

A simple computer simulation of molecular collisions leading to Maxwell distribution

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Abstract We describe a simple computer program which simulates molecular collisions in two dimensions and leads to Maxwell distribution. The results show that even with 5–10 colliding molecules the velocity distribution is quite close to Maxwell's.

Zusammenfassung Ein einfaches Computerprogramm wird beschrieben, das molekulare Stöße in zwei Dimensionen simuliert und zur Maxwell-Verteilung führt. Die Ergebnisse demonstrieren, daß bereits mit Stößen von 5–10 Molekülen nahezu Maxwell-Geschwindigkeitsverteilung erreicht wird.

When teaching molecular physics, one often illustrates the behaviour of molecules in gas by showing (on an overhead projector) collisions of little discs floating on an air pillow. Observing rapid changes of velocities of the discs, students get a feeling of the molecular chaos. But in this way it is difficult to see the appearance of statistical regularities, such as the Maxwell (1860a, b, 1866a, b, c, 1867) distribution, which are at the basis of statistical physics.

The purpose of this note is to point out that the emergence of Maxwell distribution out of the molecular chaos can be demonstrated by a simple computer experiment, which can be performed on a home computer.

We start by considering the simplest case of two molecules with equal masses moving within a given region. In order to connect the discussion with demonstrations of the molecular chaos on an overhead projector, we shall consider only the case of molecules moving in a plane. Let us suppose that at time t_0 the molecules we follow have velocities $v_1^{(0)}$ and $v_2^{(0)}$. Since our 'gas' is very rare, the molecules will be reflected many times by the walls before they collide. As the walls are never perfectly regular, the directions (but not magnitudes) of velocities will change irregularly at every reflection. Instead of trying to describe the motion of molecules within the vessel, it is much easier and more realistic to assume that the directions of the molecules' vel-

ocities are completely random at the moment they collide. We thus choose two angles $\alpha_1 \in (0, 2\pi)$ and $\alpha_2 \in (0, 2\pi)$ at random and take the velocities v_1, v_2 before the collision of molecules as

$$\begin{aligned} v_{1x} &= |v_1^{(0)}| \cos \alpha_1, & v_{1y} &= |v_1^{(0)}| \sin \alpha_1 \\ v_{2x} &= |v_2^{(0)}| \cos \alpha_2, & v_{2y} &= |v_2^{(0)}| \sin \alpha_2. \end{aligned} \quad (1)$$

When describing the collision we first pass to the centre of mass system (CMS). Its velocity V with respect to the vessel (lab. system) is $V = \frac{1}{2}(v_1 + v_2)$, and velocities of molecules in this system are

$$\begin{aligned} w_1 &= v_1 - V = \frac{1}{2}(v_1 - v_2) \\ w_2 &= -w_1. \end{aligned} \quad (2)$$

The conservation of energy and momentum says that in the CMS the direction of w_1 may change during the collision, but its magnitude remains constant. The situation is shown in figure 1, taken almost literally from Maxwell's papers (1866a, b, c, 1867). The result of the collision is thus given by a single angle γ in terms of which

$$\begin{aligned} w'_{1x} &= w_{1x} \cos \gamma + w_{1y} \sin \gamma \\ w'_{1y} &= -w_{1x} \sin \gamma + w_{1y} \cos \gamma \\ w'_2 &= -w'_1 \end{aligned} \quad (3)$$

where w'_1 and w'_2 are velocities in the CMS after the collision.

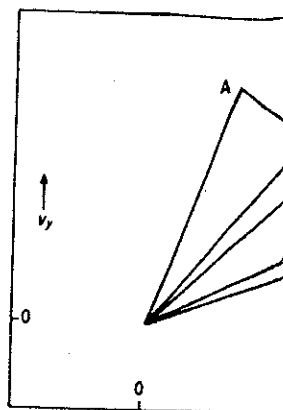


Figure 1 The vector OA represents the velocity w_1 , OB the velocity w_2 . OA' and OB' represent the velocities w'_1 and w'_2 in the CMS after the collision. The angle γ is the angle of rotation of the velocities during the collision. The magnitudes of the velocities are equal.

According to classical mechanics, the direction of the velocity of the centre of mass depends on parameters characterizing the collision (impact parameter and form of interaction between molecules). In quantum mechanics, the direction of the velocity of the centre of mass is a random variable with the distribution general on E and $W(r)$. In this model, we shall suppose that the direction of the velocity of the centre of mass is a random variable with the distribution general on $(0, 2\pi)$.

