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|  | [**DOING PHYSICS WITH MATLAB**](http://www.physics.usyd.edu.au/teach_res/mp/mphome.htm)  **THERMAL PHYSICS**  **SECOND LAW OF THERMODYNAMICS**  **Arrow of time**      Ian Cooper  School of Physics, University of Sydney  ian.cooper@sydney.edu.au    [**DOWNLOAD DIRECTORY FOR MATLAB SCRIPTS**](http://www.physics.usyd.edu.au/teach_res/mp/mscripts)    **tp\_equilibrium.m**  The mscript is for a simulation of the release of “perfume molecules” from a corner of a room and predicting how these gas molecules will distribute themselves throughout the room. The motion of the gas molecules can be saved as an **animated gif**.        **SECOND LAW OF THERMODYNAMICS**     The **Second Law of Thermodynamics** can be stated as:  Natural process in an isolated system will always spontaneously evolve to  states of greater disorder (states of greater entropy – states of greater probability)  We can think of the concept of **entropy** as a **measure of the disorder of a system**.  *But what do these statements mean?*  We will consider the act of releasing a small quantity of perfume into a fully closed room from one location within the room. Immediately after the perfume is released, we can conclude that the perfume molecules are in an **orderly** state (state with the **lowest entropy**) since all the molecules are located within a small volume element of the room. After some time interval, we know that the perfume can be detected through the room and the perfume molecules will be uniformly spread around the room. This is the most **disordered** state (state of **maximum entropy** state of **maximum probability**). If we continuously monitor the motion of all the perfume molecules we will never detect all the molecules again located in the small volume element that they were released from, although in terms of the principles of conservation of energy and momentum this state is not forbidden. Why? Because if all the perfume molecules were suddenly found within the initial volume element it would be a violation of the Second Law of Thermodynamics.  We can help clarify the meaning of order / disorder and entropy by using a simple model to account for the behavior of the perfume gas molecules. We will consider the gas to be enclosed within an area *A* = 10x10 a.u., that is, we will consider the behavior of *N* gas molecules from a two-dimensional point of view. The enclosure is divided into 100 equal size boxes of area *Abox* = 1x1 a.u. At time *t* = 0 all the gas molecules are within the box (outlined in red) located near the origin (0, 0) as shown in figure 1.    Fig. 1. The two-dimensional enclosure of the gas with an area *A* = 10x10 a.u. The area is subdivided  into 100 boxes of area *Abox* = 1x1 a.u. At time *t* = 0, all the gas molecules (*N* = 600) are released from the  box outlined in red. One of the gas molecules is marked so that you can track its movements.  **tp\_equilibrium.m**  The initial state of the gas at *t* = 0 has the most order since the molecules are located into the smallest volume element and there is only one arrangement possible for this as all the molecules are in one of the boxes. After the gas is released, each molecule moves a random distance and direction in each time step. We are interested in how the molecules arrange themselves in the 100 boxes as time flows. The movement of the gas molecules is shown in the animation of figure 2.    Fig. 2. Animation of gas molecules released from the red enclosed box at time *t* = 0.  The distribution of the gas molecules evolves to states that are more probable. This means the gas molecules after being released will eventually fill uniformly the entire enclosure. The system evolves with time to the state which has its maximum entropy and this corresponds to the most probable state. The system evolves to an equilibrium state in which each box has the same number of molecules in it since this is the state in which there is the greatest number of ways in which the gas molecules can arrange themselves in the 100 boxes.  Figures 3, 4 and 5 ( **tp\_equilibrium.m** ) show the percentage of the gas molecules in the red box (unit area *Abox* = 1x1 a.u.) – the box from which the *N* particles were released from. Since there are 100 boxes, in the equilibrium state (state with the maximum number of ways the particles can arrange themselves 🡪 the most probable state 🡪 state with the maximum entropy) has **1.00 %** of the total *N* particles in the start box. The mean and standard deviation for the average percentage of particles in the start box in the time interval from *t* = 120 to 200 a.u. are shown in each figure. The standard deviation means that in 68% of the measured time steps, the percentage was within one standard deviation of the mean. In each figure, the bottom view shows the y-axis scale reduced to 0 to 5% for the particles in the start box.    