
A Simple Experiment to Study the Statistical Properties of a Molecular Assembly with Two or Three State Dynamics

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A dice throwing game is used to develop the key concepts in statistical thermodynamics of systems with two or three energy states. The experiment will demonstrate how, according to the second law of thermodynamics, an increasing number of molecules in an assembly produces a particular distribution of microstates. It will also lead to a statistical definition of temperature.

Consider a beaker of water – an assembly of some 10^{24} molecules. Are these molecules identical? Are they all moving in the same direction with the same speed? Are they all occupying one particular molecular energy state?

The answer to all these questions is no. Yet, at the macroscopic level, the thermodynamic properties of this system are fairly well defined. For example, it has a fairly uniform temperature. But do all the molecules have the same temperature? What does temperature mean for a single molecule?

To investigate why in spite of utter chaos at the molecular level we still end up with well defined properties for the system as a whole, we use concepts of statistics. Elementary techniques of statistical mechanics applied to systems in equilibrium are included in all undergraduate texts of physical chemistry (See Atkin's book in Suggested Reading). We discuss here a simple classroom experiment to supplement the textbook material and clarify some of the questions which frequently arise.

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Box 1**What is a Micro-state?**

A micro-state is a description of a system in terms of a dynamical configuration of individual molecules or particles, such that the larger macro system obeys certain constraints. For instance, a system could be described in terms of the occupations of molecular energy states of its particles, or of the momenta and position coordinates of its particles. Suppose we have a system of free particles in which each particle has a unit mass and the system has a total energy of 100 units. Then all possible states are allowed such that the sum of the squares of the momenta of individual particles taken together is 200 units. The particles may be anywhere in space. The configuration of momenta and position of the particles at any particular time is a micro-state of the system. The constraint here is the constant total energy.

The objectives of the experiment are as follows: i) to demonstrate that as the number of molecules in a system increases, a particular distribution of micro-states (see *Box 1* for definitions) becomes overwhelmingly prominent (the values of measurements taken in a laboratory will essentially correspond to this distribution); ii) to confirm that the above observation follows from the second law of thermodynamics; and iii) to obtain a statistical definition of *temperature*.

Experiment

The experiment itself is quite simple. In fact, it was inspired by an innovative middle school exercise on probability in the Hoshangabad Science Teaching Program in Madhya Pradesh (see *Bal Vajnanik* in Suggested Reading). It is a game of throwing dice, where the value of each throw of one die represents the state occupied by an individual molecule. Let us say we have a class of students. For a large class, the students can be divided into groups to work together on the experiment. But the larger the number of experimenters in a group, the better the results. (One can even double the sampling, with each student holding one die in the left hand and another in the right hand.) Throwing the dice determines the micro-state for a collection of N



Experiment	State I	State II
A	1, 2, 3	4, 5, 6
B	1, 2, 3, 4	5, 6

Table 1 Experiments for the case where each molecule can occupy only two states; A: degenerate (equal-probability) states; B: non-degenerate states

molecules, where N is the number of members in a team. For each experiment, we can define two possible states for each molecule. For example, if the value on the die is 1, 2, or 3, we can say the molecule is in State I, and if the value is 4, 5, or 6 it is in State II. The states can be defined differently for each experiment (see *Table 1*). You can easily go further and design additional experiments with three states, which however we will not discuss here.

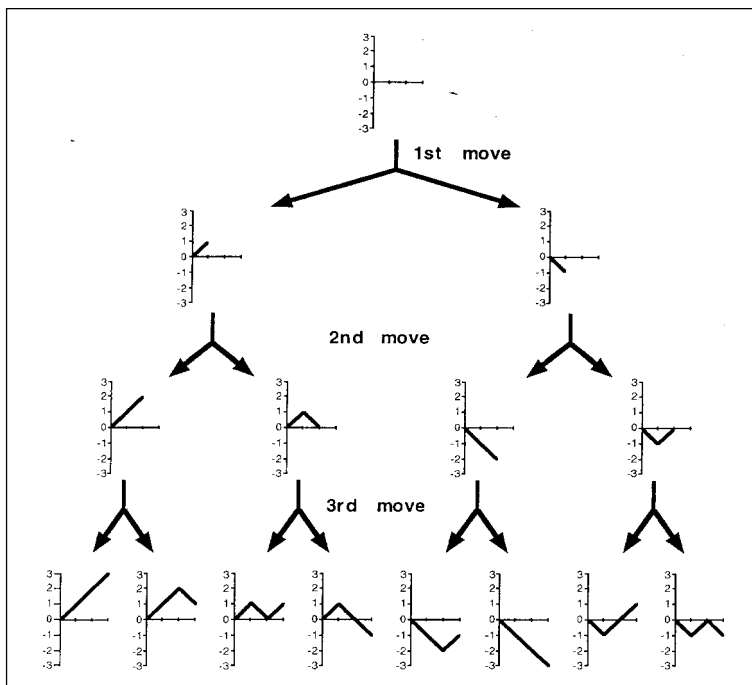
Each student throws a die 100 times and records the reading of the die in a table (see *Table 2*). The table shows the possibilities for the case where only two energy states are accessible to an individual molecule. Note that a die is not a molecule, but its

Table 2 A typical set of readings for the two different experiments A and B.

