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# “Reason for Higher Rate of Gas Flow per unit Cross-Sectional Area of Smaller Pore Aperture,,

## ABSTRACT

**Objectives:** The objectives of this research are to 1) Formulate equation that shows the effect of pore aperture (or confinement) on not just the mass movement of molecules but the movement of individual molecules and 2) elucidate the derived equation and illustrate with diameter of pipes or tubes in literature.

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**Methods:** Theoretical and calculational.

**Results:** The results reaffirm that higher volume of gas flows through pore aperture of longer diameter than the shorter diameter. The same is applicable to longer tubes. The velocity of flow (volume of gas diffusing per cross-sectional of pore aperture per unit time) is higher for shorter diameter of pore aperture than the longer diameter of pore aperture. The converse is the case for the entropy implicit in the flow of gas through pores of different diameter.

**Conclusion:** The “reduced velocity” is inversely proportional to the cube root of the diameter of the pore. The entropic value arising from the effect of diameter is directly proportional to natural logarithm of the square of half of the diameter. If the diameter of the pore is equal to the dB wavelength the gas molecule may continue its motion at a root mean square velocity.

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*Keywords: Carbon (IV) oxide; diffusion; randomness; entropy; “reduced velocity”; pore aperture, kinetic energy; root mean square velocity.*

## 1. INTRODUCTION

The kinetic energy of gases is well known, and the velocity of any gaseous particle in gas phase at 273.15 K and above can be determined without much consideration for forces of interaction that promotes a departure from ideality. Gas molecules do not have restricted motion, the movement

15 being in any direction. What seems to be ignored is the effect of gravity within the very strong  
16 gravitational field of the earth unlike in the moon where astronauts float almost randomly due to weak  
17 gravitational field force. In the absence of concentration gradient (chemical potential gradient) or  
18 pressure gradient, the random motion of gas molecules is due not only to collision between  
19 molecules, but to the weak gravitational attraction for each molecule. This helps in the distribution of  
20 gases in all direction in a three-dimensional space (3 – D space). The additional implication is that  
21 more time could be spent before a gas molecule in gas phase reaches a specific target, though the  
22 root mean square velocity remains quantitatively the same. However, according to Simpkins and  
23 Williams [1], Brown and Escombe [2], observed that pipes of smaller uniform cross-section deliver  
24 gases at a higher rate measured in unit of volume per unit cross-sectional area per unit time than  
25 pipes of larger uniform cross-section. It is presumed however, that all pipes were in contact with  
26 carbon (IV) oxide (CO<sub>2</sub>) in a vessel at the same temperature and pressure.

27         Mere fact that gas molecules diffuse from the region of higher concentration to lower  
28 concentration does not preclude randomness in the motion of the molecules because of weak  
29 gravitational attraction for the molecules by the earth. But the randomness is far more pronounced in  
30 open space at zero concentration gradient. It is suggested that confinement or restriction in the space  
31 available for the diffusion of gases may reduce randomness. The effect of confinement or restricted  
32 space on the diffusion of gases has been studied in different ways [3, 4]. Etienne et al [3], Burada et  
33 al [4], and Martens [5] expressed concern for the entropic effect of confinement on the motion of  
34 particles; Chow and Skolnick [6] investigated the effect of confinement which entails slowing down of  
35 particle motion in cellular medium in particular. The effects of confinement and crowded biological  
36 environment on the diffusion of biomolecules have been studied earlier [6 – 9]. Although some highly  
37 technical terms and much higher mathematics in particular that are poorly understood may have been  
38 used in some research papers [4], but useful information can be obtained. For instance, "in  
39 fluorescence correlation spectroscopy (FCS) analysis it is generally assumed that molecular species  
40 diffuse freely in volumes much larger than the three-dimensional FCS observation volume. However,  
41 this standard assumption is not valid in many measurement conditions, particularly in tubular  
42 structures with diameters in the micrometre range, such as those found in living cells (organelles,  
43 dendrites, etc.) and microfluidic devices (capillaries, reaction chambers etc.)"[3].