Fig. 3. *N* = 600 gas molecules. The average percentage of particles in the starting box in the time interval  from *t* = 120 to 200 a.u. is (0.93 ± 0.36).    Fig. 4. *N* = 12 000 gas molecules. The average percentage of particles in the start box in the time interval  from *t* = 120 to 200 a.u. is (0.98 ± 0.08).    Fig. 4. *N* = 60 000 gas molecules. The average percentage of particles in the start box in the time interval  from *t* = 120 to 200 a.u. is (0.99 ± 0.04).  Inspection of figures 3, 4 and 5 show that as the number of particles increase, the mean value approaches 1% and its uncertainty becomes smaller. It is clear that as *N* gets larger, the distribution becomes more uniform and the fluctuations from the mean value reduce. 60 000 particles was the maximum number of particles used in the three simulations. Consider a gas enclosed in a volume *V* = 1.00 m3 at atmospheric pressure *p* = 1.01x105 Pa and temperature *T* = 300 K. In this volume there are 2.4x1025 particles ( *pV* = *NkT* ). In a box of 1.00 m3, the gas molecules will certainly be uniformly distribution and the any fluctuations away from this equilibrium state will certainly be negligible. Hence, the process of the gas spreading around the room is **irreversible**. Although it is possible that all the particles can return to the start box at the same instant, there are no laws really preventing this, only that the probability of this occurring is exceedingly small.  When the perfume is released, the system of the enclosed gas spontaneously changes from a state of low probability to one of higher probability, that is, the entropy of the system increases. The relationship between probability and entropy is given by  ***S* = *k* loge( *w* )**  where *S* is the entropy, *k* is the Boltzmann constant and *w* is “loosely” defined as the number of molecular arrangements that correspond to the same macroscopic state. In our initial state (*t* = 0), there is only one possible arrangement of the particles – all the particles must be in the start box, *w* = 1 🡪 *S* = 0.  The **Second Law of Thermodynamics**, tells us that if an isolated system undergoes a spontaneous process, its final state will be one in which the entropy *S* and *w* are maximum.  **MATLAB MSCRIPT**  Setup for initial position of particles in start box using the Matlab command **rand** to give a set of numbers between zero and one  e.g. rand(1,5) 🡪 0.7612 0.7568 0.3738 0.5126 0.9739  % initial position of N particles within unit box ------------------------  R = 1; % max step length  P = rand(N,2); % initial (x,y) coordinates of N particles  x = P(:,1);  y = P(:,2);  Particle coordinates are updated in a for loop using the Matlab command **randn** to give random numbers which are normally  e.g. randn(1,5) 🡪 -0.0426 0.8961 -2.1927 -1.3408 0.0100  % increment the position of each particle --------------------------------  dP = R.\*randn(N,2);  dx = dP(:,1);  dy = dP(:,2);  % updated position of each particle---------------------------------------  x = x + dx;  y = y + dy;    The particles are kept inside the enclose by reflections at the sides  % particle reflected of boundaries of the box ----------------------------  for c1 = 1:N  if x(c1) < 0; x(c1) = x(c1) + abs(dx(c1)); end;  if y(c1) < 0; y(c1) = y(c1) + abs(dy(c1)); end;  if x(c1) > 10; x(c1) = x(c1) - abs(dx(c1)); end;  if y(c1) > 10; y(c1) = y(c1) - abs(dy(c1)); end;  end  To count the number of particles in the start box each time step, logical functions are used  e.g. z = rand(1,5) 🡪  0.7635 0.0078 0.8026 0.7228 0.7291 0.0627 0.7569 0.6265 0.1902 .6564  z01 = z01 < 0.5 🡪 0 1 0 0 0 1 0 0 1 0  z10 = z(z<0.5) 🡪 0.0078 0.0627 0.1902  sum of numbers less than 0.5 sum(z01) 🡪 3  % calculate the number of particles in start box --------------------------  box\_x = ones(1,N);  box\_y = ones(1,N);  box\_x(x>R) = 0;  box\_y(y>R) = 0;  N\_box(c) = sum(box\_x .\* box\_y);  Calculating the statistics for the start box  % calc. mean std sem for no. of particles in start box ---------------  ns = floor(0.6\*nt); % starting point for calc.  N\_avg = (100/N) \* mean(N\_box(ns:end));  N\_std = (100/N) \* std(N\_box(ns:end));  N\_sem = N\_std/sqrt(nt-ns+1); |  |