Move number	Readings on die	Molecular State	
		Experiment A	Experiment B
1	3	I	I
2	2	I	I
3	6	II	II
4	4	II	I
5	5	II	II
6	1	I	I
.	.	.	.
.	.	.	.
100	5	II	II



Figure 1 Possible routes of evolution of the micro-chart.



reading gives us information on the energy state occupied by the molecule. Thus, if we have just one group of ten students, we will get ten tables like the one shown representing 100 configurations (states) of ten molecules.

Although a number of experiments can be devised, *Table 1* shows only two examples. Experiments A and B represent degenerate and non-degenerate energy states respectively. In the degenerate case, both states are of equal energy and have equal probability of occupation. In the non-degenerate case, the state with a higher probability of occurrence (*which one is it?*) is the ground state, and the one with a lower probability is the excited state.

Investigating the Micro-charts: How Different are the Molecules?

For experiments A and B, each student then draws a micro-chart, as explained below and shown in *Figure 1*. We call these



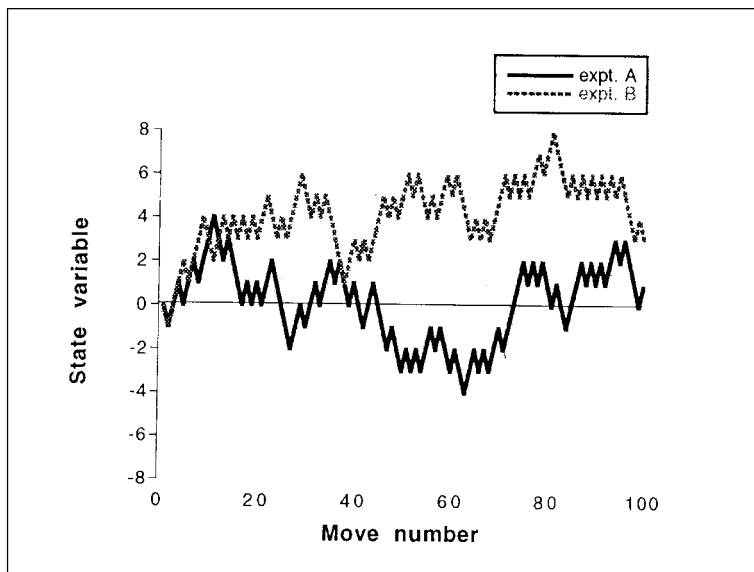


Figure 2 Typical micro-charts for the experiments A and B.

micro-charts because these depict the states occupied by individual molecules as a function of time. Starting from the origin, occupation of State I in a particular move adds +1 and that of State II adds -1 to the magnitude of a random variable plotted on the y -axis. The serial number of the move is shown on the x -axis. A typical micro-chart at the end of the experiment (100 moves) is shown in *Figure 2*. Each member of the group would find his/her micro-chart to be unique and to show no similarity with the others after the first couple of moves. This is merely a reflection of the complete randomness in the microscopic dynamics.

The Macro-chart: Towards Chemically Relevant Questions

For experiments A and B, all the experimenters in a group now work together to record a frequency table. The frequency of occurrence of a given number of molecules in State I $[n_1 \in (0, 1, \dots, N)]$, where N is the total number of molecules] is then plotted as a bar diagram (*Figure 3*). After 25, 50 and 100 moves, the following calculations are done:



(i) the probability p_i , ($i = n_1$) for a particular value of n_1 is calculated as:

$$p_i = \frac{f_i \text{ (frequency)}}{N_m \text{ (\# of moves)}}$$

(ii) the probability $p(I)$, that a molecule occupies State I, as:

$$p(I) = \frac{1}{N} \sum_i i \cdot p_i$$

(iii) A smooth plot is drawn to clearly indicate the envelope. The peak position, n_1^0 , peak height, full width at half maximum (fwhm) and standard deviation (Δ) are found. The ratio peak height/ fwhm are related quantities. Δ is calculated as

$$\Delta = \frac{1}{N_m} \sqrt{\sum_i (i - i_0)^2 \cdot f_i}$$

The target questions are:

- What is the variation in the quantities calculated above as the number of moves increases from 25 to 50? Why?
- Why does the peak position change from experiment A to experiment B?
- What is the shape of the envelope after a large number of moves? Why is it like that?