44 In the application of Einstein equation, the time it may take a particle in the gas phase or solution,  
45 and an intra-cellular medium is often given as  $x^2/2D$  where the parameters,  $x$  and  $D$ , are the root  
46 mean square distance (displacement) and diffusion coefficient respectively. However, the long  
47 dimension length of the cell or vessel containing reaction mixture components is not equal to root  
48 mean square movement. This is so because the equation is formulated based on mass diffusion of  
49 molecules such that average displacement cannot be attributed to any single molecule; each particle  
50 may cover distance different from distance covered by any other particle. Given specified condition for  
51 the determination of  $D$ , the root mean square distance,  $x$  can be correctly determined for a given time,  
52  $t$ . In other words, the parameter  $x$  is a function of  $t$ , and not the other way round. Thus within the mass  
53 movement of molecules along concentration or pressure gradient individual molecules retain its  
54 velocity influenced by potential energy intrinsic in the concentration or pressure gradient and thermal  
55 energy. This is to suggest that single molecule motion can be tracked instrumentally. Single-particle  
56 tracking (SPT) methods with hi-tech instrumentation are, according to Michalet [10] and references  
57 therein, widely used for the study of microscopic behaviour and interactions of individual molecules or  
58 tiny objects in soft matter and biological environment. Based on the kinetic theory of a case, the root  
59 means the square velocity of the gas molecule in free space is established. From point "a" to point "b"  
60 the distance apart may be » the long dimension length of the molecule such that the particle may not  
61 move in only one direction. Therefore, if the distance apart is said,  $l$  the latter divided by the total time  
62 spent in all direction in random motion should be < the root mean square velocity. It is speculated that  
63 randomness is minimised in confined space such as space within the tube. In this regard, more than  
64 100 years ago Brown and Escombe [2] observed that pipes of narrower diameter deliver carbon  
65 dioxide at the higher rate in volume per unit cross section per unit time than pipes of more full  
66 diameter. There seem not to have been any precise reason for this observation and any other  
67 observation by contemporary investigators [3, 5]. Thus, the novelty of this research lies in the fact that  
68 velocity equation different from the usual kinetic equation,  $\sqrt{\frac{3k_B\theta}{m}} \equiv v$ , but not unrelated to it was  
69 derived in a way that explains the reason why pore of smaller aperture delivers gas at a faster rate  
70 than pores of longer diameter. Therefore, the objectives of this research are to 1) Formulate equation  
71 that shows the effect of pore aperture (or confinement) on not just the mass movement of molecules  
72 but the change of individual atoms and 2) elucidate the derived equation and illustrate with a diameter  
73 of pipes or tubes in literature.

74 **2.0 Formulation of Mathematical Model**

75 This section concerns the formulation of the fundamental model which begins with the  
76 following equation.

77 
$$u = \frac{v}{n} \tag{1}$$

78 Where  $v$  and  $u$  are the root mean square (r m s) velocity and “reduced velocity” (otherwise called  
79 “pseudo-velocity”), respectively, and,  $n$  is » 1 due to time spent in other directions other than the  
80 preferred route in a straight line. It is not an overemphasis to restate that from one end of the wall to  
81 the other end, for instance, a gas molecule hardly moves in one direction such that the time taken to  
82 reach one end of the wall is longer than what it should have been if right straight course is taken.  
83 Therefore, the distance between the terms of the wall divided by the total time is taken in all directions  
84 yields the reduced velocity expressed in Eq. (1). This view is similar to the analogy expressed in  
85 literature. The difference, however, is that the diffusion of solute facing obstacles in fluid phase  
86 including intracellular environment is the case as described by Kao *et al.* [11]. The time required for  
87 an auto to reach a target destination depends on its speed, the fraction of time it is in constant motion,  
88 and its route. This is to say there may not be right straight course to the preferred destination. The  
89 continuous movement of an automobile at continual speed is analogous to not only fluid-phase solute  
90 diffusion [11], but to the dissemination or random displacement of gas molecules driven by thermal  
91 energy. It should be made transparent too, that this approach is entirely different from the transformed  
92 Einstein’s expression  $\frac{2D}{l} = \frac{l}{t}$  where  $l$  is the root mean square displacement and  $t$  is a time of transit. In  
93 this research, the total distance covered in random motion compared to what the range should have  
94 been if a straight course is taken is the case rather than the root mean square displacement or  
95 distance. This, therefore, represents a new approach that can lead to the determination of other  
96 parameters such as entropy arising from random motion in confined space as in tubes and their  
97 apertures.