After passing back to the lab. system, we find the velocities v'_1, v'_2 after the collision

$$v'_1 = w'_1 + V$$

From equations (2), (3) and (4), we find

$$(v'_{1,2})^2 = \frac{1}{2}(v_1^2 + v_2^2) \pm [v_1^2 - v_2^2] \cos \gamma$$

where $\alpha = \alpha_1 - \alpha_2$ is a random variable with the distribution general on $(0, 2\pi)$. Note that $v_1^2 + v_2^2 = v'^2_1 + v'^2_2$, the conservation of energy in the CMS.

After the scattering, the molecules are reflected many times from the walls of the vessel, and they collide again.

With two molecules, of course, the Maxwell distribution (on the total energy of the

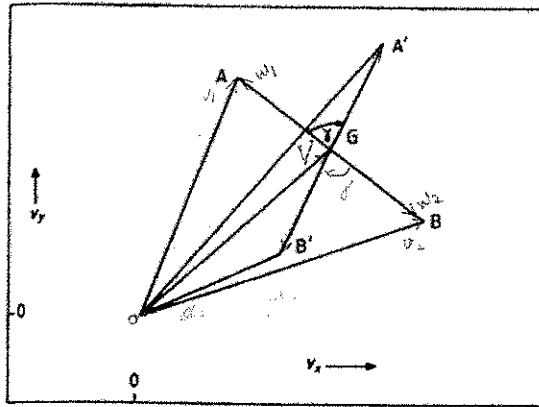


Figure 1 The vector OA represents the velocity v_1 , the vector OB the velocity v_2 . The centre of AB is denoted as G and OG represents the CMS velocity V . The velocities w_1 and w_2 in the CMS are given by vectors GA and GB . During the collision these velocities are rotated by the angle γ to new values GA' and GB' . Note that the magnitudes of velocities in the lab. system (OA' and OB') after the collision might be quite different even if the magnitudes of the original velocities were equal.

According to classical mechanics, the angle γ depends on parameters characterising the collision (impact parameter and CMS energy E) and on the form of interaction energy $W(r)$ between molecules. In quantum mechanics, the angle γ is a random variable with the distribution depending in general on E and $W(r)$. In order to have a simple model, we shall suppose that the scattering is isotropic (rigid molecules with contact interaction or s-wave scattering in quantum mechanics). Therefore we shall consider the angle γ as a uniformly distributed random variable within the interval $(0, 2\pi)$.

After passing back to the laboratory system we find the velocities v'_1, v'_2 of molecules after the collision

$$v'_1 = w'_1 + V, \quad v'_2 = w'_2 + V. \quad (4)$$

From equations (2), (3) and (4) we easily obtain

$$(v'_{1,2})^2 = \frac{1}{2}(v_1^2 + v_2^2) \pm \left[\frac{1}{2}(v_1^2 - v_2^2) \cos \gamma + v_1 v_2 \sin \alpha \sin \gamma \right] \quad (5)$$

where $\alpha = \alpha_1 - \alpha_2$ is a random variable with uniform distribution within the interval $(-2\pi, 2\pi)$. Note that $v_1^2 + v_2^2 = v_1'^2 + v_2'^2$, which shows explicitly the conservation of energy in the collision process.

After the scattering, the molecules are again reflected many times from the walls of the vessel, the directions of their velocities change in a random way and they collide again.

With two molecules, of course, we cannot obtain the Maxwell distribution (one molecule may have at most the total energy of the two molecules with

which we started) and for that purpose we have to consider a 'gas' containing more molecules. Since we do not wish to complicate the analysis by following trajectories of molecules, we select the two of them that are going to collide at random.

Our simple model thus consists of four steps that are repeated again and again:

Step 1: Choose two molecules which will collide.

Step 2: Generate randomly the angle α between their velocities (the consequence of reflections from irregular walls).

Step 3: Generate randomly the angle of scattering γ in the CMS.

Step 4: Calculate the new velocities in the lab. system.

In the appendix we list the program which represents the realisation of our model on the Sinclair ZX Spectrum computer. We did not take advantage of the modifications of BASIC offered by this computer and tried to write the program in standard BASIC. The only exceptions are the IF statements and the CLS (clear screen) statement. Instead of velocities, we work with their ratios to initial velocities, which are all made equal. From the didactical point of view a graphical output is desirable, but we have not included the corresponding part of our program, because it is machine-dependent.

The calculated velocity distributions for a 'gas' consisting of 5, 10 or 50 molecules are compared with the true Maxwell distribution in figure 2. Note that in this planar case the distribution function is proportional to $v \exp(-v^2/(v^2))$, where $\langle v^2 \rangle$ denotes the mean quadratic velocity†.

It is not surprising that the velocity distribution in a 'gas' consisting of 50 molecules is so close to Maxwell's one, but it is somewhat surprising for a 'gas' consisting of only five molecules.

