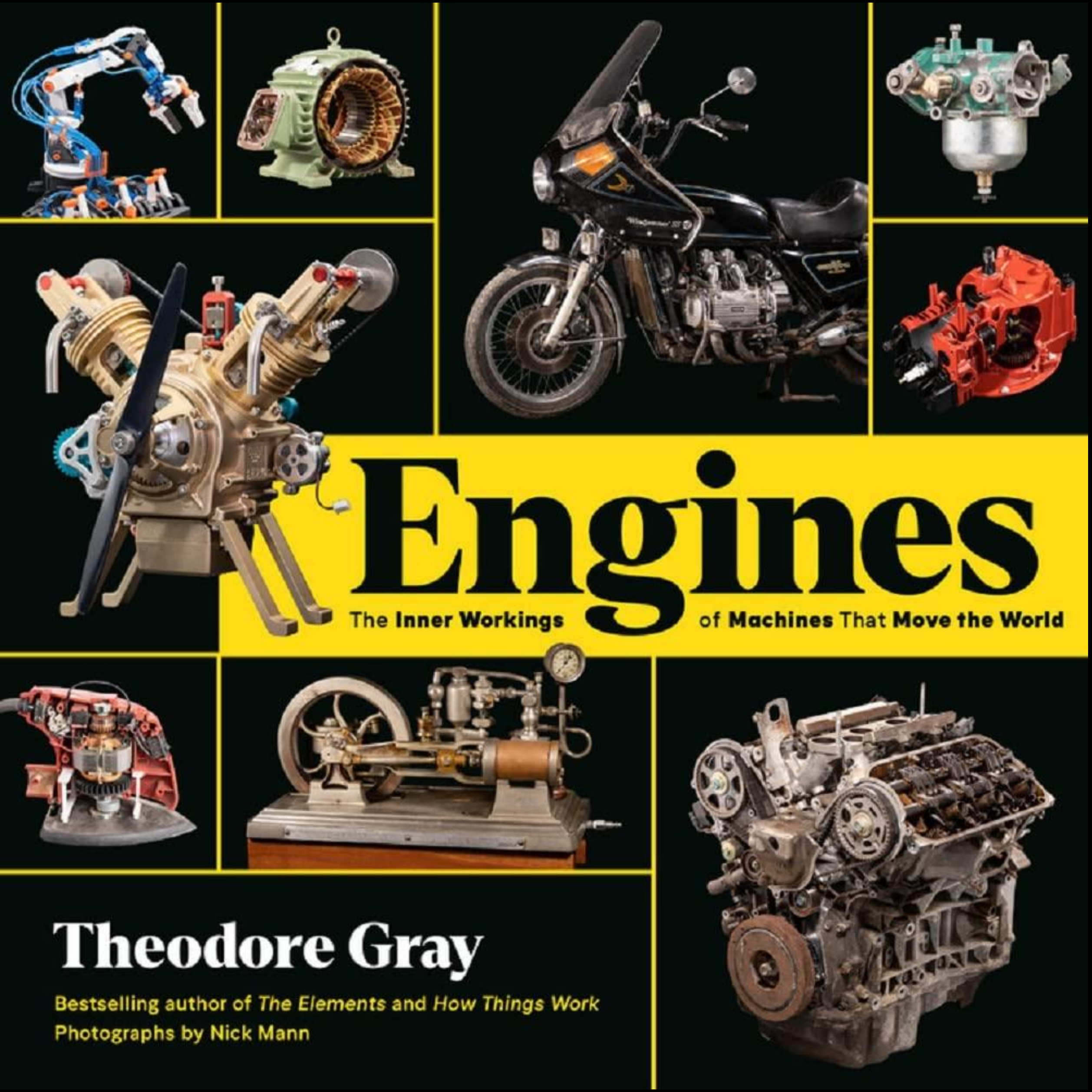
BPhO Computational Challenge

Thermodynamics

Dr Andrew French.
December 2023.

BPhO British Physics Olympiad

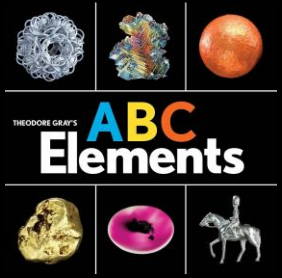


Engines

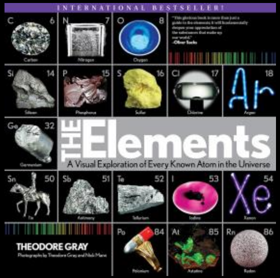
The Inner Workings of Machines That Move the World

Theodore Gray

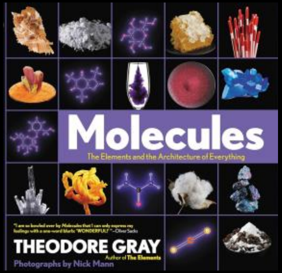
Bestselling author of *The Elements* and *How Things Work*
Photographs by Nick Mann



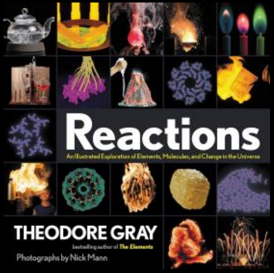
THEODORE GRAY'S
ABC
Elements



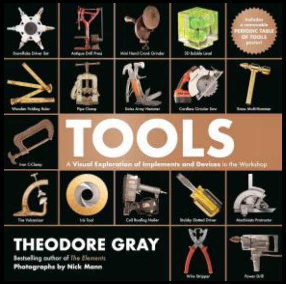
INTERNATIONAL BESTSELLER!
The Elements
A Visual Exploration of Every Known Atom in the Universe
THEODORE GRAY
Photographs by Theodore Gray and Nick Mann



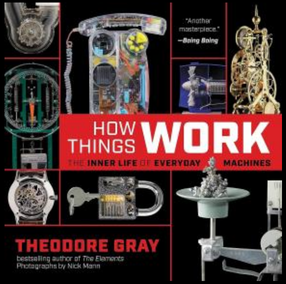
Molecules
The Elements and the Architecture of Everything
THEODORE GRAY
Author of The Elements
Photographs by Nick Mann



Reactions
An Illustrated Exploration of Elements, Molecules, and Change in the Universe
THEODORE GRAY
bestselling author of The Elements
Photographs by Nick Mann



TOOLS
A Visual Exploration of Implements and Devices in the Workshop
THEODORE GRAY
Bestselling author of The Elements
Photographs by Nick Mann



"Another masterpiece."
—Boing Boing
HOW THINGS WORK
THE INNER LIFE OF EVERYDAY MACHINES
THEODORE GRAY
bestselling author of The Elements
Photographs by Nick Mann

These books are amazing!

$$\boxed{Q_{in} = Q_{out} + W}$$ 1st law

$$\boxed{\Delta S_H = -\frac{Q_{in}}{T_H} \qquad \Delta S_C = \frac{Q_{out}}{T_C}}$$ Entropy

$$\Delta S_{total} = \Delta S_H + \Delta S_C = -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C}$$

$$\boxed{\Delta S_{total} \geq 0} \qquad \therefore -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \geq 0$$

2nd law

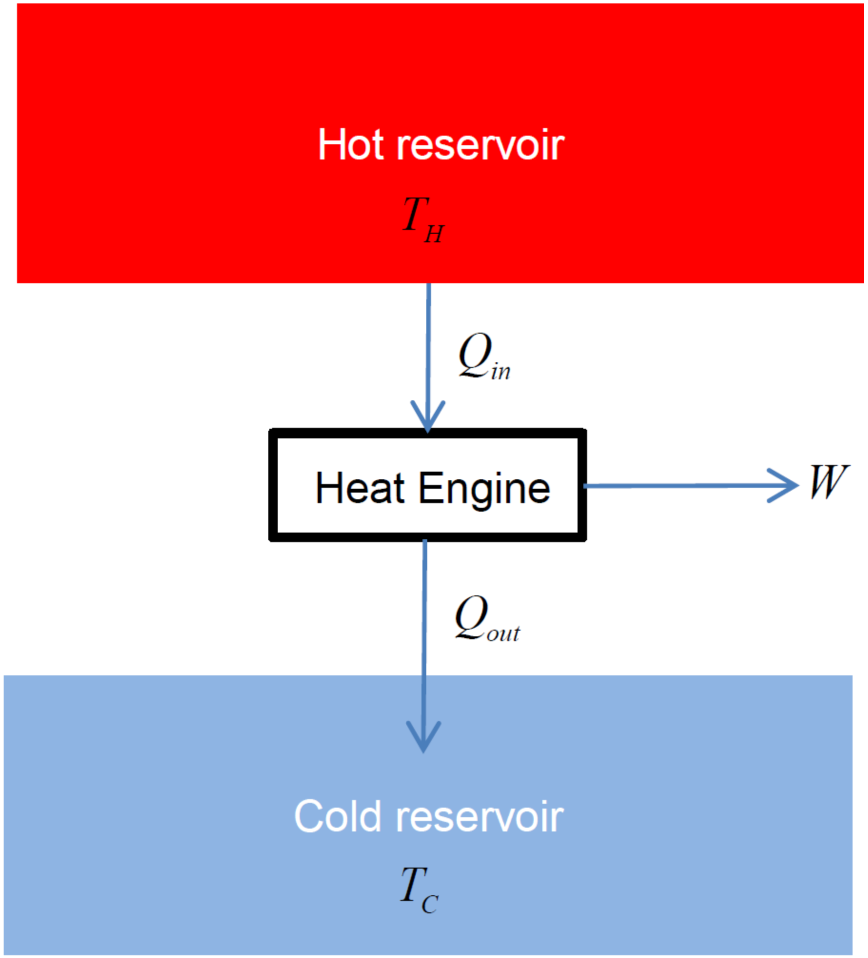
↓

$$-\frac{Q_{in}}{T_H} + \frac{Q_{in} - W}{T_C} \geq 0$$

$$\therefore -\frac{1}{T_H} + \frac{1 - \frac{W}{Q_{in}}}{T_C} \geq 0$$

$$-\frac{T_C}{T_H} + 1 - \frac{W}{Q_{in}} \geq 0$$

→



Hot reservoir

T_H

Q_{in}

Heat Engine

W

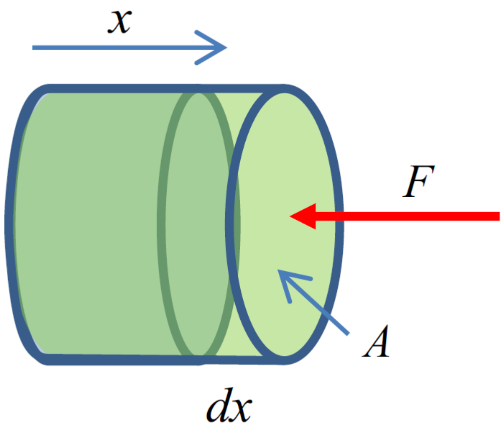
Q_{out}

Cold reservoir

T_C

$$\eta = \frac{W}{Q_{\text{in}}}$$ Engine efficiency

$$\therefore -\frac{T_C}{T_H} + 1 - \eta \geq 0 \qquad \therefore \boxed{\eta \leq 1 - \frac{T_C}{T_H}}$$



volume change

$$dV = -Adx$$

$$dW = Fdx$$

Work done *on* the gas

$$p = \frac{F}{A}$$

The pressure acting upon the gas

$$\therefore dW = pA \times -\frac{dV}{A}$$

$$\boxed{\therefore dW = -pdV}$$

If heat dQ is supplied to the gas then the **First Law of Thermodynamics** (that Energy in a closed system is conserved) means the internal energy change is

$$\boxed{dU = dQ - pdV}$$

Internal energy

Heat

Work

The internal energy for
n moles of
an ideal gas is:

$$\boxed{U = \frac{1}{2}\alpha nRT}$$

Molar gas constant 8.314 $\mathrm{Jmol^{-1}K^{-1}}$

Temperature (Kelvin K)

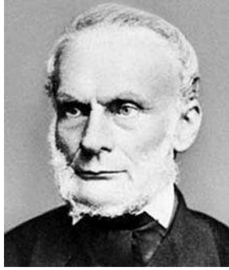
Internal energy of n moles of gas

Number of degrees of freedom of molecular motion (e.g α = 3 for x,y,z translation)

IDEAL GAS EQUATION

$$\boxed{pV = nRT}$$

$$\boxed{dS = \frac{dQ}{T}}$$



Rudolf Clausius
1822-1888

ISOTHERMAL PROCESS

$$dT = 0$$

$$\boxed{pV = \text{constant}}$$

$$\boxed{Q = W = nRT \ln\left(\frac{V}{V_0}\right)}$$

Heat input = work done by gas since no change in U

ISENTROPIC (CONSTANT ENTROPY) PROCESS

$dS = dQ = 0$ No heat exchanged

$$\boxed{\begin{gathered} pV^{\gamma} = \text{constant} \\ \gamma = \frac{c_P}{c_V} = 1 + \frac{2}{\alpha} \end{gathered}}$$

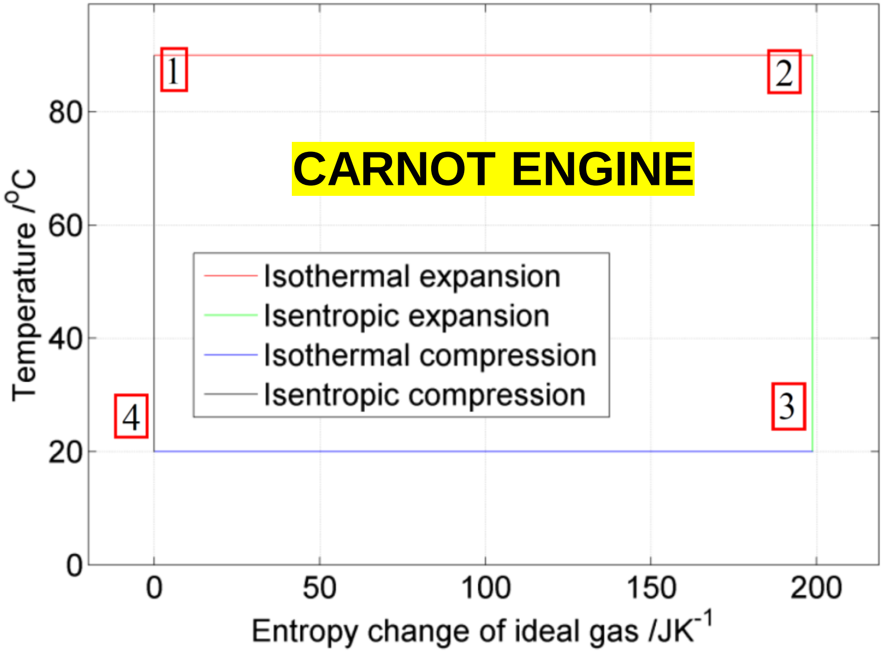
Ratio of constant pressure to constant volume process heat capacities

$$\boxed{W = \frac{p_0 V_0}{\gamma - 1}\left(1 - \left(\frac{V_0}{V}\right)^{\gamma - 1}\right)}$$

Work done by gas on the surroundings

$$\boxed{\begin{gathered} c_V = \frac{R}{M}\frac{1}{\gamma - 1} \\ c_P = \frac{R}{M}\frac{\gamma}{\gamma - 1} \end{gathered}}$$

Carnot cycle: $T_H = 90^{\circ}C$, $T_C = 20^{\circ}C$, $V_1 = 0.1 m^3$
$W = 13.9266 kJ$, $Q_{in} = 72.2194 kJ$, Efficiency = W/Q_{in} = 19.2837%



From the **First Law of Thermodynamics**

$$dU = dQ - pdV \quad \therefore dU = TdS - pdV$$

Over the whole cycle the *internal energy doesn't change*, so the work done by the gas is

$$\boxed{W = \oint pdV = \oint Tds}$$

i.e. area enclosed by cycle

$$W = (T_H - T_C)\Delta S = (T_H - T_C)nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{\Delta S = \frac{Q_{\text{in}}}{T_H} = \frac{Q_{\text{out}}}{T_C} = nR\ln\left(\frac{V_2}{V_1}\right)}$$

$$\therefore \eta = \frac{W}{Q_{\text{in}}} = \frac{(T_H - T_C)nR\ln\left(\frac{V_2}{V_1}\right)}{nRT_H\ln\left(\frac{V_2}{V_1}\right)} = \boxed{1 - \frac{T_C}{T_H}}$$