98 The main principle upon which this derivation is based is de Broglie principle (dB). Therefore,  
99 apply dB and obtain:

100 
$$m \left( \frac{v}{n} \right)^2 = hf_{dB(1)} \tag{2}$$

101 Where  $f_{dB(1)}$  is the reduced dB frequency,  $m$  is the mass of a molecule and  $h$  is the Planck’s constant.  
102 Accordingly, there should be increased dB wavelength ( $\lambda_{dB(1)}$ ). These parameters, decreased  $f_{dB(1)}$  and

103 increased  $\lambda_{dB(1)}$  are regarded as pseudo-quantities in contrast to the real quantities expected if the  
 104 total distance in all directions as against the single preferred direction to the target destination, is  
 105 divided by the total time. **This is to say that the total distance covered divided by the total time yields**  
 106 **the r ms.** From Eq. (2),

$$107 \quad f_{dB(1)} = \quad f_{dB}/n^2 \quad (3)$$

108 Equation (3) arises because  $mv^2 = hf_{dB(1)}n^2$  and  $hf_{dB(1)}n^2 = hf_{dB}$  where  $f_{dB}$  is the dB frequency at r  
 109 m s velocity,  $v$ . This is so because  $v > u$ .

110 Meanwhile,

$$111 \quad (mu)^2 = \left(\frac{h}{\lambda_{dB(1)}}\right)^2 \quad (4)$$

112 Where  $\lambda_{dB(1)}$ , is the pseudo-wavelength applicable to reduced velocity (or pseudo-velocity). From Eq.  
 113 (4),

$$114 \quad u^2 = \left(\frac{h}{m\lambda_{dB(1)}}\right)^2 \quad (5)$$

115 Since  $\left(\frac{v}{n}\right)^2 = u^2$ , then,  $\left(\frac{v}{n}\right)^2 = \left(\frac{h}{m\lambda_{dB(1)}}\right)^2$  and so,

$$116 \quad \lambda_{dB(1)} = \frac{nh}{mv} \quad (6)$$

117 Besides,  $\lambda_{dB} = \frac{h}{mv}$ . Hence,

$$118 \quad \lambda_{dB(1)} = n \lambda_{dB} \quad (7)$$

119 Where  $\lambda_{dB}$  is the dB wavelength at r m s velocity,  $v$ . As long as Eq. (1) holds, then,

$$120 \quad n = d_0/d \quad (8)$$

121 Where  $d_0$  (or  $v t$ ) and  $d$  ( $u t$ ) is the total distance covered in every direction and the distance covered  
 122 in the real direction on a straight course (*i.e.* along the preferred straight route) respectively in time,  $t$ .

123 Meanwhile,

$$124 \quad v/n = \lambda_{dB(1)}f_{dB(1)} \quad (9)$$

125 Thus,

$$126 \quad v \text{ or } \frac{d_0}{t} = n\lambda_{dB(1)}f_{dB(1)} \quad (10)$$

127 From Eq. (10),

$$128 \quad \lambda_{dB(1)} = d_0/n f_{dB(1)}t \quad (11)$$

130 However,  $mu = h/\lambda_{dB(1)}$  and so, substitution of  $\lambda_{dB(1)} = h/mu$  into Eq. (11) gives:

131 
$$u = nhf_{dB(1)}t/md_0 \quad (12)$$

132 Meanwhile, multiply both sides of Eq. (12) by  $n$  and obtain:

133 
$$nu(or v) = n^2hf_{dB(1)}t/md_0 \quad (13)$$

134 There should be a time  $t_x (t_x \neq t)$  such that  $f_{dB(1)}t_x = n$ . Therefore, if  $D_0$  is the total distance covered  
135 in all directions in  $t_x$ , at  $v$  ms velocity,  $v$ , then,

136 
$$D_0 = n^3\lambda_{dB} \quad (14)$$

137 Equation (14) arises as follows: In place of  $t$  in Eq. (13)  $t_x$  is used while in place of  $d_0$ ,  $D_0$  is used;  
138 since  $h/mv = \lambda_{dB}$ , then when  $D_0$  is made the subject of the formula, Eq. (14) remains as it is.

139 Keeping the relationship between  $you$  and  $v$  in mind, and as long as Eq. (14) holds, then,

140 
$$D_1 = n^2\lambda_{dB} \quad (15)$$

141 **Where**  $D_1$  is the distance measured in a single straight line towards the preferred destination in  $t_x$ .

