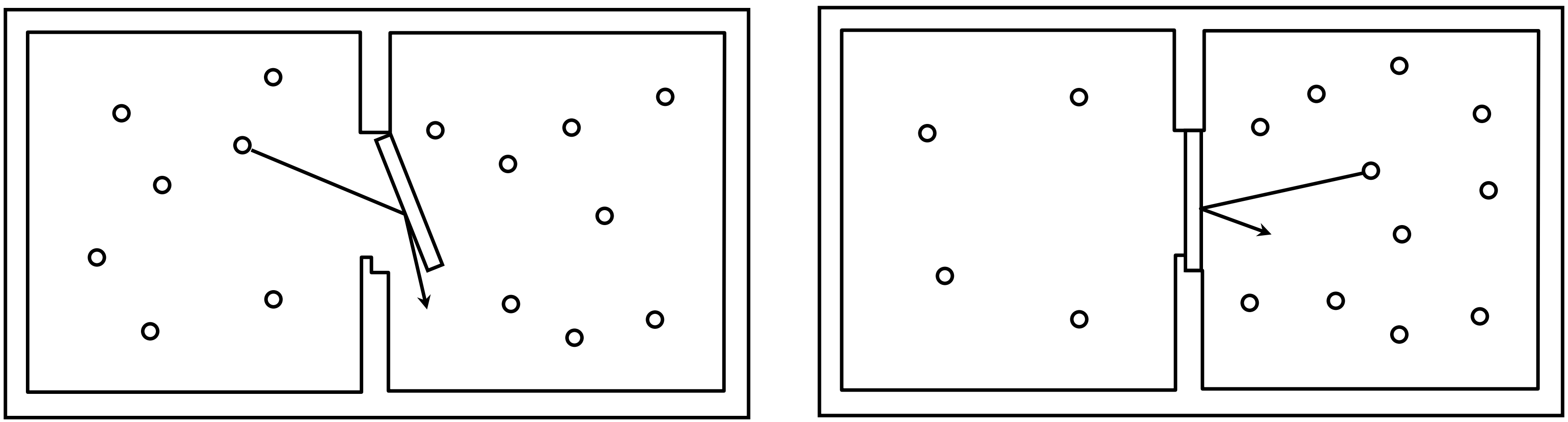
14. Fluctuation Phenomena and Maxwell's Demon

- Early 20th century thermal fluctuation phenomena:
  - Brownian motion.
  - Density fluctuations in fluids near critical states.

  } *Key characteristic:* *Completely random processes!*

- *Idea*: Exploit such phenomena to construct devices that violate 2nd Law.

(a) Smoluchowski's (1914) trapdoor device:



- Gas in separate chambers initially at equal pressures and temperatures.
- Spring-loaded trapdoor allows *randomly fluctuating* molecules to pass from one side to the other, but not *vice-versa*.
- *Expected Result*: Build-up of pressure on one side that can be exploited to perform work. Violation of 2nd Law!

Questions:

(1) Is this an example of a decrease in entropy of a thermally-isolated system?

- Yes!

(2) Can this decrease in entropy be used to perform work?

- No! Spring must be sufficiently weak, and trapdoor sufficiently light.
- But then trapdoor itself will be subject to thermal fluctuations that will prevent its intended operation.

- Smoluchowski's response to (1):
  - Weaken the 2nd Law: **In the long run, on average, a thermally isolated system's entropy will increase.**

- *New (old) question:* What if the trapdoor is replaced with an intelligent being who knows when to open/close it?

(b) Szilard on Entropy and Information

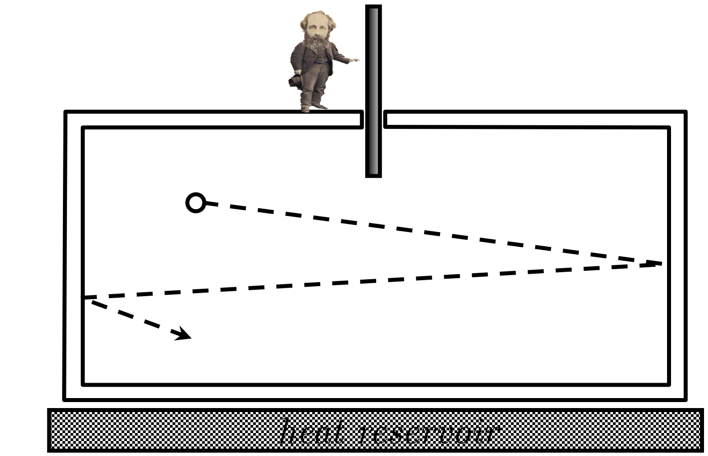
(1929) "On the Decrease of Entropy in a Thermodynamical System by the Intervention of Intelligent Beings"

- *Claim*: Any device that employs fluctuations in an attempt to violate the 2nd Law will fail since there is an inevitable hidden entropy cost in the aquisition of information needed to run the device.

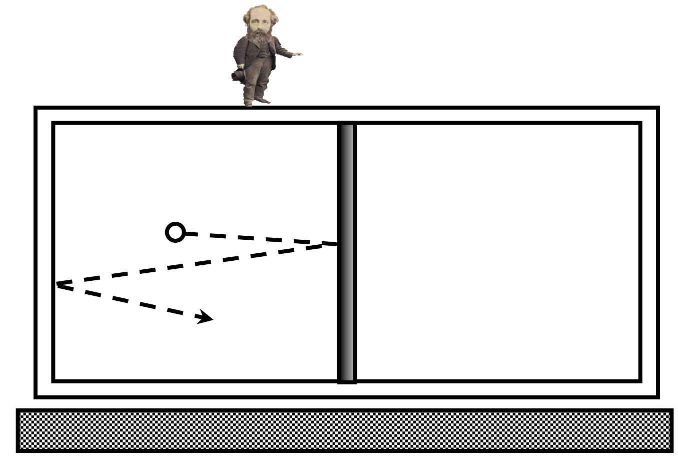
"...measurements themselves are necessarily accompanied by a production of entropy."