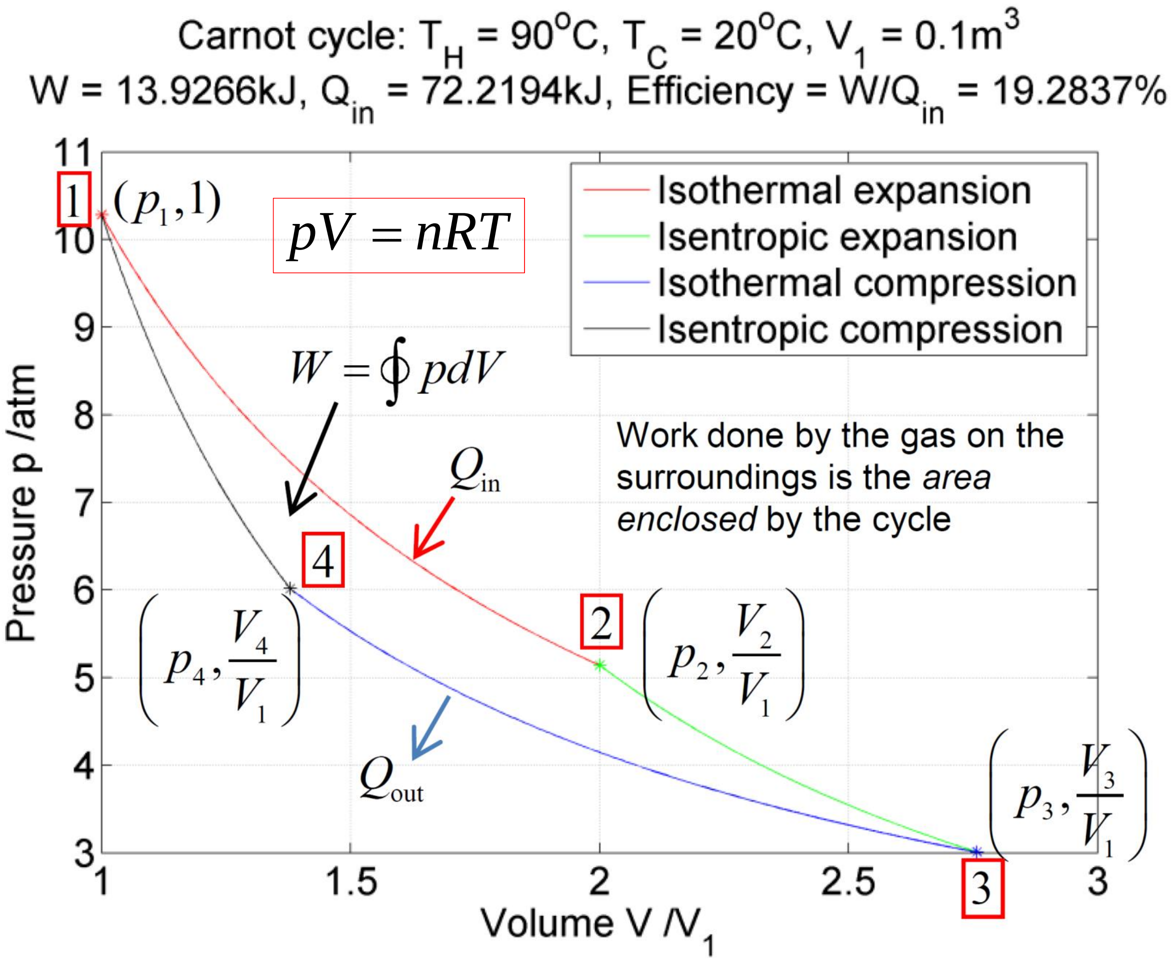
ISOTHERMAL PROCESS

$$\boxed{\begin{aligned} &dT = 0 \\ &pV = \text{constant} \\ &Q = W = nRT\ln\left(\frac{V}{V_0}\right) \end{aligned}}$$

Heat input = work done by gas
Since no change in *U*

$$\eta \le 1 - \frac{T_C}{T_H}$$

So Carnot engine is (one example) of the *most efficient heat engine possible.*



Carnot cycle: $T_H = 90^oC$, $T_C = 20^oC$, $V_1 = 0.1m^3$

$W = 13.9266kJ$, $Q_{in} = 72.2194kJ$, Efficiency = $W/Q_{in} = 19.2837\%$

$$pV = nRT$$

$$W = \oint p\,dV$$

Work done by the gas on the surroundings is the *area enclosed* by the cycle

Nicolas Léonard
Sadi Carnot
(1796-1832)

$$W = (T_H - T_C)\,nR\ln\left(\frac{V_2}{V_1}\right)$$

$$Q_{in} = nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$Q_{out} = nRT_C \ln\left(\frac{V_3}{V_4}\right)$$

Inputs

$$T_H, T_C, V_1, V_2, n$$

$$V_4 = \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} V_1$$

$$V_3 = \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma-1}} V_2$$

Next step: code up a Heat Cycle model! Start with a spreadsheet, then try MATLAB/Python etc …The key idea is to VISUALIZE your solutions.

Carnot Cycle model

Dr A. French. September 2017

Nicolas
Léonard Sadi
Carnot
(1796-1832)

Input parameters

Hot reservoir temperature /Celsius	150
Cold reservoir temperature /Celsius	20
Mass of gas /g	1.00
Volume of gas at lowest volume and hightest pressure /litres	0.40
Volume of gas after isothermal expansion /litres	1.00
Degrees of freedom of molecular motion	3
Molar mass of gas /gmol^-1	28.966

Outputs

Heat input during isothermal expansion /kJ	0.111
Heat output during isothermal compression /kJ	0.077
Total work done by gas on surroundings /kJ	0.034
Entropy change during isothermal stages /JK^-1	0.263
Efficiency (work done / heat input)	0.307

Theoretical efficiency	0.307

$$\eta = 1 - \frac{T_C}{T_H}$$

Note all temperatures incorporated into calculations
will be converted to Kelvin first - i.e. add 273 to Celsius number.

Pressure, volume coordinates of heat cycle

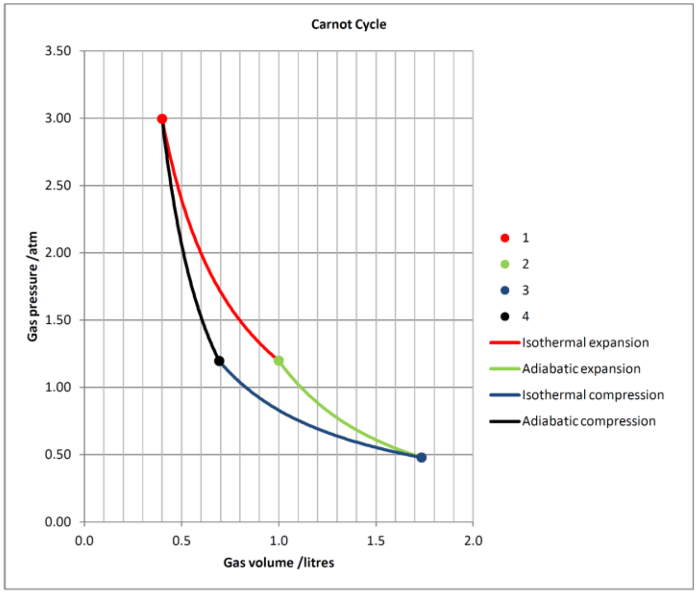
🟥	p1	3.00
	V1	0.4
🟩	p2	1.20
	V2	1.0
🟦	p3	0.48
	V3	1.73
⬛	p4	1.20
	V4	0.7

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres. T in K.

Reservoir temperatures in K

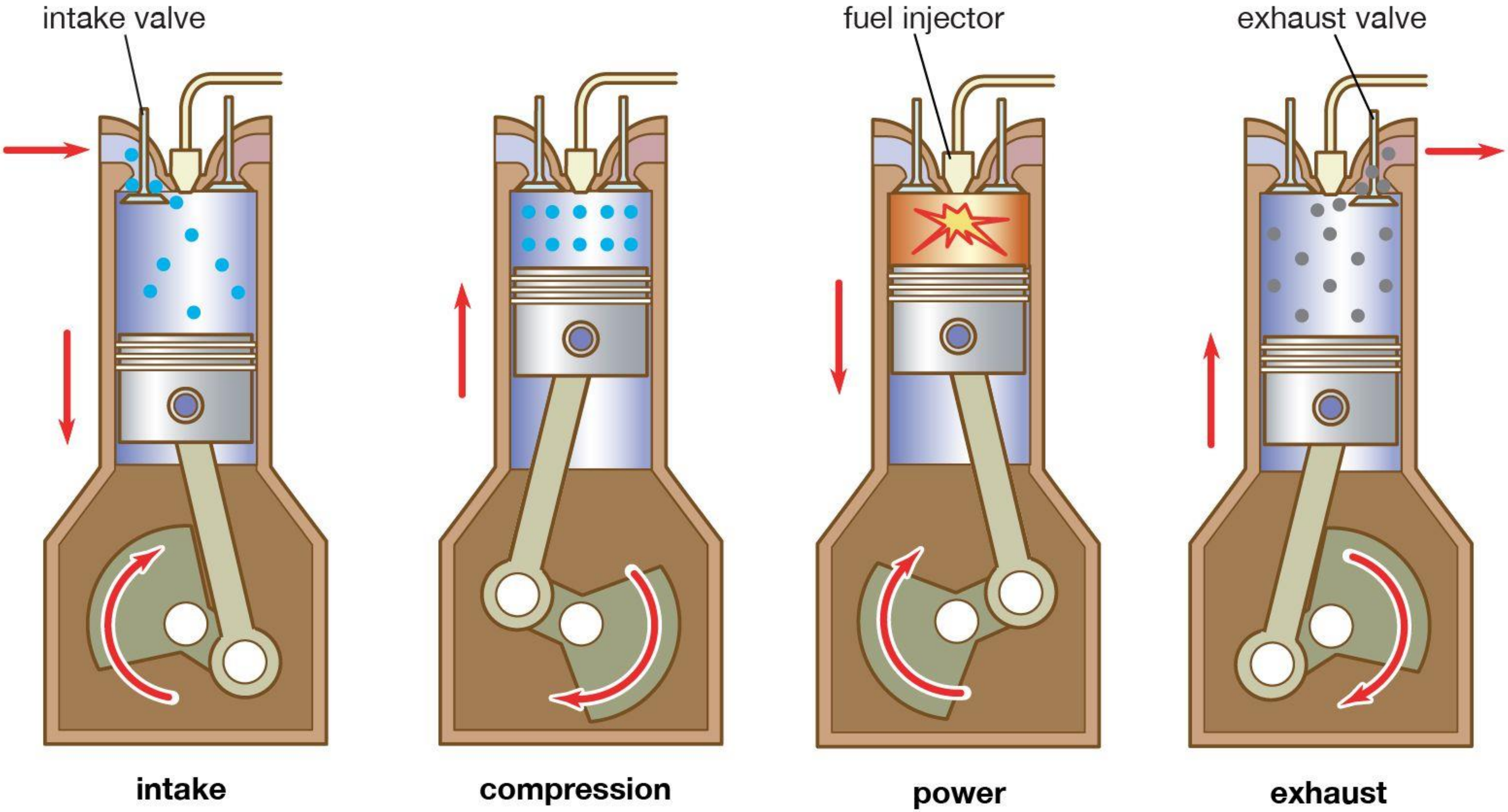
T_H	423
T_C	293

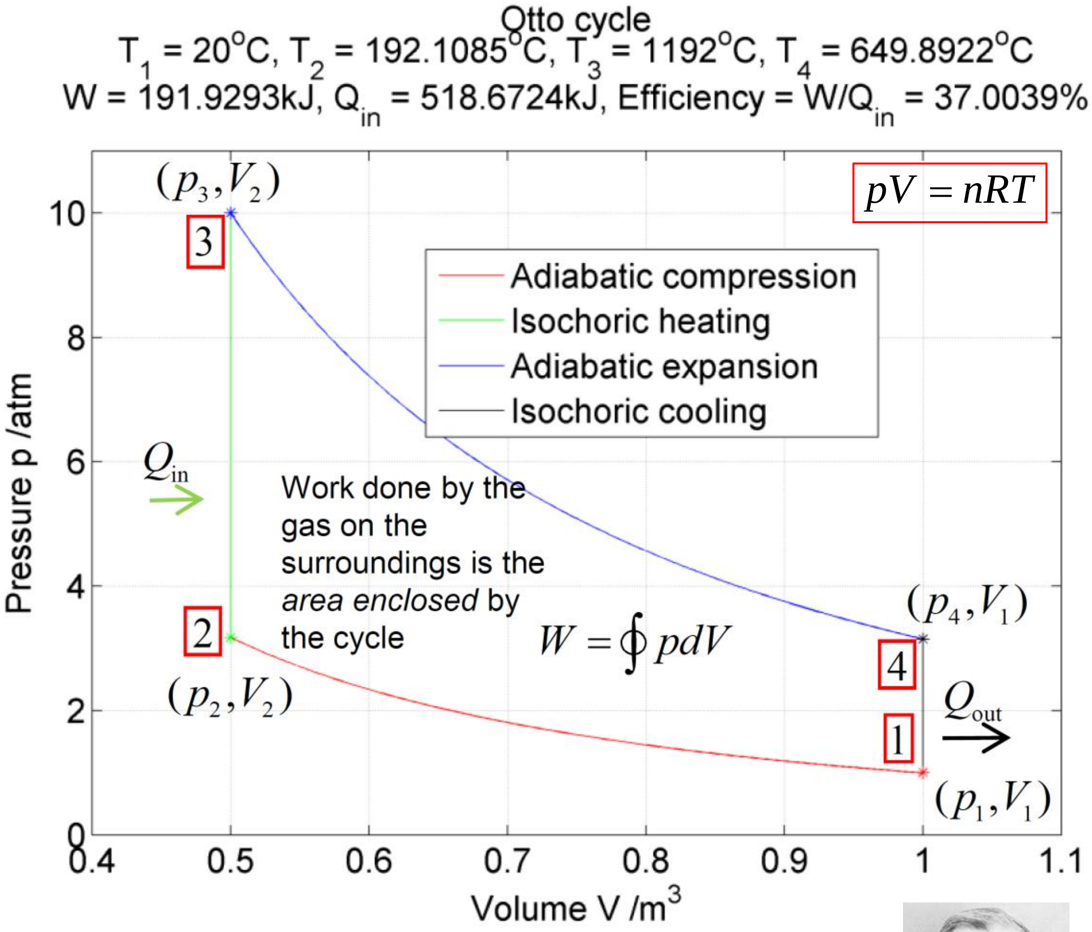
Number of moles of gas in engine	0.035
Ratio of specific heats gamma	1.667