142 **Therefore** (with a reason given below),

143 
$$D_0 = n^2\lambda_{dB(1)} \quad (16)$$

144 Equation (16) arises because  $\lambda_{dB(1)} = n\lambda_{dB}$  and,

145 
$$D_1 = n\lambda_{dB(1)} \quad (17)$$

146 Note that the above equation arises because, the dB wavelength ( $\lambda_{dB}$ ) at  $v$  is shorter than the  
147 wavelength ( $\lambda_{dB(1)}$ ) at  $u$  while the total distance ( $D_0$ ) covered in all directions in random motion in time,  
148  $t_x$  at  $v$  is always longer than  $D_1$ .

149 In Eq. (13),  $f_{dB(1)} = u/\lambda_{dB(1)}$  and so,

150 
$$v = hn^2ut/md_0\lambda_{dB(1)} \quad (18)$$

151 Substitution of Eq. (12) into Eq. (18) gives:

152 
$$v = h^2n^3t^2f_{dB(1)}/m^2d_0^2\lambda_{dB(1)} \quad (19)$$

153 In Eq. (19),  $D_0/t_x = d_0/t = v$ . So,

154 
$$v = h^2n^3t_x^2f_{dB(1)}/m^2D_0^2\lambda_{dB(1)} \quad (20)$$

155 In Eq. (20)  $n^3f_{dB(1)}$  stands for  $nf_{dB}$  (i.e.  $n(n^2f_{dB(1)}) = nf_{dB}$ ) and if Eq. (16) is squared the result can  
156 be used in place of  $D_0^2$  in Eq. (20) so that,

157 
$$v = h^2t_x^2f_{dB}/m^2n^3\lambda_{dB(1)}^3 \quad (21)$$

158 Yet,  $f_{dB} = v/\lambda_{dB}$  and so, Eq. (21) becomes:

159 
$$v = h^2 t_x^2 v / m^2 n^3 \lambda_{dB} \lambda_{dB(1)}^3 \quad (22)$$

160 Keeping in mind that  $D_0$  is the same as  $n^3 \lambda_{dB}$  and making appropriate substitution into Eq. (22), and  
 161 after rearrangement, the result is:

162 
$$m^2 \lambda_{dB(1)}^3 D_0 = h^2 t_x^2 \quad (23)$$

163 Therefore,

164 
$$\lambda_{dB(1)}^3 = h^2 t_x^2 / m^2 D_0 \quad (24)$$

165 From Eq. (24),

166 
$$\lambda_{dB(1)} = \sqrt[3]{\frac{h^2 t_x^2}{m^2 D_0}} \quad (25)$$

167 Nonetheless,  $\lambda_{dB(1)} = h/mu$  and substitution into Eq. (25) gives:

168 
$$h/mu = \sqrt[3]{\frac{h^2 t_x^2}{m^2 D_0}} \quad (26)$$

169 Making  $u$  in Eq. (26) subject of the formula gives:

170 
$$u = \frac{h}{m} \sqrt[3]{\frac{m^2 D_0}{h^2 t_x^2}} \quad (27a)$$

171 But  $t_x^2 = D_0^2/v^2$  and  $v^2 = 3k_B\theta/m$  such that substitutions into Eq. (27a) give:

172 
$$u = \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}} \quad (27b)$$

173 Equation (27b) is subject to analysis in the results and discussion section.

## 174 2.1 Derivable equation of entropy arising from random motion of gases

175 Given that the rate of flow or flux per cross-sectional area through a given pore of known diameter is:

176  $R_v/\pi r^2$ , then,

177 
$$u = \sqrt[3]{\left(\frac{3k_B\theta h}{m^2 n^3 \lambda_{dB}}\right)} = R_v/\pi r^2 \quad (28)$$

178 Where,  $r$  and  $R_v$  are the radius of the pore and rate of gas flow in volume per unit time respectively.

179 There is need to add that if  $X$  volume of a gas diffused through a pipe in time  $t$ , regardless of length,

180 the total distant along the length of the pipe whose uniform cross-section is known **is X/cross-sectional**

181 **area**. In Eq. (28),  $n^3 \lambda_{dB}$  takes the place of  $D_0$  defined in Eq. (14). Making  $n^3$  subject of the formula