The question (a) mostly addresses aspects of statistics. For instance, the standard deviation calculated for a typical set of data as shown in the macro-chart (*Figure 3*) are shown below (*Table 3*).

Number of moves (N_m)	Mean	Δ
25	4.60	0.3622
50	4.64	0.2593
100	4.89	0.1726

Table 3 Standard deviations from the macro-chart (i_0 is assumed to be equal to the mean)



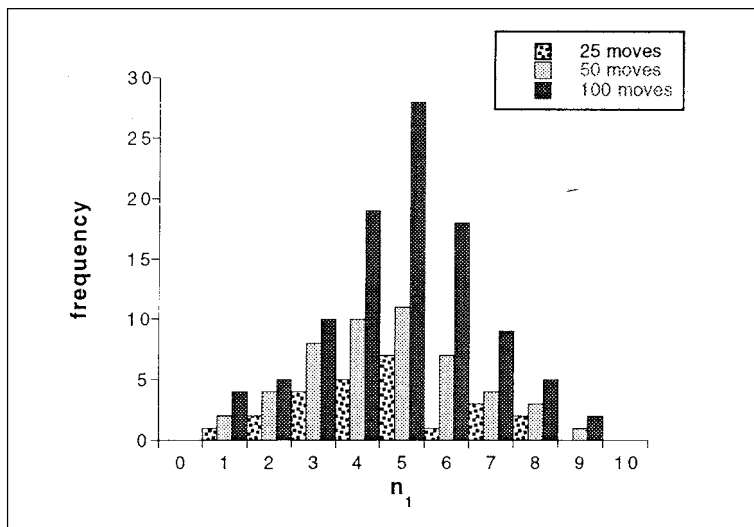


Figure 3 A typical macro-chart for experiment A.

Thus we see both visually as well as in terms of statistical calculations how the system of 10 independent molecules tends towards a most probable distribution after a large number of moves (or, in other words, a particular distribution is most likely to occur in any particular observation on a large number of molecules).

The sharpening of peak position for a particular distribution is expressed in classical thermodynamics in terms of a maximal value for the entropy, $S = k_b \cdot \ln W$, where W is the thermodynamic probability or the number of possible microstates for a particular distribution and k_b is the Boltzmann constant.

It is meaningful to calculate here the values of entropy corresponding to a couple of different distributions, including the most probable one (see *Box 2*).

Question (b) on the other hand poses an interesting learning exercise. If entropy were the only deciding factor, the peak position in the macro-charts obtained for both the experiments A and B would be the same. Is the second law of thermodynamics violated here (see *Box 3*)?



Box 2
Micro-states and Entropy

For a two state problem, with say, 10 molecules, the following table shows the values of entropy function corresponding to some of the distributions:

Number of molecules		W	S cals/degree/mole
State I	State II		
3	7	$10!/(3!7!) = 120$	9.513
4	6	$10!/(4!6!) = 210$	10.625
5	5	$10!/(5!5!) = 252$	10.988
6	4	$10!/(4!6!) = 210$	10.625

It is thus apparent that the distribution (5, 5) corresponds to the maximum value of entropy. The difference in entropy for two different distributions does not appear to be large here, but as we increase the number of molecules (to say 1000), the difference is going to increase and the value will peak sharply for the distribution with an equal number of molecules in each state (this is shown rigorously by differentiating $\ln W$ and finding the values of N_1 and N_2 corresponding to the maximum). (See McQuarrie's book in Suggested Reading)

For a three state problem the thermodynamic probability is calculated using the trinomial distribution, $W = N!/(N_1! N_2! N_3!)$.

For the non-degenerate case, since the occupation probabilities for the two different states are known (either a priori or from the frequency probabilities obtained from the macro-chart), we can now evaluate the *statistical* temperature, as

$$T^{-1} = \left(\frac{\Delta E}{R} \right) \cdot \ln \frac{p(\text{I})}{p(\text{II})}.$$

This follows from the Boltzmann distribution (see *Box 4*).

Here we will talk of temperature in units of $\Delta E/R$, since we are dealing with an arbitrary separation of energy states.



Box 3**The Second Law of Thermodynamics and the Most Probable Distribution**

The second law of thermodynamics states that the entropy of an isolated system tends to increase in a natural process. For a system in equilibrium, the entropy remains constant at its maximal value. For a system with a fixed composition and with only one set of degenerate energy states, interaction with the surroundings is impossible. There is no mechanism for the transfer of mass or energy; hence the system is effectively isolated. However, if there are non-degenerate states, there can be an exchange of energy with the surroundings and thus the system is not isolated any more. In such a case, the equilibrium molecular distribution depends on the collective property of thermal equilibrium. The Helmholtz free energy, $A = U - TS$ (or with appropriate conditions, the Gibbs' free energy, $G = H - TS$) determines the most probable distribution; here U is the internal energy of the system, H is the enthalpy, and T is the temperature parameter (quantifying the property of thermal equilibrium, as stated in the zeroth law of thermodynamics).