	1 to 2		2 to 3		3 to 4		4 to 1	
	Isothermal expansion		**Adiabatic expansion**		**Isothermal compression**		**Adiabatic compression**	
V diff fraction	p	V	p	V	p	V	p	V
0	2.996	0.400	1.198	1.000	0.478	1.735	1.196	0.694
0.01	2.951	0.406	1.184	1.007	0.481	1.724	1.205	0.691
0.02	2.908	0.412	1.169	1.015	0.484	1.714	1.213	0.688
0.03	2.867	0.418	1.155	1.022	0.487	1.703	1.222	0.685
0.04	2.826	0.424	1.142	1.029	0.490	1.693	1.231	0.682
0.05	2.787	0.430	1.128	1.037	0.493	1.683	1.240	0.679
0.06	2.748	0.436	1.115	1.044	0.496	1.672	1.249	0.676
0.07	2.711	0.442	1.102	1.051	0.499	1.662	1.258	0.673
0.08	2.675	0.448	1.089	1.059	0.503	1.651	1.267	0.670
0.09	2.639	0.454	1.077	1.066	0.506	1.641	1.276	0.667
0.1	2.605	0.460	1.065	1.073	0.509	1.631	1.286	0.664
0.11	2.571	0.466	1.053	1.081	0.512	1.620	1.295	0.662
0.12	2.539	0.472	1.041	1.088	0.516	1.610	1.305	0.659
0.13	2.507	0.478	1.029	1.096	0.519	1.599	1.315	0.656
0.14	2.476	0.484	1.018	1.103	0.522	1.589	1.324	0.653
0.15	2.445	0.490	1.007	1.110	0.526	1.579	1.334	0.650
0.16	2.416	0.496	0.996	1.118	0.529	1.568	1.345	0.647
0.17	2.387	0.502	0.985	1.125	0.533	1.558	1.355	0.644
0.18	2.359	0.508	0.974	1.132	0.536	1.547	1.365	0.641
0.19	2.331	0.514	0.964	1.140	0.540	1.537	1.376	0.638
0.2	2.304	0.520	0.953	1.147	0.544	1.526	1.386	0.635
0.21	2.278	0.526	0.943	1.154	0.547	1.516	1.397	0.632
0.22	2.252	0.532	0.933	1.162	0.551	1.506	1.408	0.629
0.23	2.227	0.538	0.924	1.169	0.555	1.495	1.419	0.626
0.24	2.203	0.544	0.914	1.176	0.559	1.485	1.430	0.623
0.25	2.179	0.550	0.905	1.184	0.563	1.474	1.441	0.620
0.26	2.155	0.556	0.895	1.191	0.567	1.464	1.453	0.617
0.27	2.132	0.562	0.886	1.198	0.571	1.454	1.465	0.615
0.28	2.110	0.568	0.877	1.206	0.575	1.443	1.476	0.612
0.29	2.088	0.574	0.868	1.213	0.579	1.433	1.488	0.609
0.3	2.066	0.580	0.860	1.220	0.584	1.422	1.500	0.606
0.31	2.045	0.586	0.851	1.228	0.588	1.412	1.512	0.603
0.32	2.024	0.592	0.843	1.235	0.592	1.402	1.525	0.600
0.33	2.004	0.598	0.834	1.242	0.597	1.391	1.537	0.597
0.34	1.984	0.604	0.826	1.250	0.601	1.381	1.550	0.594
0.35	1.964	0.610	0.818	1.257	0.606	1.370	1.563	0.591
0.36	1.945	0.616	0.810	1.264	0.610	1.360	1.576	0.588
0.37	1.926	0.622	0.803	1.272	0.615	1.350	1.589	0.585
0.38	1.908	0.628	0.795	1.279	0.620	1.339	1.603	0.582
0.39	1.890	0.634	0.787	1.287	0.625	1.329	1.616	0.579
0.4	1.872	0.640	0.780	1.294	0.630	1.318	1.630	0.576

Four-stage engine (modelled by Diesel or Otto cycles)





FORD MOTOR CO.

1.0L ECOBOOST DOHC DI I-3

Displacement: 999 cc

Block / head material: cast iron / aluminum

Horsepower (SAE net): 123 @ 6,000 rpm

Torque: 125 lb.-ft. (169 Nm) @ 2,500 rpm

Specific output: 123 hp/L

Bore x stroke: 71.9 x 82 mm

Compression ratio: 10.0:1

EPA city / highway: 31 / 43 mpg

Assembly site: Cologne, Germany; Craiova, Romania

Application tested: '14 Ford Fiesta SE

Additional applications: Ford Focus, C-Max, Mondeo, Transit Courier (Europe); B-Max (Europe, Asia/Pacific); EcoSport (Asia/Pacific)

Nikolaus Otto
(1832-1891)

$$W = \frac{V_2}{\gamma - 1}\left(1 - \frac{1}{r^{\gamma-1}}\right)\left\{p_3 - p_1 r^\gamma\right\}$$

Inputs

$$p_1, p_3, V_1, V_2, T_1, n$$

$$r = \frac{V_1}{V_2}$$

$$Q_{out} = Q_{in} - W$$

Molar mass of gas

$M_{air} \approx 29 \mathrm{gmol}^{-1}$

$$\eta_{otto} = 1 - \frac{1}{r^{\gamma-1}}$$

$$Q_{in} = \frac{V_2\left(p_3 - p_1 r^\gamma\right)}{\gamma - 1}$$

Otto Cycle model
Dr A. French. September 2017

Nikolaus Otto
(1832-1891)

Input parameters

Temperature T1 of air draw into piston /Celsius	20
Low pressure state p1 /atm	1.00
High pressure state p3 /atm	100
Volume V1 of uncompressed gas /litres	1
Volume V2 of compressed /litres	0.1
Degrees of freedom of molecular motion	3
Molar mass of gas /gmol^-1	28.966

Outputs

Heat input during isochoric heating /kJ	0.814
Heat output during isochoric cooling /kJ	0.175
Total work done by gas on surroundings /kJ	0.639
Efficiency (work done / heat input)	0.785

Theoretical efficiency	0.785

$$\eta = 1 - \frac{1}{r^{\gamma - 1}}$$

$$r = \frac{V_1}{V_2} \quad \gamma = \frac{c_P}{c_V}$$

Note all temperatures incorporated into calculations
will be converted to Kelvin first - i.e. add 273 to Celsius number.

Pressure, volume, temperature coordinates of heat cycle

🟥	p1	1.00
	V1	1.000
	T1	293
🟩	p2	46.42
	V2	0.100
	T2	1360
🟦	p3	100.00
	V3	0.100
	T3	2930
⬛	p4	2.15
	V4	1.000
	T4	631

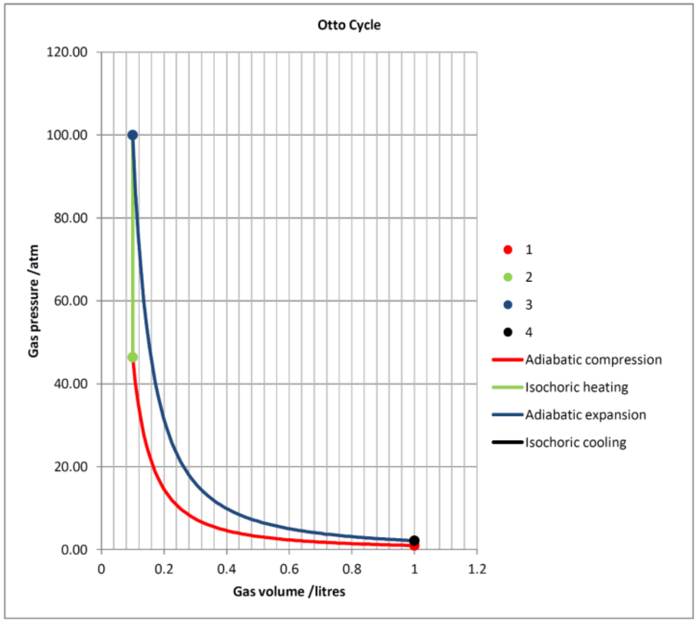
Power per cylinder

Engine RPM	6500
Power output /kW	69.21979

Number of cylinders	1
Total power output /kW	69.22

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres. T in K.

Number of moles of gas in engine	0.042
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718



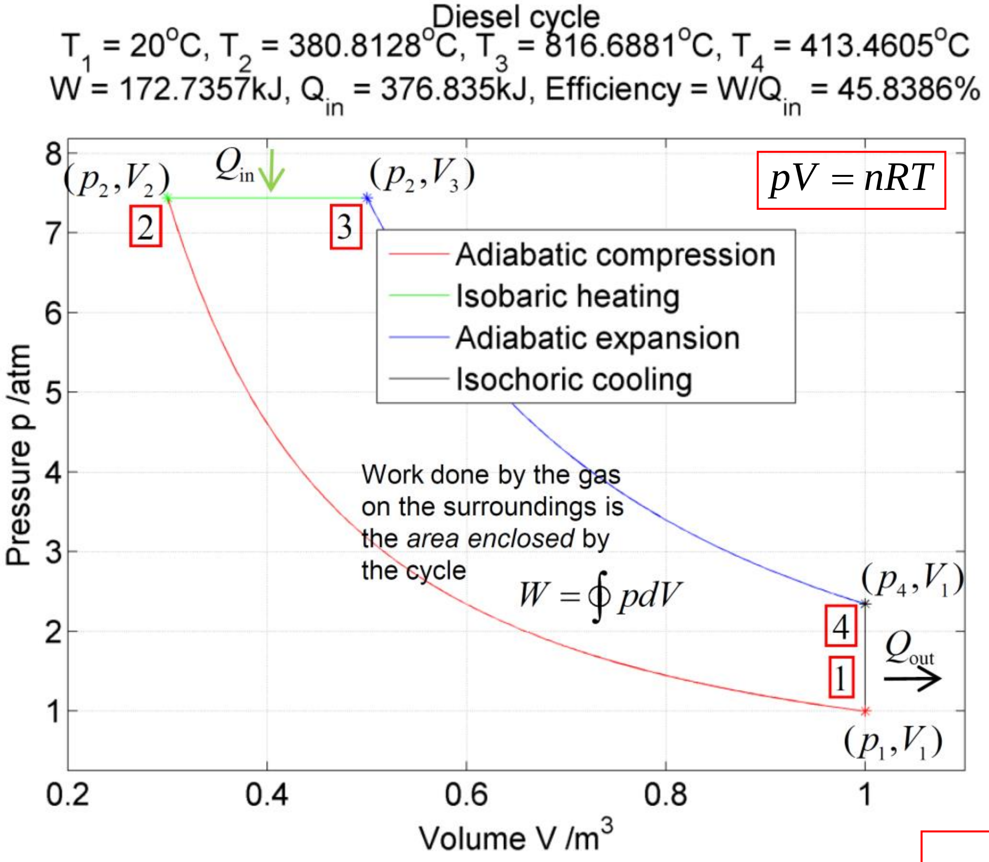
Note real petrol engines have an efficiency of more like 20%, whereas diesels can be up to 40%. In other words, significant losses!

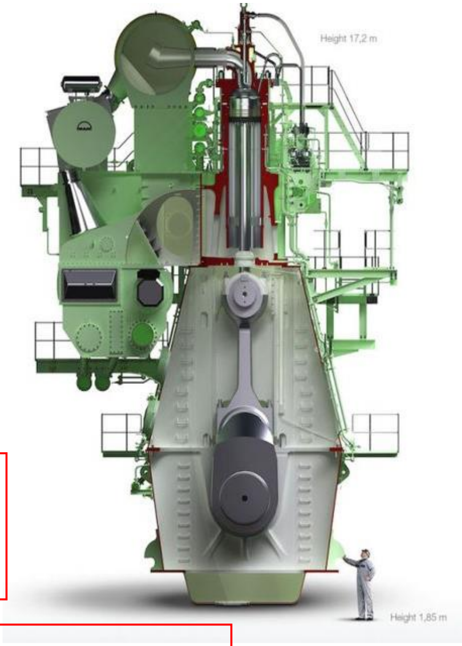
FORD MOTOR CO.
1.0L ECOBOOST
DOHC DI I-3

Displacement:
999 cc
Block / head material:
cast iron / aluminum
Horsepower (SAE net):
123 @ 6,000 rpm
Torque:
125 lb.-ft. (169 Nm)
@ 2,500 rpm
Specific output:
123 hp/L
Bore x stroke:
71.9 x 82 mm
Compression ratio:
10.0:1

EPA city / highway:
31 / 43 mpg
Assembly site:
Cologne, Germany;
Craiova, Romania
Application tested:
'14 Ford Fiesta SE
Additional applications:
Ford Focus, C-Max,
Mondeo, Transit Courier
(Europe); B-Max (Europe,
Asia/Pacific); EcoSport
(Asia/Pacific)

	1 to 2		2 to 3		3 to 4		4 to 1	
	Adiabatic compression		**Isochoric heating**		**Adiabatic expansion**		**Isochoric cooling**	
V or p diff fraction	**p**	**V**	**p**	**V**	**p**	**V**	**p**	**V**
0	1.000	1.000	46.416	0.100	100.000	0.100	2.154	1.000
0.01	1.015	0.991	46.952	0.100	86.621	0.109	2.143	1.000
0.02	1.031	0.982	47.488	0.100	75.892	0.118	2.131	1.000
0.03	1.047	0.973	48.023	0.100	67.142	0.127	2.120	1.000
0.04	1.063	0.964	48.559	0.100	59.901	0.136	2.108	1.000
0.05	1.080	0.955	49.095	0.100	53.834	0.145	2.097	1.000
0.06	1.097	0.946	49.631	0.100	48.693	0.154	2.085	1.000
0.07	1.115	0.937	50.167	0.100	44.295	0.163	2.074	1.000
0.08	1.133	0.928	50.703	0.100	40.500	0.172	2.062	1.000
0.09	1.151	0.919	51.238	0.100	37.199	0.181	2.051	1.000
0.1	1.170	0.910	51.774	0.100	34.309	0.190	2.039	1.000
0.11	1.190	0.901	52.310	0.100	31.762	0.199	2.027	1.000
0.12	1.210	0.892	52.846	0.100	29.505	0.208	2.016	1.000
0.13	1.230	0.883	53.382	0.100	27.494	0.217	2.004	1.000
0.14	1.252	0.874	53.918	0.100	25.693	0.226	1.993	1.000
0.15	1.273	0.865	54.454	0.100	24.074	0.235	1.981	1.000
0.16	1.296	0.856	54.989	0.100	22.613	0.244	1.970	1.000
0.17	1.319	0.847	55.525	0.100	21.288	0.253	1.958	1.000
0.18	1.343	0.838	56.061	0.100	20.083	0.262	1.947	1.000
0.19	1.367	0.829	56.597	0.100	18.984	0.271	1.935	1.000
0.2	1.392	0.820	57.133	0.100	17.978	0.280	1.924	1.000
0.21	1.418	0.811	57.669	0.100	17.054	0.289	1.912	1.000
0.22	1.444	0.802	58.204	0.100	16.205	0.298	1.900	1.000
0.23	1.472	0.793	58.740	0.100	15.421	0.307	1.889	1.000
0.24	1.500	0.784	59.276	0.100	14.696	0.316	1.877	1.000
0.25	1.529	0.775	59.812	0.100	14.024	0.325	1.866	1.000
0.26	1.559	0.766	60.348	0.100	13.400	0.334	1.854	1.000
0.27	1.590	0.757	60.884	0.100	12.819	0.343	1.843	1.000
0.28	1.622	0.748	61.419	0.100	12.277	0.352	1.831	1.000
0.2								00
0.								00
0.3								00
0.3								00
0.3								00
0.3								00
0.3								00
0.3								00
0.3								00
0.3								00
0.3								00
0.								00
0.41	2.154	0.631	68.385	0.100	7.610	0.469	1.681	1.000
0.42	2.206	0.622	68.921	0.100	7.373	0.478	1.670	1.000
0.43	2.261	0.613	69.457	0.100	7.147	0.487	1.658	1.000
0.44	2.317	0.604	69.993	0.100	6.932	0.496	1.646	1.000
0.45	2.376	0.595	70.529	0.100	6.727	0.505	1.635	1.000
0.46	2.437	0.586	71.065	0.100	6.532	0.514	1.623	1.000





$$r = \frac{V_1}{V_2}$$

$$s = \frac{V_3}{V_2}$$

$$Q_{out} = Q_{in} - W$$

$$Q_{\text{in}} = \frac{\gamma}{\gamma - 1} r^{\gamma} (s - 1) p_1 V_2$$

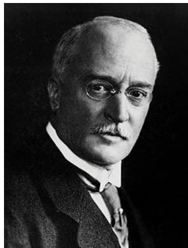
$$W = \frac{p_1 V_2}{\gamma - 1} \left\{ r(1 - s^{\gamma}) + r^{\gamma} (s - 1) \gamma \right\}$$

$$\eta_{\text{diesel}} = 1 - \frac{1}{r^{\gamma - 1}} \left(\frac{s^{\gamma} - 1}{\gamma (s - 1)} \right)$$

Inputs

$$p_1, V_1, V_2, V_3, T_1, n$$

Rudolf Diesel
(1858-1913)



Diesel Cycle model
Dr A. French. September 2017

Rudolf Diesel
(1858-1913)

Input parameters

Temperature T1 of air draw into piston /Celsius	25
Low pressure state p1 /atm	1.00
Volume V1 of uncompressed gas /litres	1820
Volume V2 of compressed gas /litres	79
Volume V3 of compressed gas after isobaric heating /litres	170
Degrees of freedom of molecular motion	3
Molar mass of gas /gmol^-1	28.966

Outputs

Heat input during isobaric heating /kJ	4267
Heat output during isochoric cooling /kJ	710
Total work done by gas on surroundings /kJ	3557
Efficiency (work done / heat input)	0.834

Theoretical efficiency	0.834

$$\eta = 1 - \frac{1}{r^{\gamma-1}}\left(\frac{s^{\gamma}-1}{\gamma(s-1)}\right)$$

$$r = \frac{V_1}{V_2} \quad s = \frac{V_3}{V_2} \quad \gamma = \frac{c_P}{c_V}$$

Note all temperatures incorporated into calculations will be converted to Kelvin first
- i.e. add 273 to Celsius number.