If one forgets for a moment what one learned at university about velocity distributions, and the students at the appropriate age fortunately do not have this knowledge, one can perhaps feel the emergence of the velocity distribution as something great and will be able to appreciate Maxwell's intuition, which led him to the discovery of these regularities at a time when even talking about the existence of atoms and molecules was often considered as a fantasy. Maxwell, as it is well known, arrived at his distribution in two different ways. The former derivation (Maxwell 1860a, b) was based on the assumption that in the state of molecular chaos the probability $f(v_x) dv_x$ for a molecule to have its x component of velocity within the interval $(v_x, v_x + dv_x)$ is completely independent

†The factor $\frac{1}{2}$ present in the exponent in Maxwell distribution in three dimensions is absent in the planar case. This is seen from the fact that the v_x distribution is proportional to

$$\exp(-v_x^2/2\langle v^2 \rangle) \quad \text{and} \quad \langle v_x^2 \rangle = \langle v^2 \rangle = \frac{1}{2}\langle v^2 \rangle.$$

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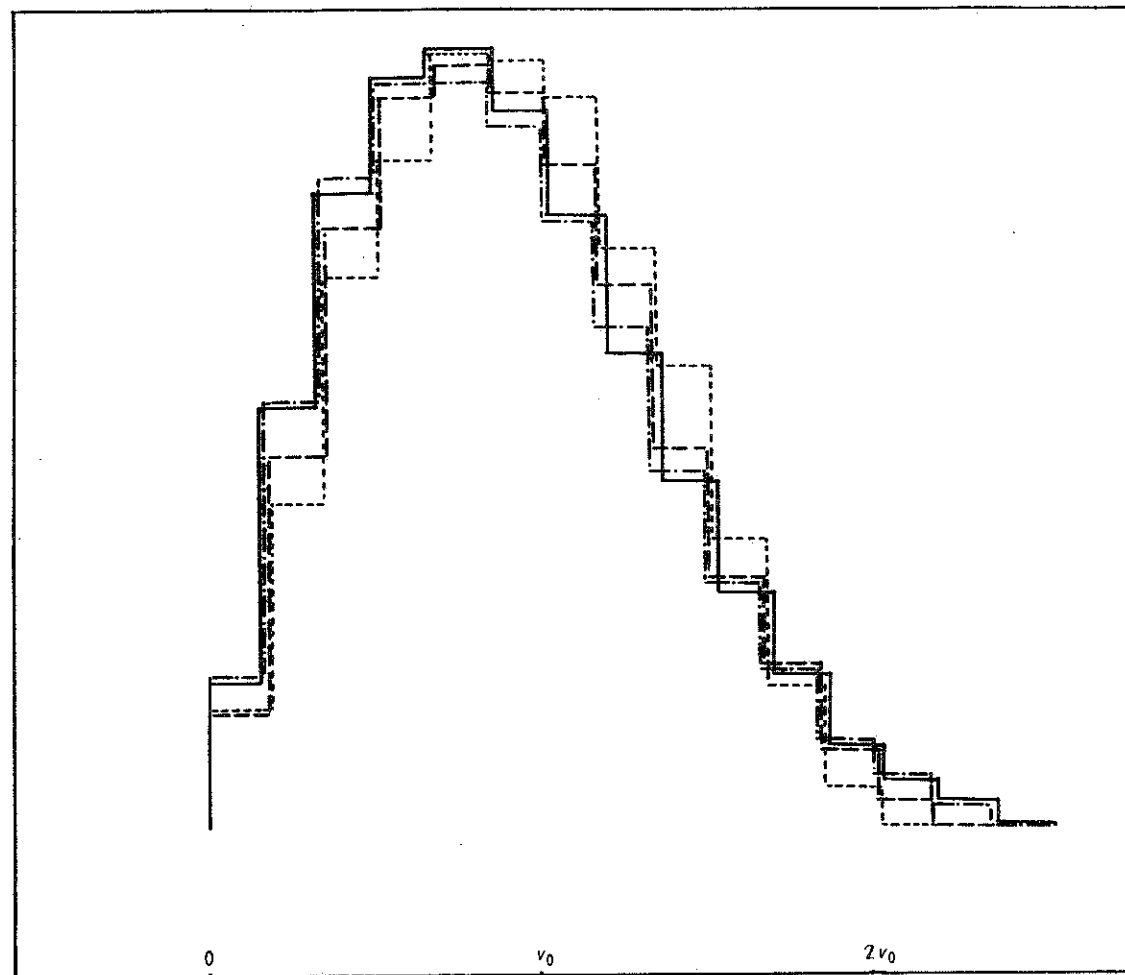


Figure 2 The distribution of molecular velocities in a 'gas' consisting of five (dotted lines), 10 (broken lines) and 50 molecules (chain lines) compared with the planar Maxwell distribution (full lines). In each case the histogram corresponds to about 5000 'snapshots' of the molecular velocities.

of y and z components of its velocity. After minor modifications, the model presented in this note can be used to check this assumption by looking at the correlations between v_x and v_y of the same molecule.