182 gives:

183 
$$n^3 = \left(\frac{\pi r^2}{R_v}\right)^3 \frac{3k_B\theta h}{m^2 \lambda_{dB}} \quad (29)$$

184 Replacing  $\lambda_{dB}$  in Eq. (29) with  $h/\sqrt{3mk_B\theta}$  gives after rearrangement:

185 
$$n^3 = \left(\frac{\pi r^2}{R_v}\right)^3 \left(\sqrt{\frac{3k_B\theta}{m}}\right)^3 \quad (30)$$

186 If volume ( $V_{(t)}$ ) swept out in specific direction is given as  $V_{(t)} = A n^2 \lambda_{dB}$  where  $A$  is the cross –  
 187 sectional area and if the volume ( $V$ ) swept out in multiple directions in random motion is given as  
 188  $V = A n^3 \lambda_{dB}$ , then  $\frac{V}{V_{(t)}} = n$ . Therefore, the entropic expression is:

189 
$$\Delta S = R \ln n$$

190 
$$\Delta S = R \ln \left( \frac{\pi r^2}{R_v} \sqrt{\frac{3k_B\theta}{m}} \right) \quad (31)$$

191 Equation (31) is explainable based on simple equation of entropy of expanding gas given as  $\Delta S =$   
 192  $R \ln \frac{v_1}{v_0}$  where  $v_1$  and  $v_0$  are the final and initial volume of the gas at constant pressure and  $v_1 > v_0$ . This  
 193 is purely an analogy which explains why  $\frac{V}{V_{(t)}}$  can be used to determine the entropy due to random  
 194 motion of the gas molecule.

195 At the earliest part of diffusion through the pore the rate of flow or diffusion concerning volume  
 196 per cross-sectional area of pore per unit time is given by Eq. (27) or Eq. (28) Where  $D_0$  is replaced by  
 197 the diameter of the pore. The earliest rate of diffusion ( $R_{vE}$ ) otherwise called conductance through the  
 198 pore regarding volume per unit time is therefore given as:

199 
$$R_{vE} = \pi r^2 \cdot \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}} \quad (32)$$

200 Substitution of Eq. (32) into entropy equation, Eq. (31) (the replacement of  $R_v$  with  $R_{vE}$ ), gives after  
 201 rearrangement the equation of entropy at the earliest stage of diffusion through the pore.

202 
$$\Delta S = R \ln \left( \left( \sqrt[6]{3mk_B\theta} \right) \cdot \sqrt[3]{\frac{d_{ia}}{h}} \right) \quad (33)$$

203 Where  $d_{ia}$  is the diameter of a pore.

204 The advantage of transport of particles through restricted channels in fluid medium and pores  
 205 has been put to good use. For instance, the advent of nanotechnology has its application in civil  
 206 engineering (effectively dispersing engineered nanomaterials in fiber-reinforced composites during  
 207 processing involves transport through a polymer solution or melt as well as through the rigid fiber  
 208 network) and medicine (delivering drugs, diagnostics, or therapeutic agents to targeted tissues in the  
 209 human body requires transport through the rigid extracellular matrix and the extracellular fluid volume  
 210 or through the highly selective blood-brain barrier) [7]. The issue is that nanoparticles move through



211 pores or spaces that are not less than nano-scale size. It is , therefore that the point of pore size is  
212 fundamental or has handy application in both biological and physical processes. But it is not yet  
213 known if pore size or extra – or intracellular space is shorter than nanoscale length. Porous structures  
214 (metal – organic framework materials), possessing big surface area, have potential application as  
215 novel adsorbents and catalysts [12]. Possible use for greenhouse gases removal, hydrogen storage  
216 for future clean energy technologies, and for highly selective separation of gaseous mixtures has  
217 according to Sartowska *et al.* [12] and references therein been the motivation for the interest in  
218 porous structures. Construction at the nanometre length scale of porous materials which may be  
219 needed at present, for many potential applications has been proposed by Sartowska *et al.* and  
220 references therein [12]. Although the fluid media as can be found in other – or intracellular medium,  
221 presents different hydrodynamic environment from the gas phase, both media have one thing in  
222 common, and that is just diffusion phenomenon. However, in support of the difference in the rate of  
223 diffusion between fluid medium and gas phase, is the observation that the distribution of dye  
224 molecules being confined in single conical nanopore channels is slower than that in the bulk solution  
225 [13] unlike the report by Brown and Escombe [2]. Whatever be the case, it is not sure yet if a pore size  
226 or intermolecular space within the cell in particular or through the membrane can be as short as the  
227 dB wavelength of the smallest molecule, the hydrogen molecule let alone larger or heavier particles.  
228 Related to this concern is the discussion on quantum aspects of the center-of-mass motion of  
229 complex particles, *i.e.* on the coherent splitting of their dB wavefronts, their recombination and  
230 interference and most importantly the experiments, in which dB wavelengths range between  $\lambda_{dB} = h =$   
231  $mv = 0.3 - 5 \exp(-12) \text{ m}$ , which is typically  $10 \exp(3) - 10 \exp(4)$  times smaller than the size of the  
232 molecule itself and comparable to the shortest wavelengths in high-resolution transmission electron  
233 microscopy [14]. The implication or effect of radius as short as dB wavelength is to be stated in the  
234 results and discussion section.