Pressure, volume, temperature coordinates of heat cycle

🟥	p1	1.0
	V1	1820
	T1	298
🟩	p2	186.0
	V2	79.1
	T2	2410
🟦	p3	186.0
	V3	169.7
	T3	5168
⬛	p4	3.6
	V4	1820.0
	T4	1063

Single cylinder power output

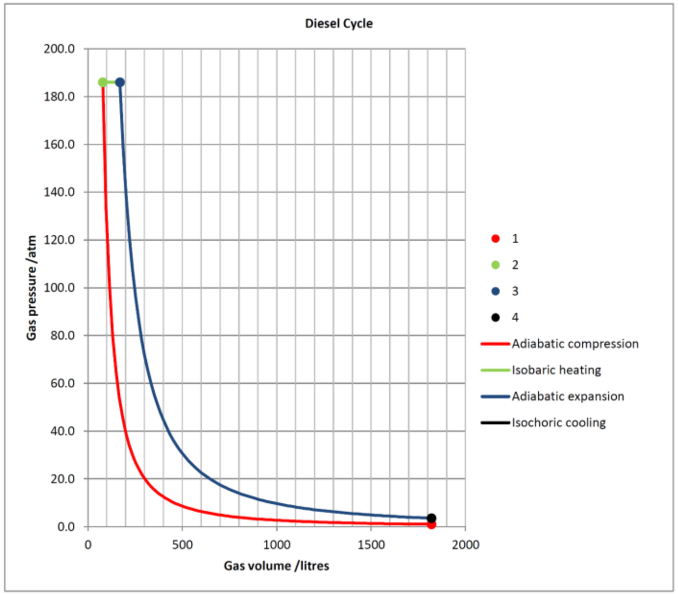
Engine RPM	84
Power output /kW	4,980

Number of cylinders	14
Total power output /kW	69,717

Note all pressures are quoted in atmospheres. 1atm = 101,325 Pa. Volumes in litres, T in K

Number of moles of gas in engine	74
Ratio of specific heats gamma	1.667
Constant volume specific heat capacity /Jkg^-1K^-1	431
Constant pressure specific heat capacity /Jkg^-1K^-1	718

Note real petrol engines have an efficiency of more like 20%, whereas diesels can be up to 40%. In other words, significant losses!



World's largest container ship in 2014
MV CSCL Globe

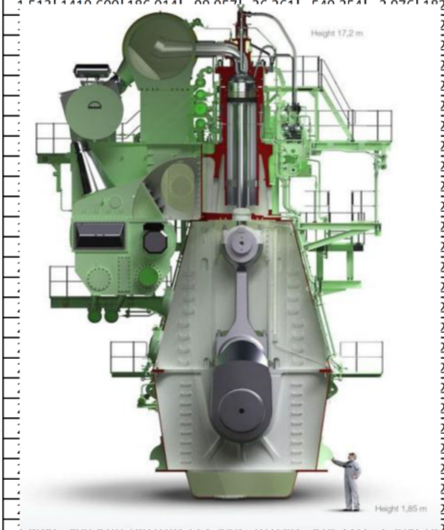
MAN B&W 12S90ME-C Mark 9.2 diesel engine. 69,720kW at 84RPM

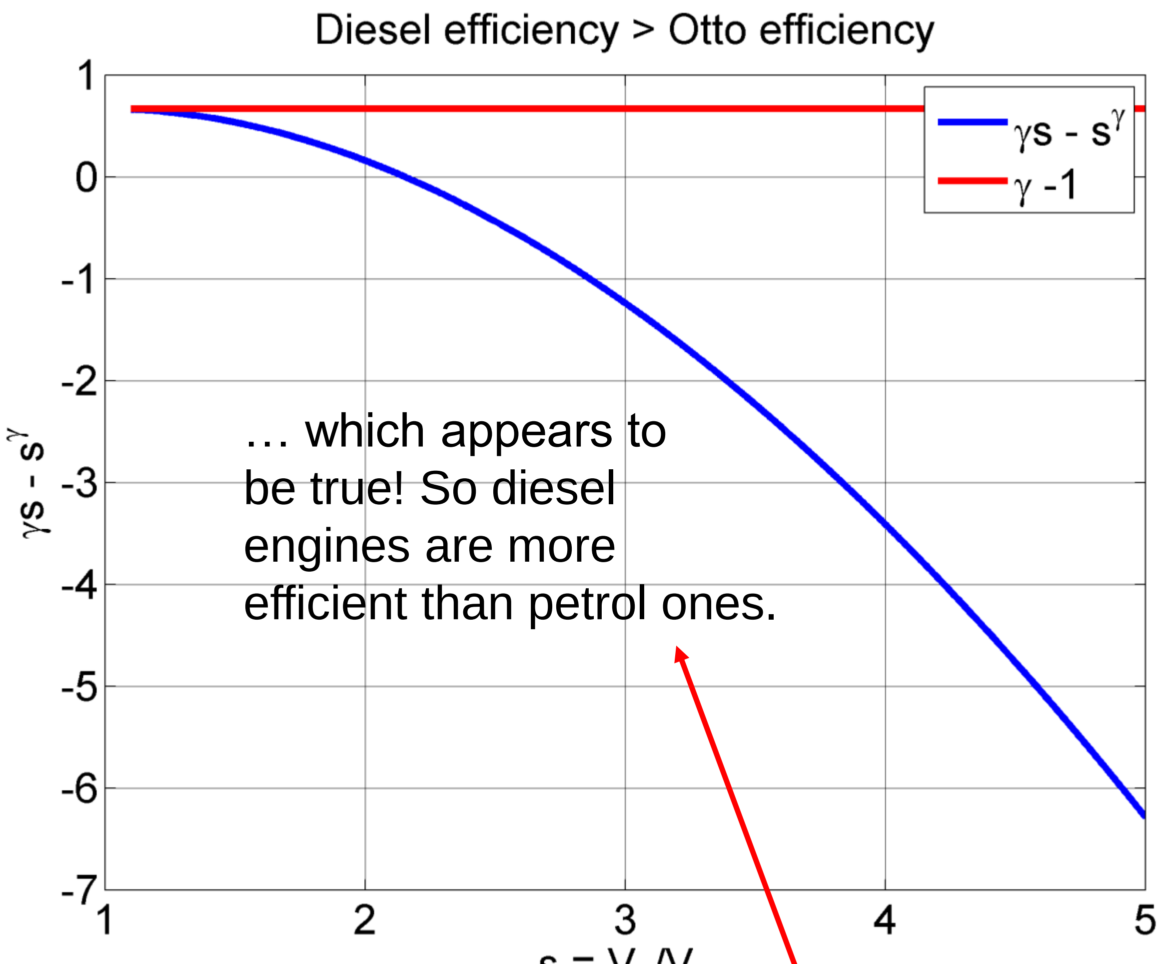
Assume about 1820 litre
cylinder volume V1

Max compression ratio:
V1/V2 = 23

V3 guessed at:
V1/10.726

	1 to 2		2 to 3		3 to 4		4 to 1	
	Adiabatic compression		**Isobaric heating**		**Adiabatic expansion**		**Isochoric cooling**	
V or p diff fraction	**p**	**V**	**p**	**V**	**p**	**V**	**p**	**V**
0	1.000	1820.000	186.014	79.130	186.014	169.681	3.566	1820.000
0.01	1.016	1802.591	186.014	80.036	159.354	186.184	3.540	1820.000
0.02	1.033	1785.183	186.014	80.941	138.322	202.688	3.514	1820.000
0.03	1.050	1767.774	186.014	81.847	121.404	219.191	3.489	1820.000
0.04	1.067	1750.365	186.014	82.752	107.569	235.694	3.463	1820.000
0.05	1.085	1732.957	186.014	83.658	96.095	252.197	3.437	1820.000
0.06	1.104	1715.548	186.014	84.563	86.461	268.700	3.412	1820.000
0.07	1.122	1698.139	186.014	85.469	78.285	285.203	3.386	1820.000
0.08	1.142	1680.730	186.014	86.374	71.279	301.707	3.360	1820.000
0.09	1.162	1663.322	186.014	87.280	65.225	318.210	3.335	1820.000
0.1	1.182	1645.913	186.014	88.186	59.954	334.713	3.309	1820.000
0.11	1.204	1628.504	186.014	89.091	55.332	351.216	3.284	1820.000
0.12	1.225	1611.096	186.014	89.997	51.256	367.719	3.258	1820.000
0.13	1.248	1593.687	186.014	90.902	47.639	384.223	3.232	1820.000
0.14	1.271	1576.278	186.014	91.808	44.414	400.726	3.207	1820.000
0.15	1.295	1558.870	186.014	92.713	41.525	417.229	3.181	1820.000
0.16	1.319	1541.461	186.014	93.619	38.925	433.732	3.155	1820.000
0.17	1.344	1524.052	186.014	94.524	36.577	450.235	3.130	1820.000
0.18	1.370	1506.643	186.014	95.430	34.447	466.739	3.104	1820.000
0.19	1.397	1489.235	186.014	96.335	32.508	483.242	3.078	1820.000
0.2	1.425	1471.826	186.014	97.241	30.739	499.745	3.053	1820.000
0.21	1.453	1454.417	186.014	98.146	29.119	516.248	3.027	1820.000
0.22	1.483	1437.009	186.014	99.052	27.631	532.751	3.001	1820.000
0.23	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1820.000
0.24	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.25	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.26	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.27	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.28	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.29	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.31	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.32	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.33	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.34	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.35	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.36	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.37	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.38	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.39	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.41	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.42	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.43	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.44	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.45	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.46	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.47	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.48	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000
0.49	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.000





… which appears to be true! So diesel engines are more efficient than petrol ones.

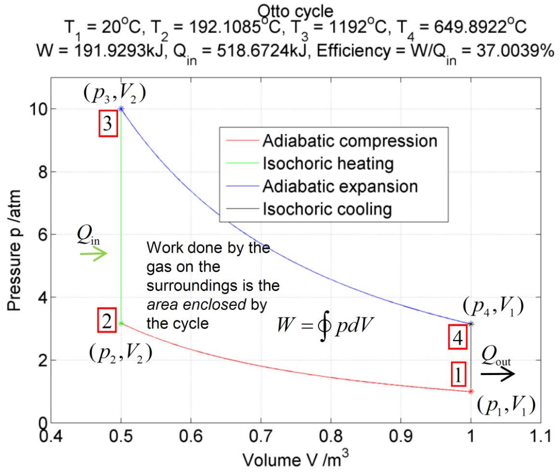
$$r = \frac{V_1}{V_2}$$

$$s = \frac{V_3}{V_2}$$

$$\eta = \frac{W}{Q_{\text{in}}}$$

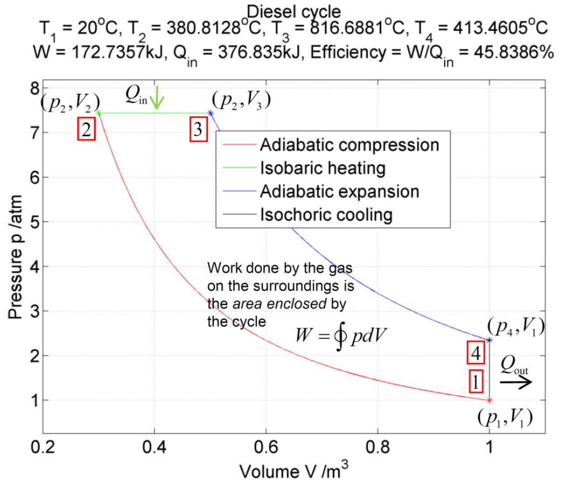
$$\eta_{\text{diesel}} = 1 - \frac{1}{r^{\gamma-1}}\left(\frac{s^{\gamma}-1}{\gamma(s-1)}\right)$$

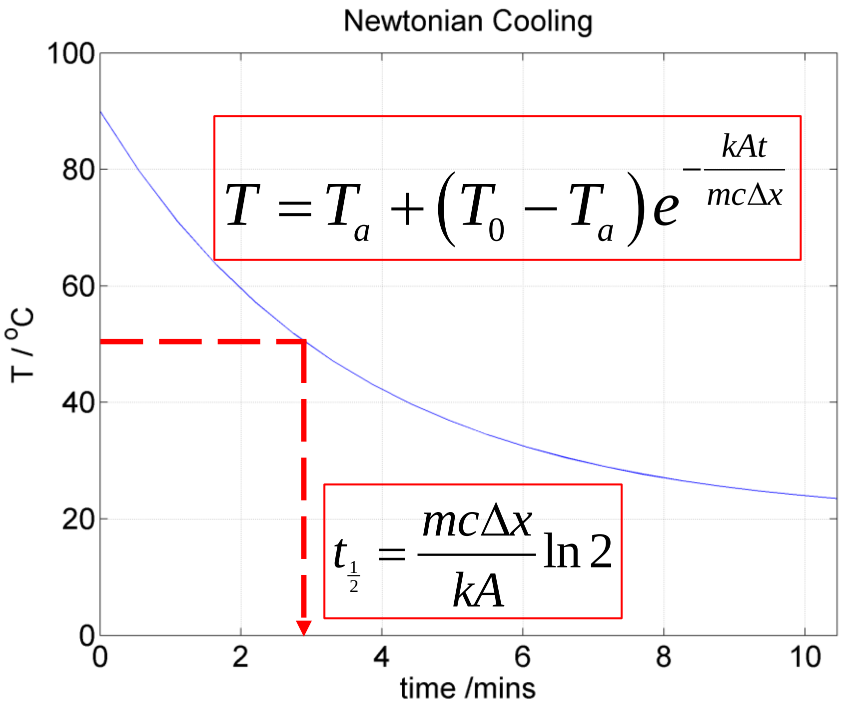
$$\eta_{\text{otto}} = 1 - \frac{1}{r^{\gamma-1}}$$



$$\eta_{\text{diesel}} > \eta_{\text{otto}}$$

$$\Rightarrow \gamma - 1 > \gamma s - s^{\gamma}$$



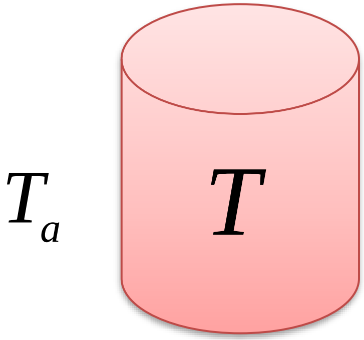


$$T = T_a + \left(T_0 - T_a\right)e^{-\frac{kAt}{mc\Delta x}}$$

$$t_{\frac{1}{2}} = \frac{mc\Delta x}{kA}\ln 2$$

Q is the heat transferred from the vessel to the surroundings
k is the thermal conductivity of the vessel
Δx is the thickness of the vessel
A is the surface area of the vessel

$$\frac{dQ}{dt} = kA\frac{\left(T - T_a\right)}{\Delta x}$$



Joseph Fourier
(1768-1830)

"Heat flow via conduction is proportional to temperature gradient"

If the specific heat capacity of the fluid is c, and the vessel contains m kg of fluid

$$dQ = -mcdT$$

If we assume the heat capacity is independent of temperature

$$\frac{dT}{dt} = -\frac{kA}{mc\Delta x}\left(T - T_a\right)$$

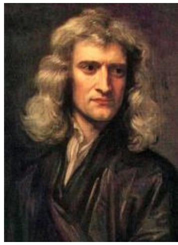
$$\int_{T_0}^{T}\frac{dT}{T - T_a} = -\frac{kA}{mc\Delta x}\int_0^t dt$$

$$\left[\ln\left|T - T_a\right|\right]_{T_0}^{T} = -\frac{kAt}{mc\Delta x}$$

$$\ln\left(\frac{T - T_a}{T_0 - T_a}\right) = -\frac{kAt}{mc\Delta x}$$

$$\frac{T - T_a}{T_0 - T_a} = e^{-\frac{kAt}{mc\Delta x}}$$

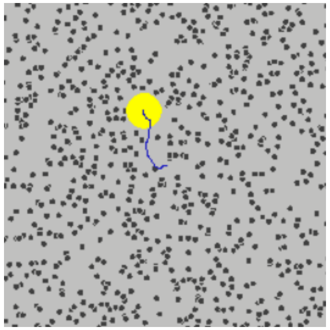
$$T = T_a + \left(T_0 - T_a\right)e^{-\frac{kAt}{mc\Delta x}}$$



Isaac Newton
(1643-1727)

Brownian motion – a *random walk*

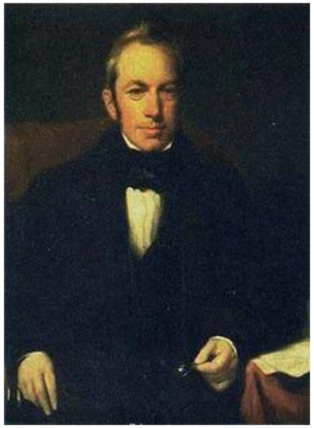
Brownian motion, initially observed as the random jittering of pollen grains in a microscope slide, is due to the random jostling of molecular motion. In the base of the pollen grains, it is the smaller (invisible) air molecules which are colliding at random. How far will a given particle move in a specified time, given its motion is random?