The latter derivation (Maxwell 1866a, b, c, 1867) based on the idea of detailed balance is probably more difficult to study using the present model.

Using computers in teaching statistical physics is becoming quite popular and for an interested reader we give a few references to earlier works. A quantum shuffling game simulating the Einstein model of a solid by transferring at random the quanta of energy on a planar lattice is described by Black *et al* (1971). A set of programs concerning the use of computers in statistical physics is given in an excellent book by Merrill (1976). Further prog-

rams simulating some statistical physics phenomena are described by Murch (1979) and Sauer (1981).

It seems to us that the difference between our program and the earlier works on simulating the Maxwell distribution lies in the fast thermalisation of the initial state caused by the randomisation of directions of molecular velocities by collisions with irregular walls of the vessel. This enables the user to find Maxwell distribution in a relatively short time with a 'gas' containing only a very small number of molecules.

Acknowledgment

The authors are indebted to Dr R Zajac for interesting discussions about the evolution of basic ideas of statistical mechanics.

References

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Appendix

Line	Code	Line	Code
10	REM Computer simulation of molecular velocity distribution	400	RETURN
15	DIM M(20)	410	REM -----
20	DIM Q(20)	500	REM Subroutine performing N collisions
25	DIM V(50)	510	FOR J=1 TO N
30	LET P2=2*PI	520	REM Random choice of two colliding molecules
35	REM Integer RN gen parameters:	530	LET H=N3*A1
40	LET N3=100	540	LET L1=INT(N5*(H-INT(H))+1)
45	LET A1=SQR(2)	550	LET L2=INT(N5*(H+A1-INT(H+A1))+1)
50	REM Collisions counter:	560	LET N3=N3+2
55	LET M1=0	570	REM The angle between velocities prior to collision
60	REM Scannings counter:	580	LET A=P2*RND
65	LET M2=0	590	REM Scattering angle in the CMS
70	REM Number of data counter:	600	LET G=P2*RND
75	LET N7=0	610	REM Calculating new velocities
80	REM Starting velocities:	620	LET V1=V(L1)
85	FOR J=1 TO 50	630	LET V2=V(L2)
90	LET V(J)=1	640	LET S=0.5*(V1*V1+V2*V2)
95	NEXT J	650	LET R=0.5*(V1*V1-V2*V2)*COS(G)
100	GO SUB 300		+V1*V2*SIN(A)*SIN(G)
105	INPUT "Number of molecules: ";N5	660	LET V(L1)=SQR(S+R)
110	INPUT "Number of collisions prior the first scanning: ";N	670	LET V(L2)=SQR(S-R)
115	INPUT "Number of collisions between two successive scannings: ";M4	680	NEXT J
120	INPUT "Required number of scannings: ";M3	690	LET M1=M1+N
125	GO SUB 500	700	RETURN
130	GO SUB 800	710	REM -----
135	LET N=M4	800	REM The scanning subroutine
140	FOR F=2 TO M3	810	FOR J=1 TO N5
145	GO SUB 500	820	LET I=INT(6*V(J))+1
150	GO SUB 800	830	IF I>20 THEN GO TO 850
155	NEXT F	840	LET M(I)=M(I)+1
160	GO SUB 900	850	NEXT J
165	INPUT "Stop = 0, Improve statistics = 1";R	860	LET N7=N7+N5
170	IF R=1 THEN GO TO 120	870	LET M2=M2+1
175	STOP	880	RETURN
180	REM -----End of main program-----	890	REM -----
300	REM Planar Maxwell distribution integrated over bins	900	REM Displaying results
310	LET R=1	910	CLS
320	LET S=1/6	915	PRINT "Bin";TAB(6);"Simulation";
330	LET B=0		TAB(20);"True Maxwell"
340	FOR J=1 TO 20	918	PRINT
350	LET B=B+S	920	FOR J=1 TO 18
360	LET H=EXP(-B*B)	925	LET S=1E-4*INT(1E4*M(J)/N7)
370	LET Q(J)=1E-4*INT(1E+4*(R-H))	930	PRINT J;TAB(8);S;TAB(23);Q(J)
380	LET R=H	940	NEXT J
390	NEXT J	943	PRINT
		946	PRINT "Bin width = ";1/6
		950	RETURN
		960	REM -----

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