235           The advantage of pore size has application in domestic kerosene stove where the combustion  
236 chamber is surrounded by two perforated cylinders with open ends. The hydrocarbon (HC), kerosene  
237 which according to Matveev *et al* [15] contains dozens of various HC components has been the object  
238 of intense research with intention of determining ways of obtaining maximum energy value available  
239 in it. Its total combustion in Jet engine [15], lantern [16] combustion chamber and use of ethanol –  
240 kerosene mixture [17] require sufficient supply of oxygen that can be made possible with device that

241 can reduce randomness like pores with very short diameter ranging from few nanometers to few  
242 micrometers.

### 243 **3. Methods**

244 The research is mainly theoretical which attempts to derive equations (based on de Broglie  
245 principle) that can elucidate qualitatively and quantitatively the reason why narrower apertures allows  
246 larger volume of gas diffusion per unit cross-sectional area per unit time than pores of longer  
247 diameter. The degree of randomness and cognate entropic parameter were determined by  
248 substituting appropriate data in literature to the appropriate equations derived in this research.

### 249 **4. Results and Discussion**

250 A series of stepwise derivation based essentially on dB principle – the wave-particle duality –  
251 ended in two major equations, Eq. (27b) and Eq. (31). Before, proceeding with the mathematical  
252 equation, it is instructive to realize that dB principle seems to be applicable mainly to components of  
253 the electromagnetic spectrum as the paper by [14] suggests. Although the issues in the paper by  
254 Brand *et al* [14] are not very clear as expected for non-specialist, but they go to illustrate almost the  
255 universality in the application of dB theory *vis-à-vis* its application in this research in the elucidation of  
256 physicochemical phenomenon. In other words dB model can be applied to both micro – and macro –  
257 particles in motion. This research does not cover diffraction experiment but reference to double – or  
258 multiple – split diffraction experiment is intended to support the premise that dB model can apply to  
259 almost every particle: According to Brand *et al* [14] and references therein, double – and multi-slit  
260 diffraction experiments with massive matter have been realized with electrons, neutrons, atoms and  
261 their clusters, as well as small and large molecules. This issue is therefore, connected to the view that  
262 a relationship between physical constants from the microcosms (subatomic world) and the  
263 macrocosms (cosmos) plays an important role in physics [18]; this implies that Planck's constant may  
264 be "a bridge" between microcosm and macrocosm which seems to be accomplished by writing  
265 Newton's gravitational constant as a function of Planck's constant [18]. But there is also a role for  
266 Planck's constant in the concept of wave-particle duality in which the particle aspect can best be  
267 described as a deterministic property in addition to its description as discrete local particle subject to  
268 detection and in which the wave aspect which is probabilistic or stochastic in nature is also described  
269 as the indistinguishable delocalized wave nature that explains the interference pattern [14]

270 characteristic of typical wave as observed in double slit experiment. What is relevant is that dB  
 271 wavelength and frequency as used in this research may be justified.