Brownian motion simulation

Consider motion in one direction in N steps of fixed length l. The caveat is that each step is either forward or backwards, and the direction is ‘chosen’ randomly.

The total displacement is $\boxed{x = l\sum_{i=1}^{N} a_i}$ where $\boxed{a_i = -1 \text{ or } 1}$



Robert Brown
(1773-1858)

A sensible measure of the distance travelled is the *root-mean-square (RMS) displacement:*

$$\sqrt{\langle x^2\rangle} = l\sqrt{\left\langle \left(\sum_{i=1}^{N} a_i\right)^2 \right\rangle} = l\sqrt{\left\langle \sum_{i=1}^{N} a_i^2 + \sum_{i=1,i\neq j}^{N} \sum_{j=1}^{N} a_i a_j \right\rangle}$$

$$\left\langle \sum_{i=1}^{N} a_i^2 \right\rangle = N \quad \text{and} \quad \left\langle \sum_{i=1,i\neq j}^{N} \sum_{j=1}^{N} a_i a_j \right\rangle = 0 \longleftarrow$$

Since a is a random choice between -1 and 1

$$\therefore \boxed{\sqrt{\langle x^2\rangle} = l\sqrt{N}}$$

$$\boxed{\begin{aligned} x &= l\sum_{i=1}^{N} a_i \\ a_i &= -1 \,\mathrm{or}\, 1 \end{aligned}}$$

1D random walk

$$\sqrt{\langle x^2\rangle} = l\sqrt{\left\langle\left(\sum_{i=1}^{N} a_i\right)^2\right\rangle} = l\sqrt{\left\langle \sum_{i=1}^{N} a_i^2 + \sum_{i=1, i\neq j}^{N}\sum_{j=1}^{N} a_i a_j\right\rangle}$$

$$\left\langle \sum_{i=1}^{N} a_i^2 \right\rangle = N \quad \text{and} \quad \left\langle \sum_{i=1, i\neq j}^{N}\sum_{j=1}^{N} a_i a_j \right\rangle = 0$$

$$\therefore \boxed{\sqrt{\langle x^2\rangle} = l\sqrt{N}}$$

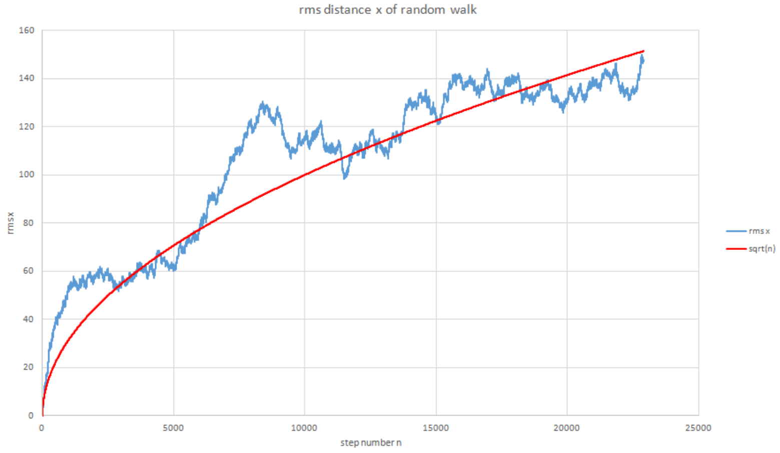
$\sqrt{\langle v^2\rangle}$ We might use the RMS speed here

If the average molecular speed is $\langle v\rangle$, the number of steps in t seconds is: $N = \dfrac{\langle v\rangle t}{l}$

Hence the RMS random walk displacement in t seconds is predicted to be:

$$\boxed{\sqrt{\langle x^2\rangle} = l\sqrt{N} = \sqrt{l\langle v\rangle t}}$$

The step size l can be associated with the **mean free path** between molecular collisions. We can define the mean free path to be the average distance travelled by a molecule in time t divided by the number of molecules it will likely collide with in that time.



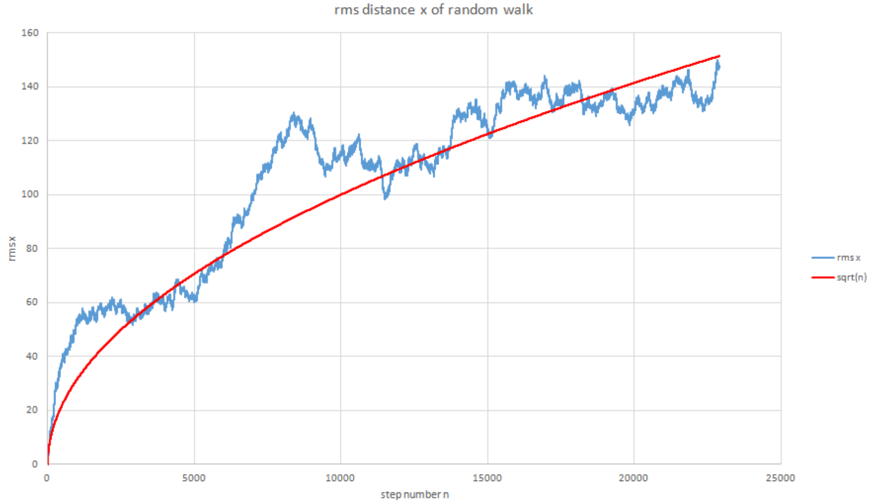
Mean free path

$$l = \frac{\sqrt{\langle v^2\rangle}t}{\underbrace{\pi d^2\sqrt{2}\sqrt{\langle v^2\rangle}t}\times n}$$

Distance travelled by molecule

'Interaction volume'

number of molecules per unit volume

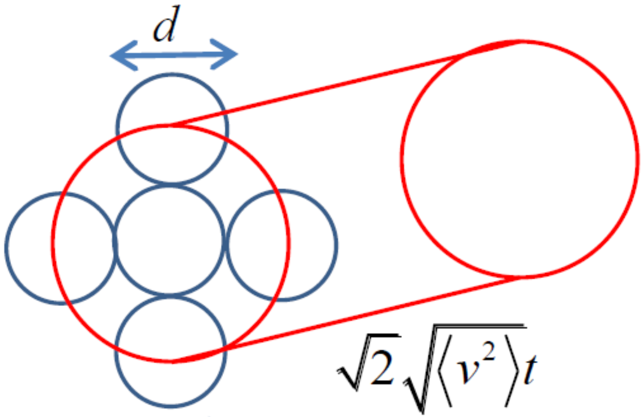


$$\boxed{l = \frac{1}{\pi\sqrt{2}d^2 n}}$$

Mean free path

Average distance between collisions

The interaction volume is root 2 larger because all molecules are in *relative* motion. Hence the length of the 'interaction tube' is proportional to the average *relative* speed



Colliding particles, assumed to be circular with diameter d

$$\langle v_{rel}\rangle = \sqrt{\left\langle \left|\mathbf{v}_i - \mathbf{v}_j\right|^2\right\rangle}$$

velocities of molecules i and j

$$\langle v_{rel}\rangle = \sqrt{\left\langle \left(v_i^2 + v_j^2 - 2\mathbf{v}_i\cdot\mathbf{v}_j\right)\right\rangle}$$

$$\langle v_{rel}\rangle = \sqrt{2\langle v^2\rangle - 2\langle \mathbf{v}_i\cdot\mathbf{v}_j\rangle}$$

$$\langle v_{rel}\rangle = \sqrt{2}\sqrt{\langle v^2\rangle}$$

We can determine the **mean free path** for an ideal gas by using the **Ideal Gas Equation**

Since the number of moles is $\frac{nV}{N_A} \leftarrow$ volume

$$\text{pressure} \rightarrow pV = \frac{nV}{N_A}RT \leftarrow \text{Absolute temperature}$$

Molar gas constant

$$R = 8.314\,\mathrm{J mol^{-1} K^{-1}}$$

$$\therefore n = \frac{p}{k_B T}$$

Boltzmann's constant $k_B = 1.38 \times 10^{-23}\,\mathrm{JK^{-1}}$

Hence $$\boxed{l = \frac{k_B T}{\pi\sqrt{2}d^2 p}}$$

If we divide this by the particle diameter d we arrive at **Knudsen's number (Kn)**. This dimensionless constant determines whether our statistical mechanics argument is valid, or whether a 'continuum' concept is needed.

The latter model is what is used to describe much of **fluid mechanics** i.e. where we consider the fluid as a continuously varying entity rather than a series of discrete, and randomly moving, molecules colliding.

$$\boxed{l = \frac{k_B T}{\pi \sqrt{2} d^2 p}}$$

$$\boxed{\begin{array}{ll} \mathrm{Kn} \ll 1 & \text{Continuum} \\ \mathrm{Kn} > 1 & \text{Statistical mechanics} \end{array}}$$

For a typical air molecule on Earth

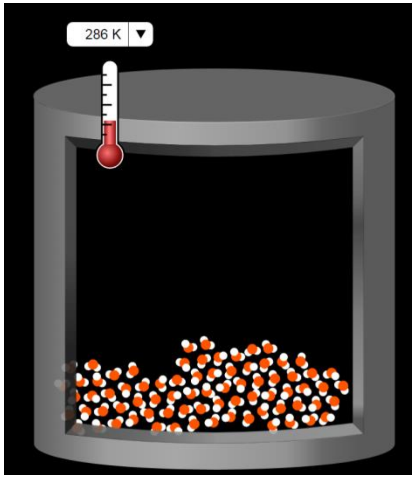
$$d = 0.3\text{nm},\ p = 10^5\,\text{Pa},\ T = 293K$$

$$\therefore l = 1.0 \times 10^{-7}\,\text{m}$$

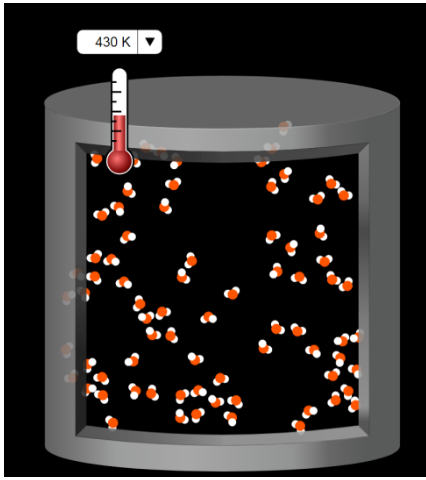
$$\therefore \mathrm{Kn} = \frac{l}{d} = \boxed{333}$$