Leo Szilard

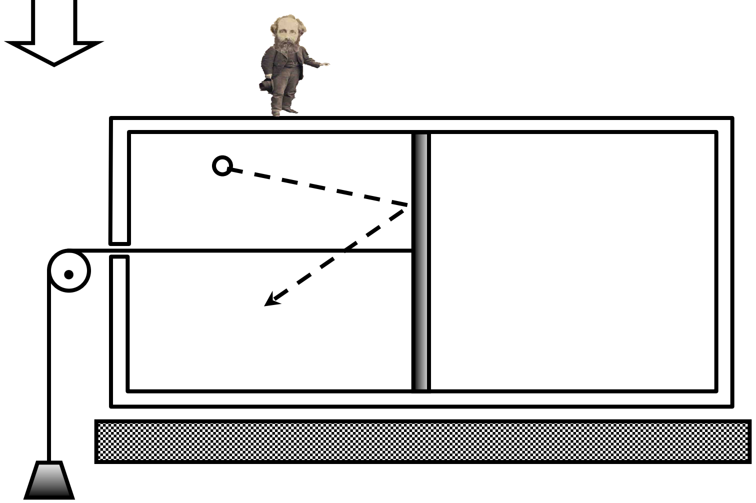
• *Szilard's One-Molecule Engine*



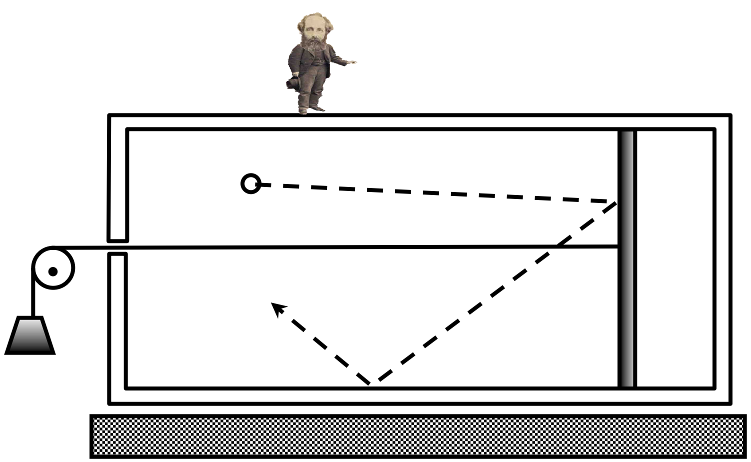
(a) Single molecule exhibiting thermal fluctuations. System at const. temp.



(b) Being inserts partition/piston and determines which side molecule is on.



(c) Being attaches weight to side with molecule. Gas expands reversibly and isothermally by absorbing heat from reservoir. Work performed on weight.



(d) Weight is detached. Partition/piston removed. Cycle returns to (a).

- *Result:* ***Violation of 2nd Law!*** Heat converted to work with no exhaust.

- *In particular*:

$$Q = W = \int_{V_i}^{V_f} P dV$$

$$= \int_{V_i}^{V_f} \frac{kT}{V} dV$$ ← *for an ideal gas*

$$= kT \log \frac{V_f}{V_i} = kT \log 2$$ ← *assuming partition is inserted down the middle ($V_f = 2V_i$)*

  - *So*: Change in entropy is $\Delta S = {}_R\int_i^f \frac{\delta Q_R}{T} = 0 - \frac{kT \log 2}{T} = \boxed{-k \log 2}$

    A decrease in entropy (in reservoir)!

- *Szilard's Solution:* There must be an entropy increase in the being which balances the entropy decrease in the reservoir.

- *Szilard's entropy associated with measurement:*

- Assume only two possible measurement outcomes (simplest case).
- Let $\overline{S}_1, \overline{S}_2$ be the entropies associated with outcomes 1 and 2, respectively.
- Then a lower bound on these entropies is given by:

$$e^{-\overline{S}_1/k} + e^{-\overline{S}_2/k} \leq 1$$

- *Why*?
- Let w_1, w_2 be the probabilities of getting outcomes 1 and 2, respectively.
- Then (it turns out), lower bounds for $\overline{S}_1$ and $\overline{S}_2$ are given by:

$$\overline{S}_1 \geq -k \log w_1 \qquad \overline{S}_2 \geq -k \log w_2$$

or

$$w_1 \geq e^{-\overline{S}_1/k} \qquad w_2 \geq e^{-\overline{S}_2/k}$$

- *And*: Lower-bound constraint follows from $w_1 + w_2 = 1$.

- *Definition*: The average entropy cost of measurement per cycle is

$$\overline{S} = w_1\overline{S}_1 + w_2\overline{S}_2$$

- Now show that for any values of $\overline{S}_1$, $\overline{S}_2$ that satisfy lower-bound constraint, the resulting value for $\overline{S}$ is no less than the entropy decrease that violates the 2nd Law.
  - *Example*: Szilard choses $\overline{S}_1 = \overline{S}_2 = k\log 2$.
  - *Then*: $e^{-\overline{S}_1/k} + e^{-\overline{S}_2/k} = 2e^{-\log 2} \leq 1$
  - *And*: $\boxed{\overline{S} = k\log 2}$

- *Thus*: *On average*, the entropy increase due to measurement is no less than the entropy decrease from the conversion of heat to work.

- *So*: The 2nd Law is saved.