In the case of experiment B, the most probable distribution corresponds to a minimum value of A (or G). This is only valid if the macroscopic system at thermal equilibrium is constrained to have a constant volume (or pressure).

Question (c) aims at introducing the Gaussian distribution. At this juncture, another exercise may be introduced. The students may be asked to draw bar diagrams for distributions showing the number of particles in one of the two a priori equiprobable states for 2, 3, 4, 5, . . . particles. It can be easily seen that these distributions are the coefficients in a binomial expansion (the W 's discussed above in *Box 2*). In the limit of large number of particles, the binomial distribution becomes a Gaussian (see McQuarrie's book in Suggested Reading).

Further Experiments

Further experiments can be designed as variations of experiments A and B. For example, a three state problem can be designed with either degenerate (e.g., I: 1, 2; II: 3, 4; III: 5, 6) or non-degenerate (e.g., I: 1, 2, 3; II: 4, 5; III: 6) states. Micro-charts for



Box 4**The Boltzmann Distribution**

Perhaps the most fundamental concept in equilibrium thermodynamics, the Boltzmann distribution provides a statistical definition of temperature.

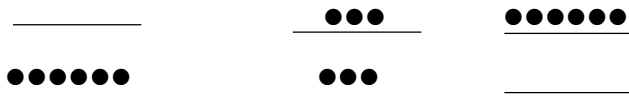
If the probability of occupation of two states with different energies are $p(I)$ and $p(II)$, then

$$\frac{\Delta E}{RT} = \ln \frac{p(I)}{p(II)}$$

where ΔE is the energy difference between the two states (*Figure 4*). The temperature, T , provides a measure of the thermal energy, $k_B T$ available to each molecule (or RT to each mole).

This holds strictly for equilibrium. In a given situation, the prevalence of equilibrium in one degree of freedom, say, translational (the velocity distribution), does not necessarily imply equilibrium in another mode. There can be different values of T for the vibrational and rotational states, each being in a local thermodynamic equilibrium.

Using the Boltzmann distribution in a nonequilibrium situation can give rise to anomalies, as for instance, in the case of population inversion (e.g., for lasers). Given below is an exercise. Find the temperature corresponding to the following distributions:



the individual molecules can be drawn with the values -1 , 0 and 1 assigned to a random variable corresponding to the occupation of states I, II and III respectively. This provides qualitative information similar to that of the micro-charts from experiments A and B, on randomness at the micro-level.

One could improvise on the macro-charts and draw a 3-D plot. Obviously, this is sensible (timewise) only if a computer is accessible. Otherwise, the probability of being in a particular state is calculated directly from the bar diagram after 25, 50 and



100 moves and the results are compared with the theoretical probability. Finally, the quantity $\Delta E/RT$ is calculated for the different energy states (I and II, I and III) using the Boltzmann distribution.

Conclusion

The purpose of designing this experiment was to demonstrate how the macroscopic properties of a system are seen as statistical outputs of the collective behaviour of random microscopic structures. We have avoided the use of a computer, though its use to simulate much larger numbers of dice throws would enhance the pedagogical value of the experiment and hence, when accessible, it is highly recommended (see Loetz article in Suggested Reading). In the HSTP exercise, the macro-charts are prepared teamwise as well as for the whole class. The difference in going from a team of a few members to an entire class is quite remarkable.

Further exercises involving the distribution function can be designed. A number of mathematical concepts, e.g., the algebra of the random walk problem as well as further questioning in the physics of the problem, e.g., the concept of phase space and the ensemble of systems with identical macroscopic properties and different microscopic descriptions, can be developed. The subject of fluctuations and nonequilibrium populations can also be invoked in an elementary manner while discussing the stochastic origins of the equilibrium distribution.

Suggested Reading

- ◆ D McQuarrie. *Statistical Mechanics*. Harper Collins. NY, 1983.
- ◆ F Reif. *Fundamentals of Statistical and Thermal Physics*. McGraw Hill. NY, 1988.
- ◆ Bal Vajinank. *Science text for class VIII. Hoshangabad Science Teaching Program. Madhya Pradesh Pathya Pustak Nigam, 1989.*
- ◆ P W Atkins. *Physical Chemistry*. 5th ed., Oxford, 1994.
- ◆ A Loetz. *J. Chem. Ed.* Vol 72. p 128, 1995.

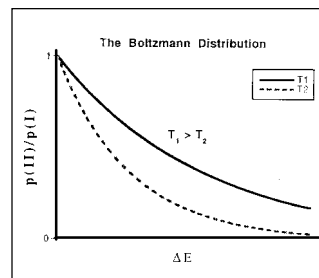


Figure 4 The Boltzmann distribution of populations in two energy states.

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