So a statistical argument is justified

Fluid

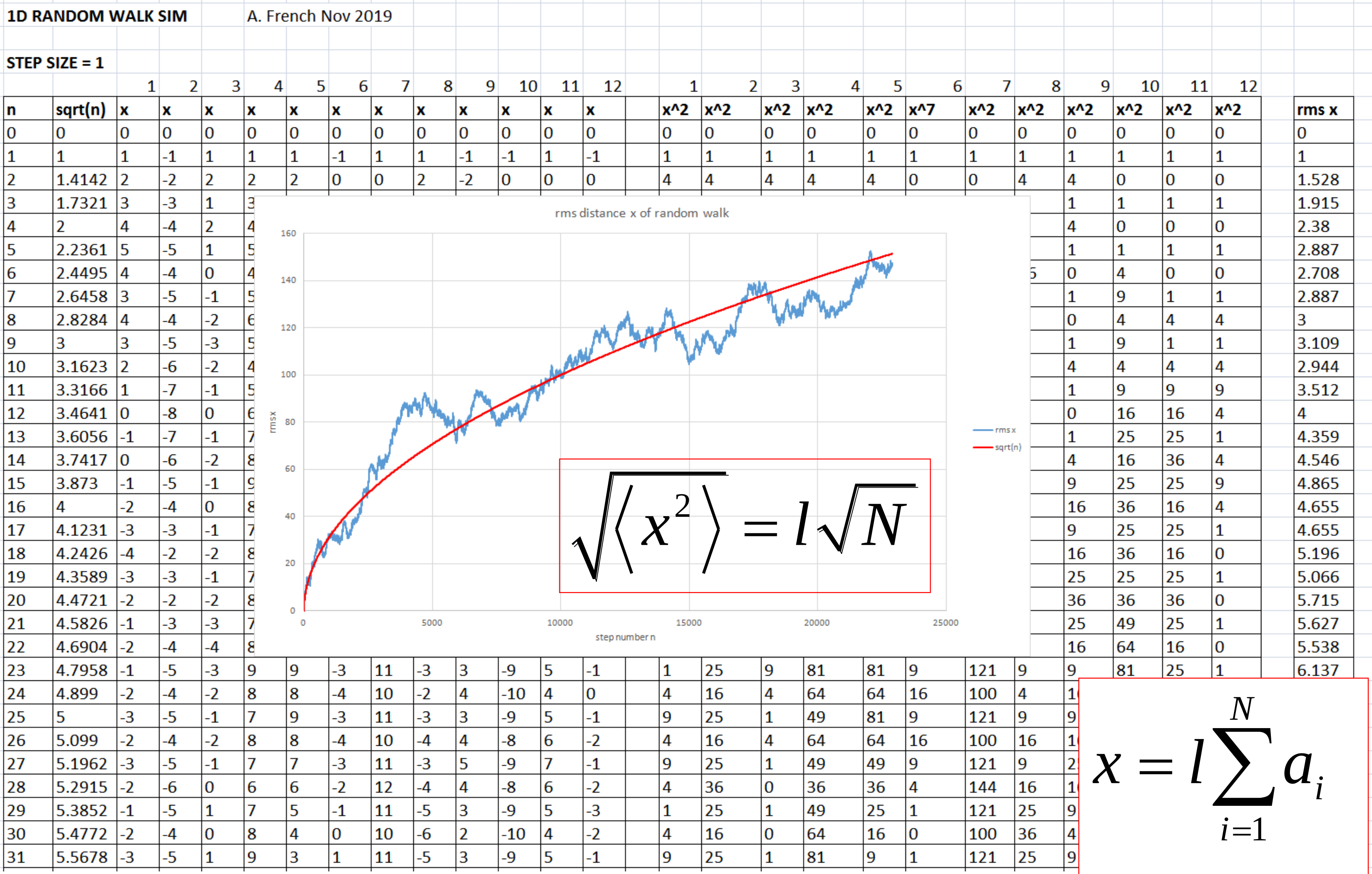


Gas



PhET States of Matter

1D random walk simulation in Excel



1D RANDOM WALK SIM A. French Nov 2019

STEP SIZE = 1

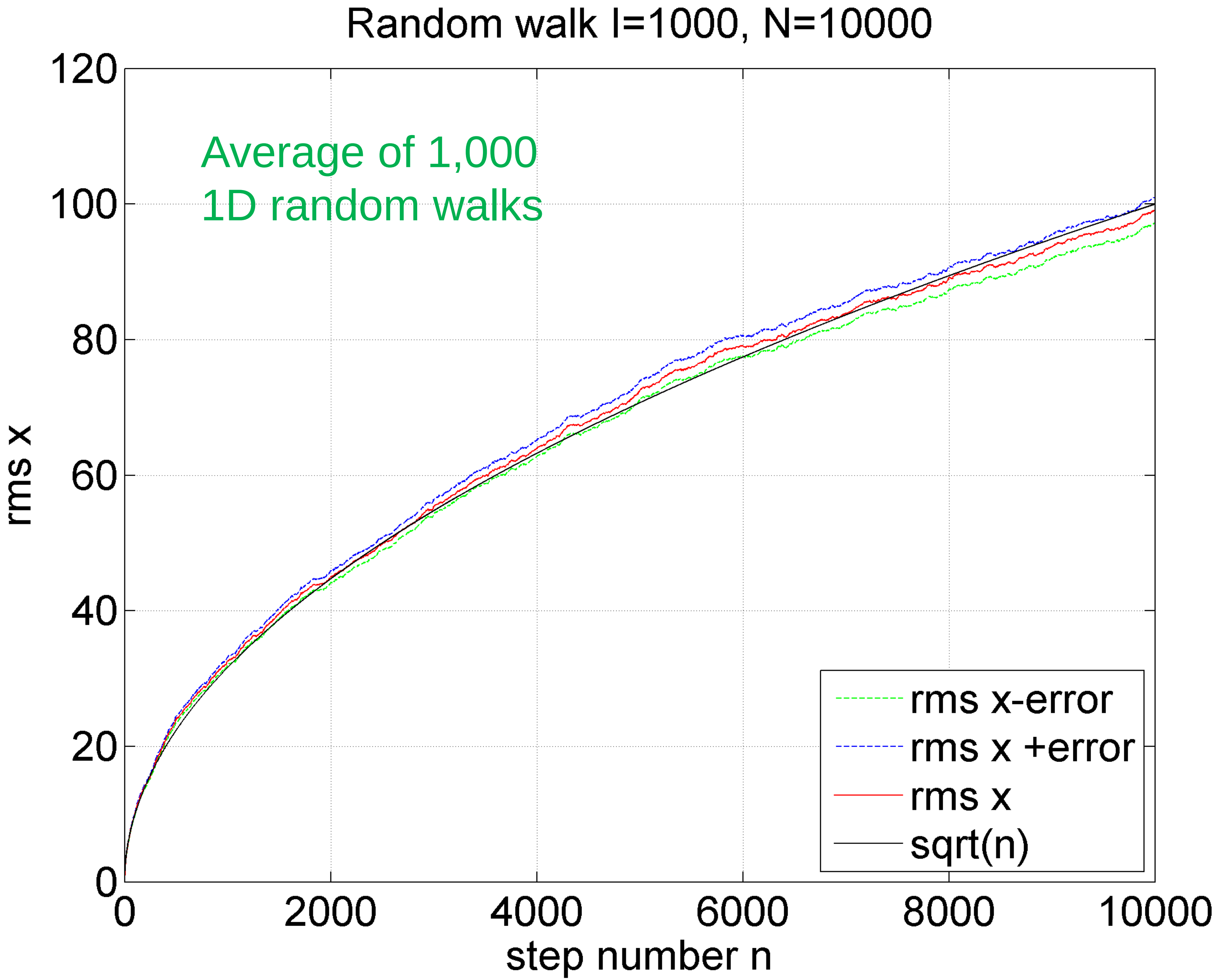
		1	2	3	4	5	6	7	8	9	10	11	12		1	2	3	4	5	6	7	8	9	10	11	12		
n	**sqrt(n)**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**		**x^2**	**x^2**	**x^2**	**x^2**	**x^2**	**x^7**	**x^2**	**x^2**	**x^2**	**x^2**	**x^2**	**x^2**		**rms x**
0	0	0	0	0	0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0	0		0
1	1	1	-1	1	1	1	-1	1	1	-1	-1	1	-1		1	1	1	1	1	1	1	1	1	1	1	1		1
2	1.4142	2	-2	2	2	2	0	0	2	-2	0	0	0		4	4	4	4	4	0	0	4	4	0	0	0		1.528
3	1.7321	3	-3	1	3																		1	1	1	1		1.915
4	2	4	-4	2	4																		4	0	0	0		2.38
5	2.2361	5	-5	1	5																		1	1	1	1		2.887
6	2.4495	4	-4	0	4																	5	0	4	0	0		2.708
7	2.6458	3	-5	-1	5																		1	9	1	1		2.887
8	2.8284	4	-4	-2	6																		0	4	4	4		3
9	3	3	-5	-3	5																		1	9	1	1		3.109
10	3.1623	2	-6	-2	4																		4	4	4	4		2.944
11	3.3166	1	-7	-1	5																		1	9	9	9		3.512
12	3.4641	0	-8	0	6																		0	16	16	4		4
13	3.6056	-1	-7	-1	7																		1	25	25	1		4.359
14	3.7417	0	-6	-2	8																		4	16	36	4		4.546
15	3.873	-1	-5	-1	9																		9	25	25	9		4.865
16	4	-2	-4	0	8																		16	36	16	4		4.655
17	4.1231	-3	-3	-1	7																		9	25	25	1		4.655
18	4.2426	-4	-2	-2	8																		16	36	16	0		5.196
19	4.3589	-3	-3	-1	7																		25	25	25	1		5.066
20	4.4721	-2	-2	-2	8																		36	36	36	0		5.715
21	4.5826	-1	-3	-3	7																		25	49	25	1		5.627
22	4.6904	-2	-4	-4	8																		16	64	16	0		5.538
23	4.7958	-1	-5	-3	9	9	-3	11	-3	3	-9	5	-1		1	25	9	81	81	9	121	9	9	81	25	1		6.137
24	4.899	-2	-4	-2	8	8	-4	10	-2	4	-10	4	0		4	16	4	64	64	16	100	4	1					
25	5	-3	-5	-1	7	9	-3	11	-3	3	-9	5	-1		9	25	1	49	81	9	121	9	9					
26	5.099	-2	-4	-2	8	8	-4	10	-4	4	-8	6	-2		4	16	4	64	64	16	100	16	1					
27	5.1962	-3	-5	-1	7	7	-3	11	-3	5	-9	7	-1		9	25	1	49	49	9	121	9	2					
28	5.2915	-2	-6	0	6	6	-2	12	-4	4	-8	6	-2		4	36	0	36	36	4	144	16	1					
29	5.3852	-1	-5	1	7	5	-1	11	-5	3	-9	5	-3		1	25	1	49	25	1	121	25	9					
30	5.4772	-2	-4	0	8	4	0	10	-6	2	-10	4	-2		4	16	0	64	16	0	100	36	4					
31	5.5678	-3	-5	1	9	3	1	11	-5	3	-9	5	-1		9	25	1	81	9	1	121	25	9					

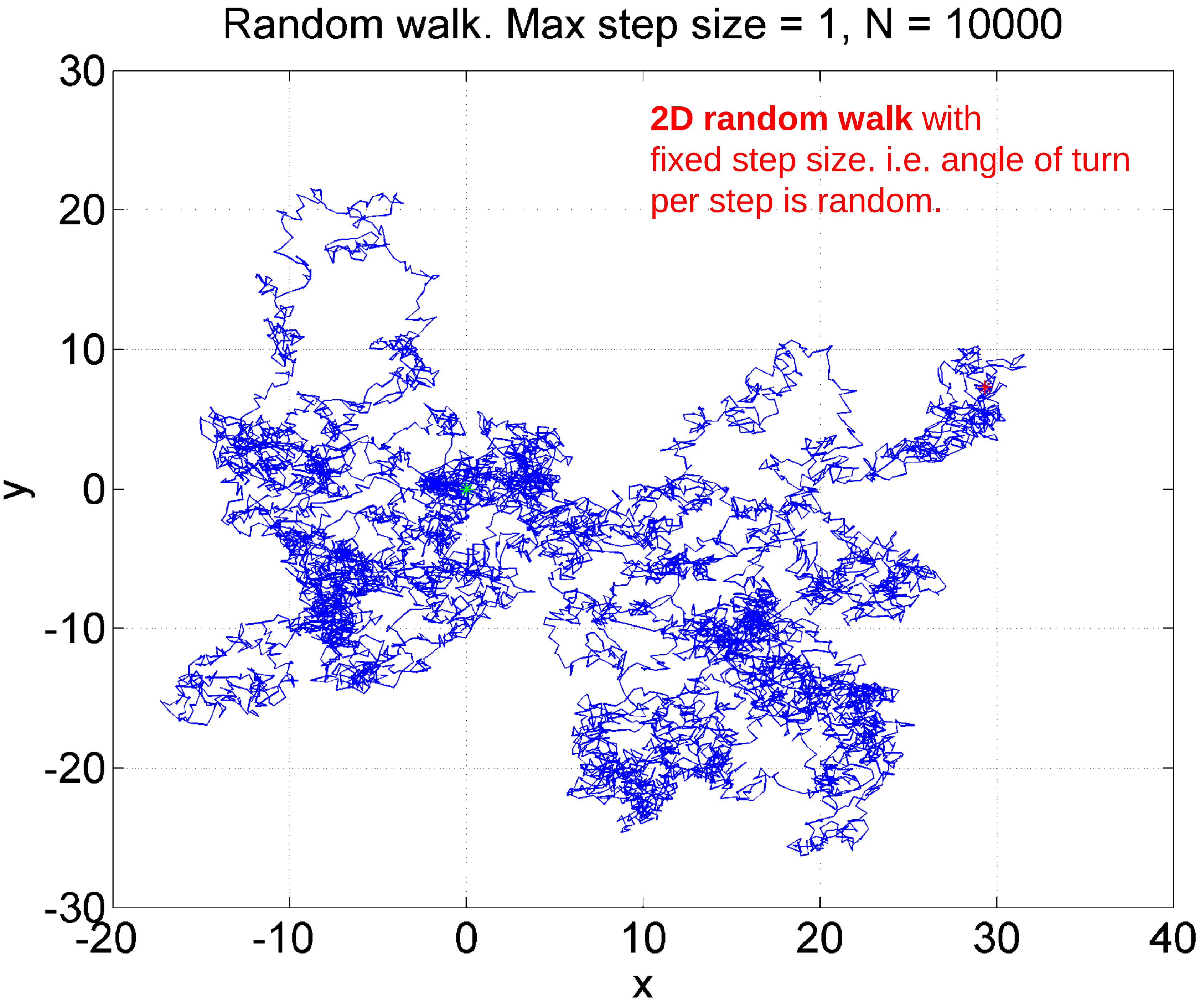
$$\sqrt{\left\langle x^2 \right\rangle} = l\sqrt{N}$$

$$x = l\sum_{i=1}^{N} a_i$$

$$a_i = -1 \text{or} 1$$

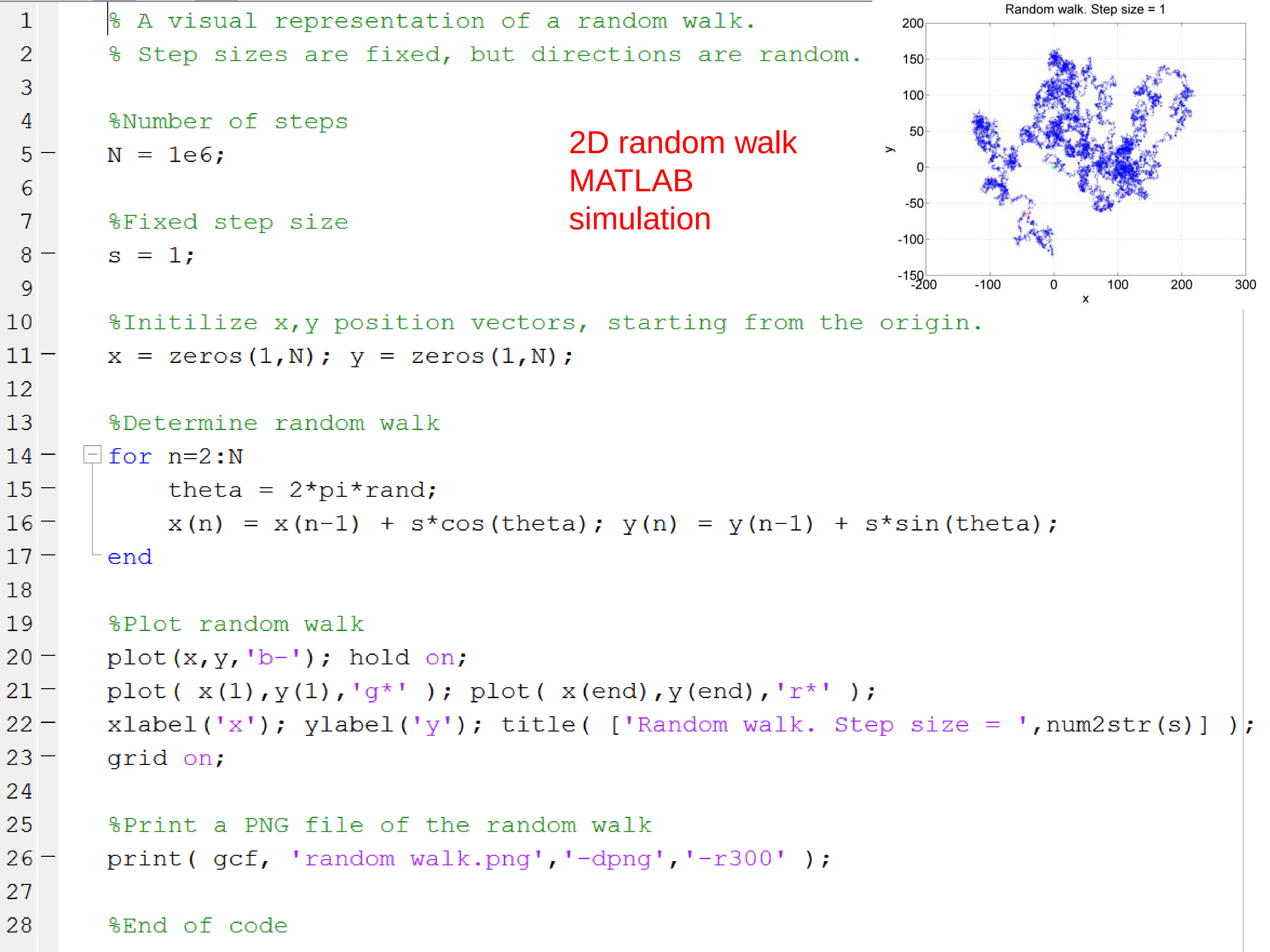
$$l = 1$$


Random walk l=1000, N=10000
Average of 1,000
1D random walks
rms x
step number n
0
20
40
60
80
100
120
0
2000
4000
6000
8000
10000
rms x-error
rms x +error
rms x
sqrt(n)

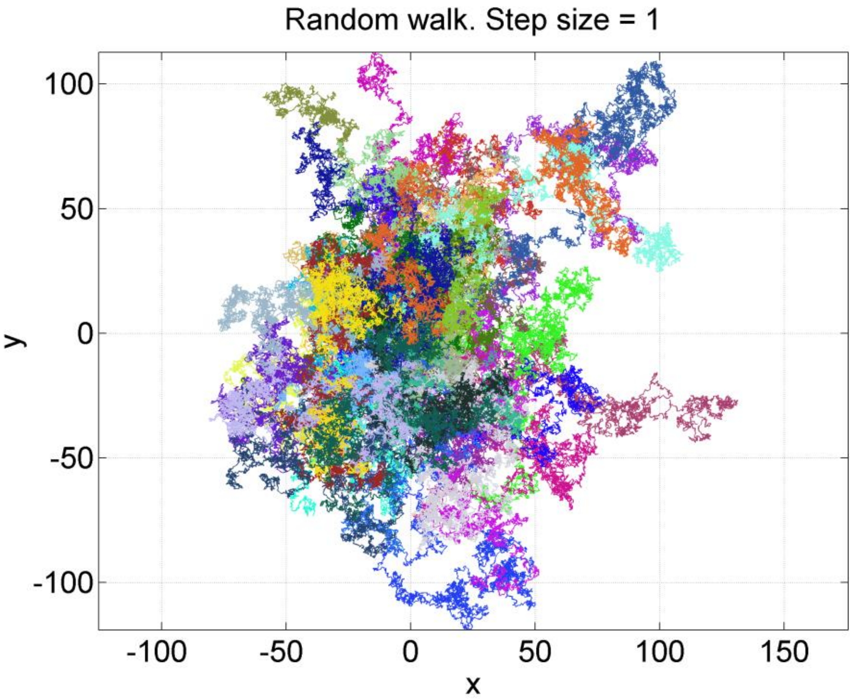


2D random walk with
fixed step size. i.e. angle of turn
per step is random.

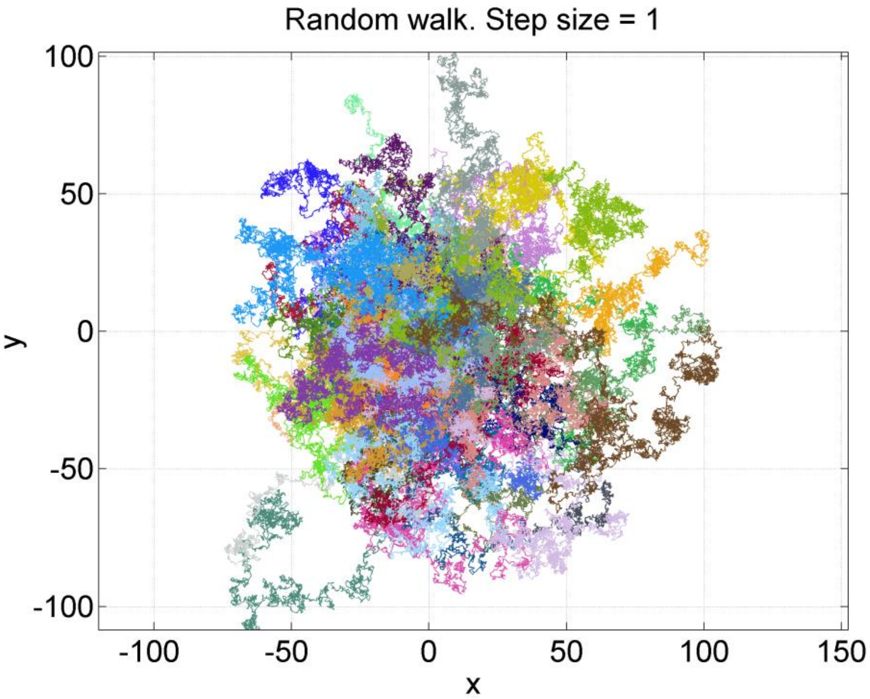
2D random walk
MATLAB
simulation



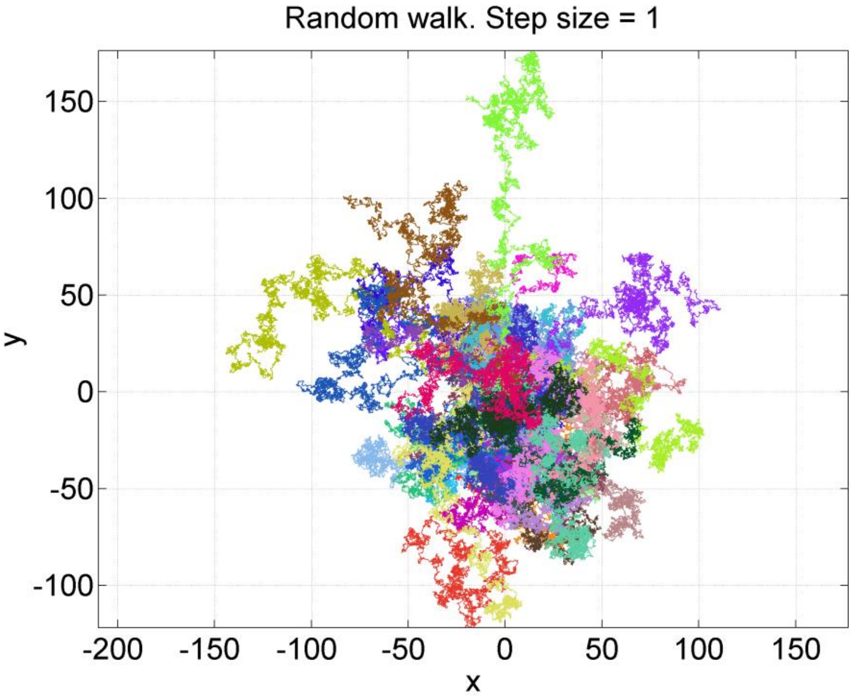
```
% A visual representation of a random walk.
% Step sizes are fixed, but directions are random.

%Number of steps
N = 1e6;

%Fixed step size
s = 1;

%Initilize x,y position vectors, starting from the origin.
x = zeros(1,N); y = zeros(1,N);

%Determine random walk
for n=2:N
    theta = 2*pi*rand;
    x(n) = x(n-1) + s*cos(theta); y(n) = y(n-1) + s*sin(theta);
end

%Plot random walk
plot(x,y,'b-'); hold on;
plot( x(1),y(1),'g*' ); plot( x(end),y(end),'r*' );
xlabel('x'); ylabel('y'); title( ['Random walk. Step size = ',num2str(s)] );
grid on;

%Print a PNG file of the random walk
print( gcf, 'random walk.png','-dpng','-r300' );

%End of code
```



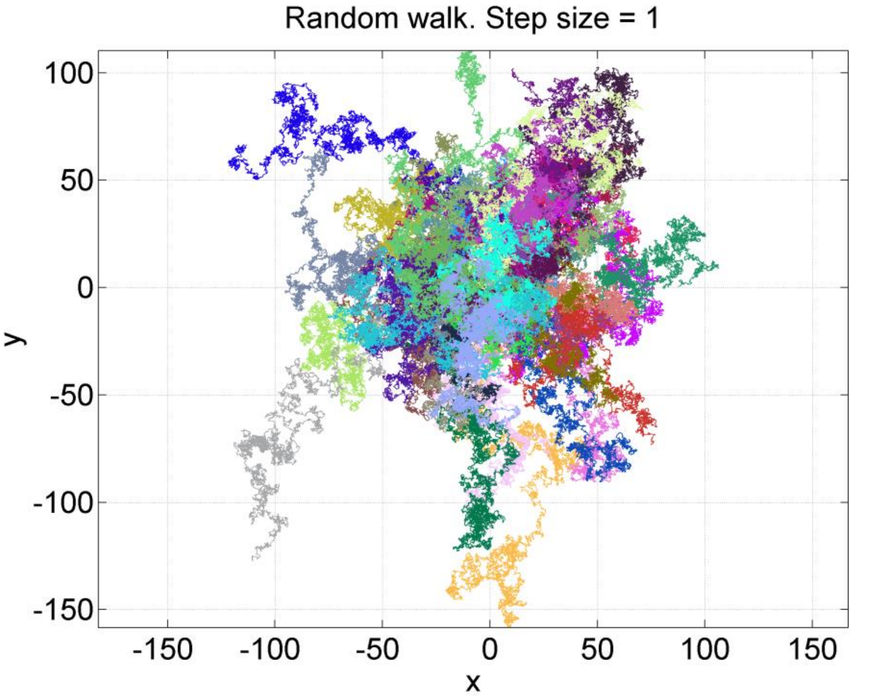
Random walk. Step size = 1



Random walk. Step size = 1

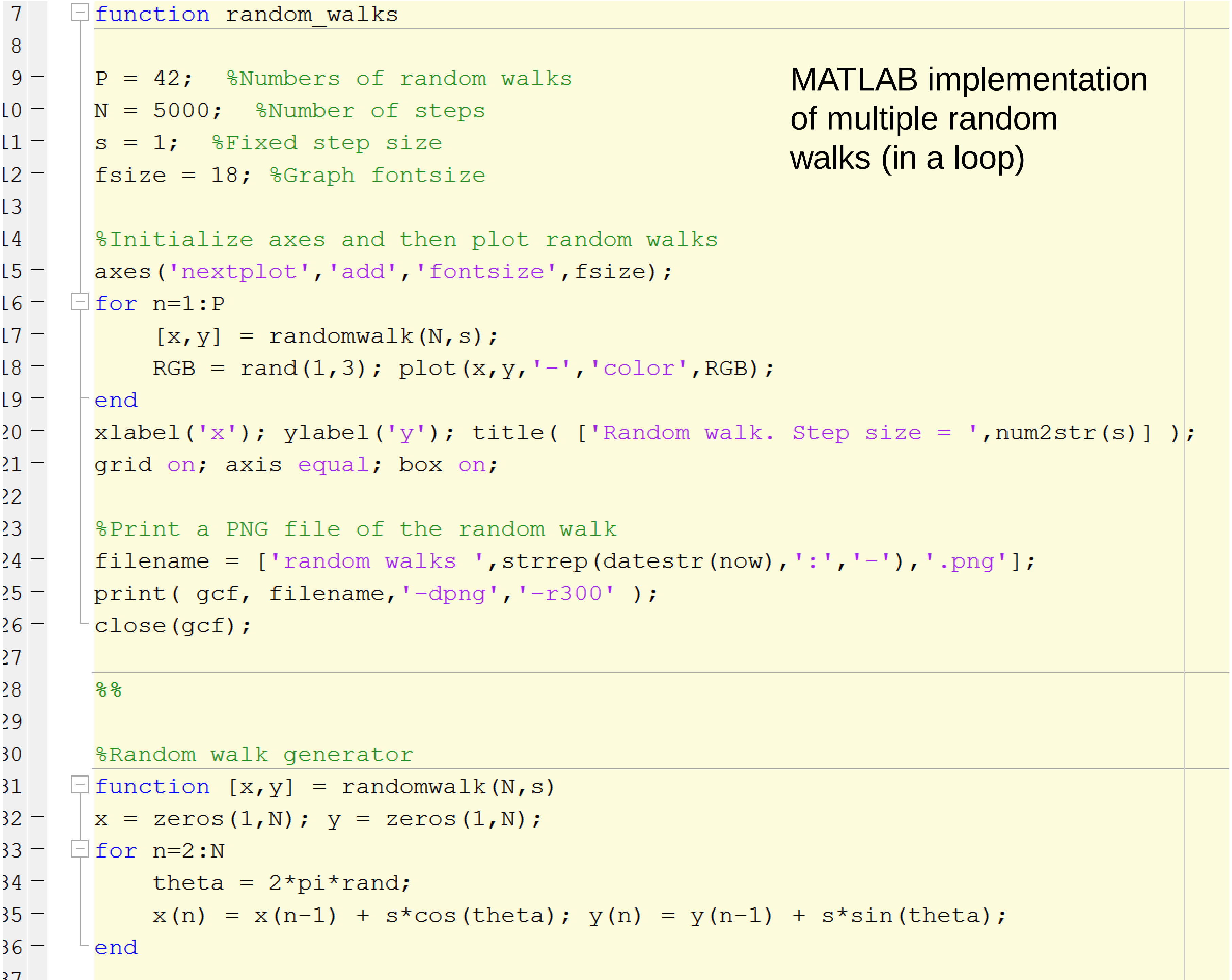


Random walk. Step size = 1

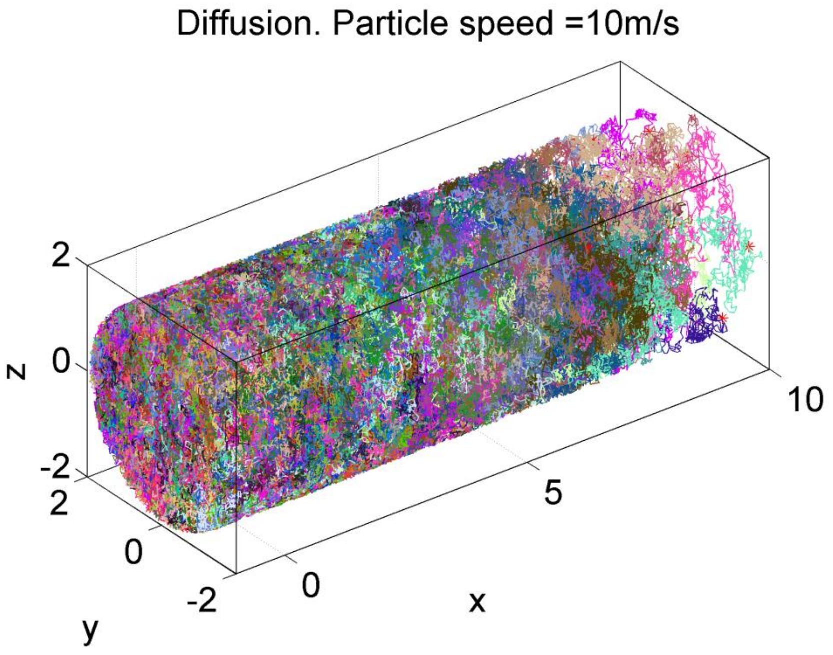


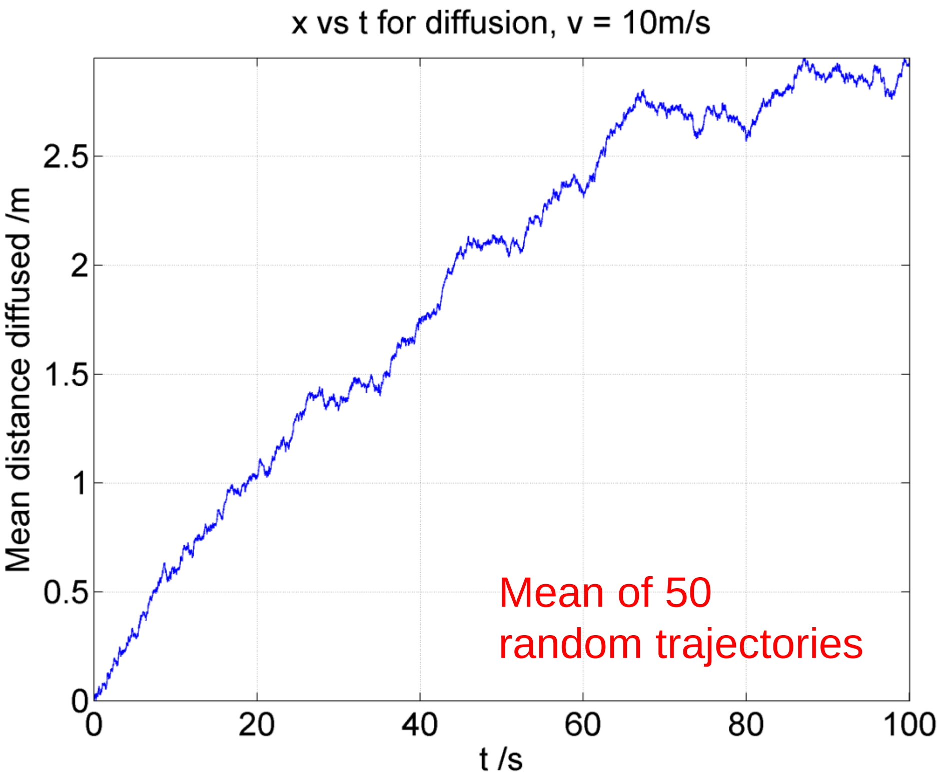
Random walk. Step size = 1

MATLAB implementation of multiple random walks (in a loop)

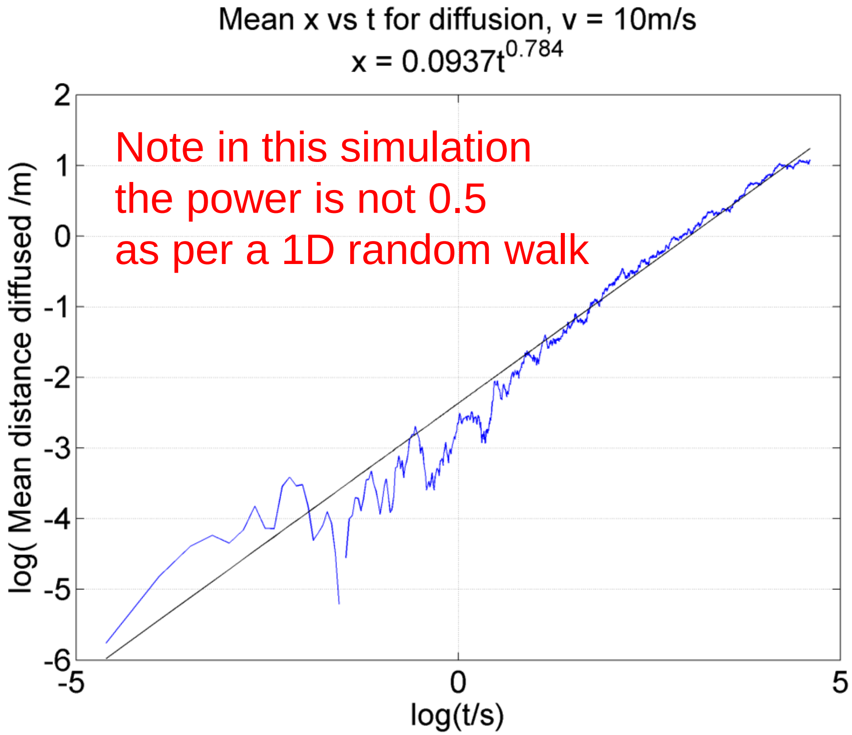


```
function random_walks

P = 42;  %Numbers of random walks
N = 5000;  %Number of steps
s = 1;  %Fixed step size
fsize = 18; %Graph fontsize

%Initialize axes and then plot random walks
axes('nextplot','add','fontsize',fsize);
for n=1:P
    [x,y] = randomwalk(N,s);
    RGB = rand(1,3); plot(x,y,'-','color',RGB);
end
xlabel('x'); ylabel('y'); title( ['Random walk. Step size = ',num2str(s)] );
grid on; axis equal; box on;

%Print a PNG file of the random walk
filename = ['random walks ',strrep(datestr(now),':','-'),'.png'];
print( gcf, filename,'-dpng','-r300' );
close(gcf);

%%

%Random walk generator
function [x,y] = randomwalk(N,s)
x = zeros(1,N); y = zeros(1,N);
for n=2:N
    theta = 2*pi*rand;
    x(n) = x(n-1) + s*cos(theta); y(n) = y(n-1) + s*sin(theta);
end
```





Mean of 50
random trajectories

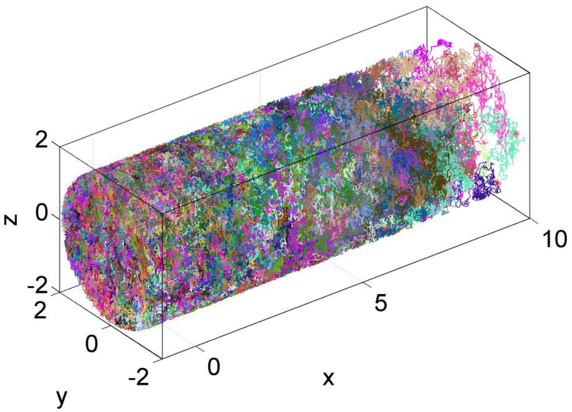


Note in this simulation
the power is not 0.5
as per a 1D random walk

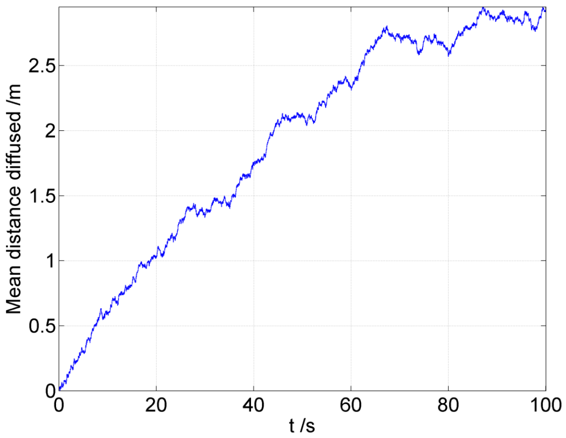
We can compute a 3D **diffusion** model *efficiently* by using a random walk.

The random walk gets around the need to keep track of thousands of particles and their collisions.

Diffusion. Particle speed =10m/s

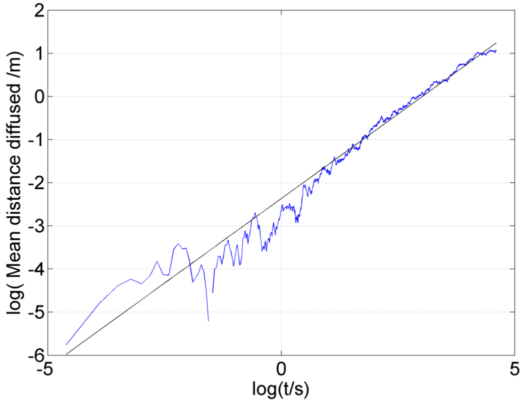


x vs t for diffusion, v = 10m/s



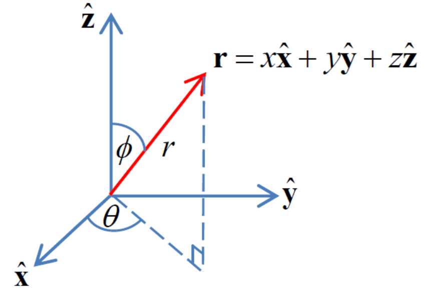
Mean x vs t for diffusion, v = 10m/s

$x = 0.0937t^{0.784}$

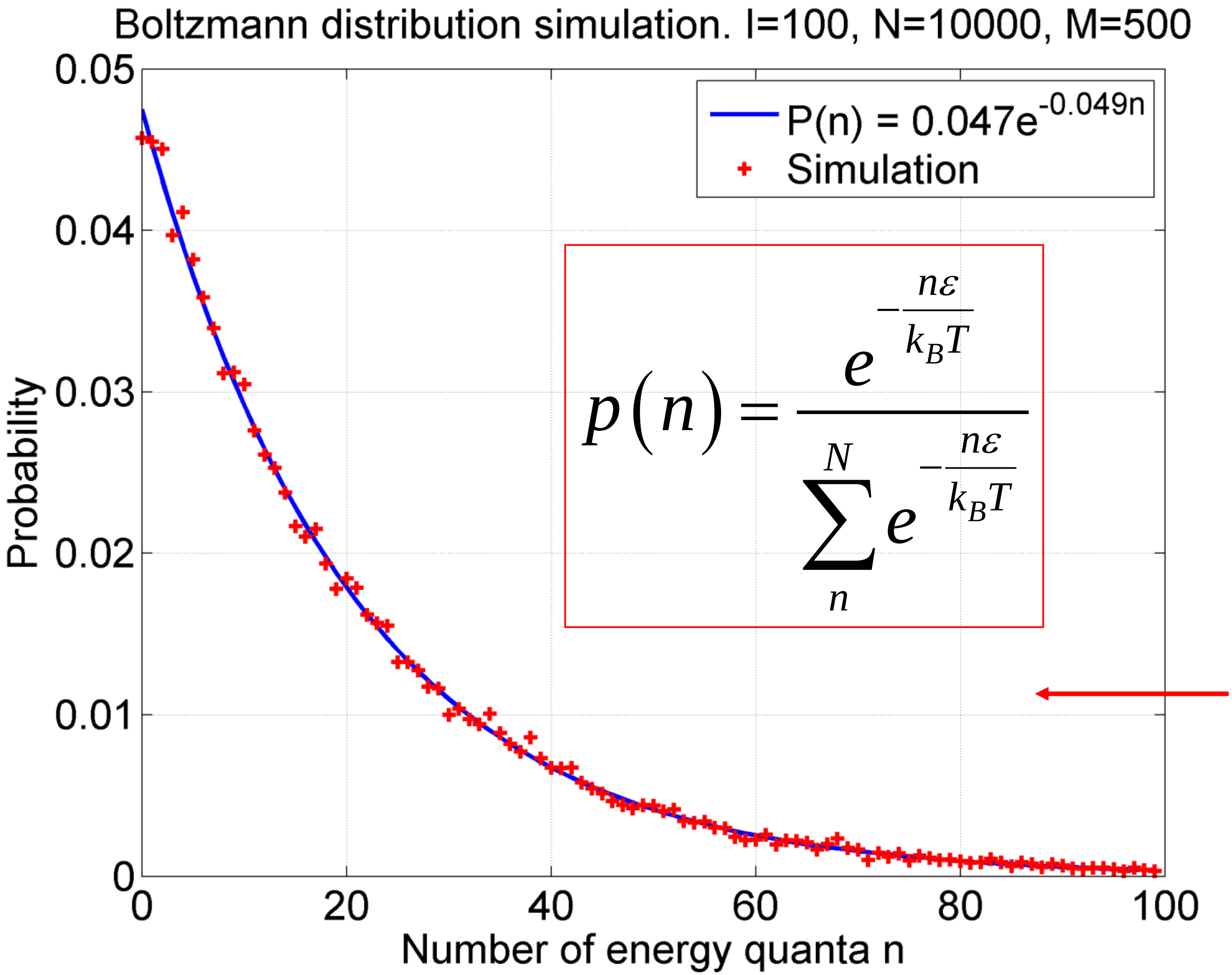


```
%Determine trajectory
function [x,y,z,t] = diffusion_trajectory(a,r,s,dt,tmax)

%Initialize x,y,z,t coordinates
x = 0; y = 0; z = 0; t = 0;

%Compute the random walk!
n=1;
while t(end) < tmax

    %Choose random direction angles
    azi = 2*pi*rand; elev = -0.5*pi + pi*rand;

    %Define magnitude of displacement during timestep
    d = s*dt;

    %Compute next x,y position
    dx = d*cos(elev)*cos(azi);
    dy = d*cos(elev)*sin(azi);
    dz = d*sin(elev);

    %Check if particle has hit a side wall
    if ( ( y(end)+dy )^2 + ( z(end) + dz )^2 ) > r^2
        dz = -dz; dy = -dy;
    end

    %Check if particle has hit back wall
    if ( x(end) + dx ) < a
        dx = -dx;
    end

    %Update x,y,z trajectory
    x(n+1) = x(n) + dx; y(n+1) = y(n) + dy; z(n+1) = z(n) + dz;
    t(n+1) = t(n) + dt; n = n+1;
end
```

Random angles
in azimuth and elevation



Assume elastic
collisions with walls

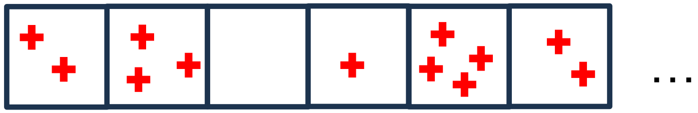


$$p(n) = \frac{e^{-\frac{n\varepsilon}{k_B T}}}{\sum_n^N e^{-\frac{n\varepsilon}{k_B T}}}$$

N = 10,000 energy quanta shared randomly among M = 500 molecules

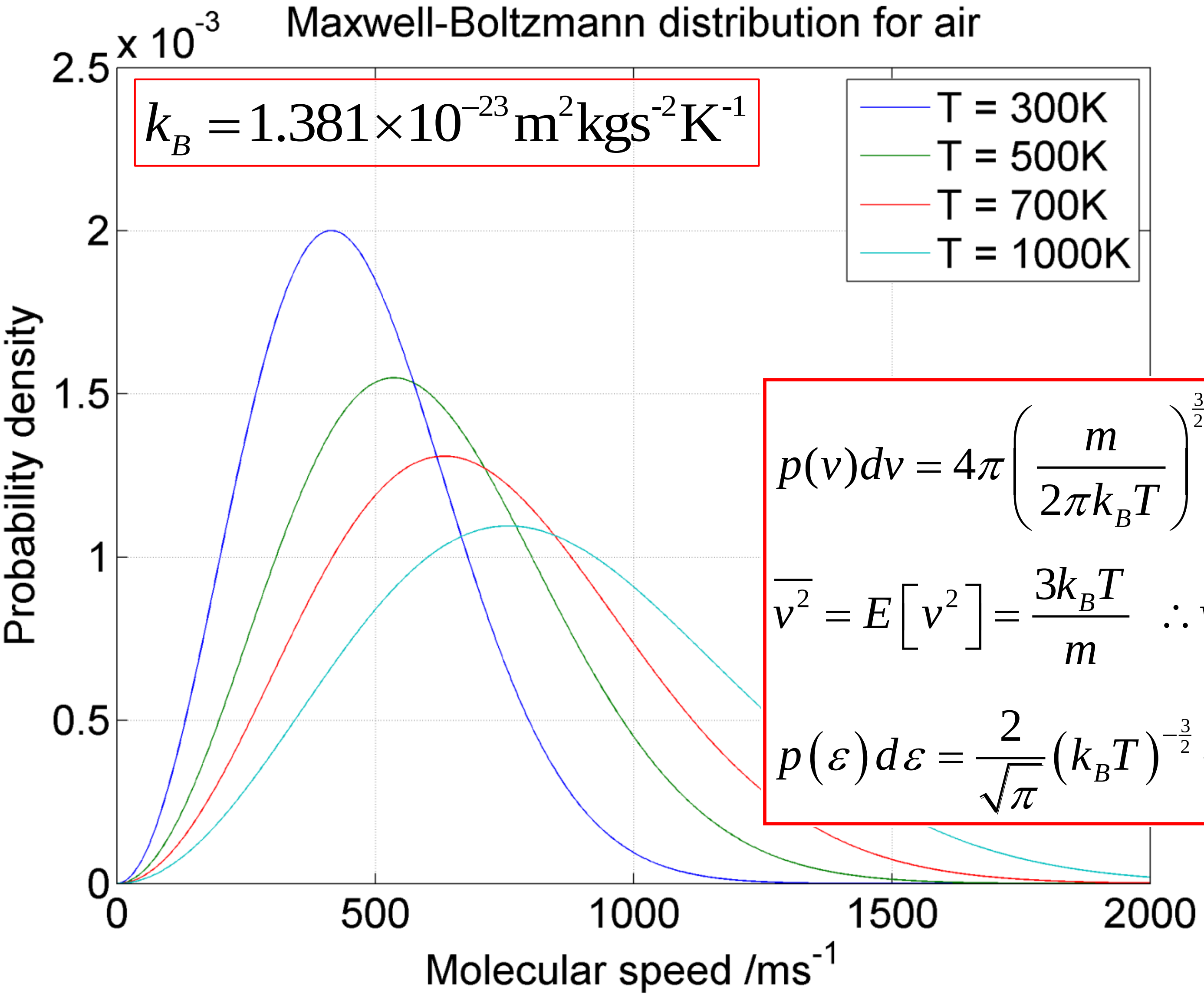
Process repeated 100 times

Normalized histogram



$$k_B = 1.38 \times 10^{-23}\,\mathrm{JK}^{-1}$$

Ludwig Boltzmann
1844-1906



$$k_B = 1.381\times 10^{-23}\,\mathrm{m^2kgs^{-2}K^{-1}}$$

James Clerk Maxwell
(1831–1879)

$$p(v)dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{\frac{1}{2}mv^2}{k_B T}}\,dv$$

$$\overline{v^2} = E\left[v^2\right] = \frac{3k_BT}{m} \quad \therefore v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}}$$

$$p(\varepsilon)\,d\varepsilon = \frac{2}{\sqrt{\pi}}\left(k_BT\right)^{-\frac{3}{2}}\sqrt{\varepsilon}\,e^{-\frac{\varepsilon}{k_BT}}\,d\varepsilon$$

$$E\left[\tfrac{1}{2}mv^2\right] = \tfrac{3}{2}k_BT$$

i.e. absolute temperature is proportional to mean KE of molecules

Ludwig Boltzmann
1844-1906