272 At this junction Eq. (27b) and Eq. (28) can be re-examined. If  $D_0 \rightarrow \lambda_{dB}$ , that is, if  $n^3 \rightarrow 1$ ,  $u \rightarrow$   
 273  $v$ . This can be shown as follows: With  $n = 1$ , substitution of  $h/\sqrt{3mk_B\theta}$  into Eq. (28) expressing  $u$ ,  
 274 should give:

$$275 \quad u = \sqrt[3]{\frac{3k_B\theta h \cdot \sqrt{3mk_B\theta}}{m^2 h}} \quad (34a)$$

276 Taking the cube of Eq. (34a) and simplifying gives:

$$277 \quad u^3 = \left( \sqrt[2]{\frac{3k_B\theta}{m}} \right)^3 \quad (34b)$$

278 Taking the cube root gives:

$$279 \quad u = \sqrt[2]{\frac{3k_B\theta}{m}} \equiv v \quad (34c)$$

280 Equation (34c) is very likely because in Eq. (1)  $u = v/n$ . Consequently,  $\frac{v}{n} = \sqrt[3]{\left(\frac{3k_B\theta h}{m^2 n^3 \lambda_{dB}}\right)}$ ; squaring of  
 281 both sides of the equation should eliminate  $n^3$  such that re – the substitution of  $h/\sqrt{3mk_B\theta}$  into the  
 282 resulting equation reproduces the root mean square velocity,  $v$ .

283 The equations, Eq. (27b) and Eq. (28) – the reduced velocity equation – and Eq. (31), the  
 284 comparison of entropic effect were derived to quantify the parameters they stand for. However, there  
 285 are models in the literature [19, 20] that may not yield the same results as applicable to the models in  
 286 this research. Indeed the flow rate of carbon (IV) oxide in volume per hour in particular as reported by  
 287 Brown and Escombe [2] is « the results (Table 1) obtainable from the use of models such as  $C_{mL} =$

288  $\frac{d^3}{3l} \sqrt[2]{\frac{\pi R_0 T}{2M_m}}$  [20] where  $C_{mL}$ ,  $d$ ,  $l$  and  $R_0$  are the conductance through long tube of uniform circular cross

289 section, diameter of the tube's orifice, length of the tube and universal gas constant respectively;  $T$   
 290 and  $M_m$  are the thermodynamic temperatures and molar mass of the gas respectively. The same  
 291 scenario also played out when the results (Table 1), that is the values of the conductance of an

292 aperture whose equation is given as  $C_a = A \cdot \sqrt[2]{\frac{R_0 T}{2\pi M_m}}$  [20] (where  $A$  is the cross-sectional area of

293 aperture) is compared with results from Brown and Escombe [2]. At a glance in Table 1, one sees that  
 294 all parameters determined by different models, the model in this research and model in literature,  
 295 were higher with the longer diameter (or radius) of the aperture. In Table 2, are parameters generated

296 at the earlier part of diffusion or flow of gas through the aperture of the tube. Expectedly the “reduced  
297 velocity” of flow is lower for longer tubes than shorter tubes, but the conductance values were higher  
298 for shorter tubes than for longer tubes. Also, the entropic parameters (Table 1 – 3 ) were higher for  
299 longer pore diameter than for shorter pore diameters for tubes in line with the models, Eq. (31) and  
300 Eq. (33), in this research. One should also consider the fact that flow at the earlier part is around the  
301 thickness of the pore aperture.

302 Table 3 shows the parameters generated at the earlier stage of diffusion through the pore  
303 aperture. The conductance  $C_a$  like the reduced velocity, you, and the entropy,  $\Delta S$  are respectively,  
304 lower and higher with longer diameter than with smaller opening. This scenario is what may be  
305 prevalent in kerosene stove in which there are two perforated open-ended cylinders, the inner and  
306 outer cylinders. The small apertures reduce the random diffusion or more technically the entropy in  
307 gas flow thereby concentrating the air/oxygen around the ignited weak soaked in kerosene. A lot has  
308 been expressed regarding the combustion of kerosene [15 – 16, 18]. However, it is a commonplace  
309 observation that in the absence of perforated cylinders around the combustion chamber or the weak,  
310 high degree of the luminosity of the flame is the case due to the insufficient air supply. But with the  
311 perforated cylinders, massive amount of air in higher concentration leads to complete combustion that  
312 gives bluish flame with much less luminosity.

313 One may recall the fact that this research aims to proffer answer or reason why smaller  
314 apertures allow the faster rate of gas flow per cross-sectional area per unit time. Equation (27b)  
315 seems to explain this observation. In this research the “reduced velocity” at the initial stage of gas flow  
316 is on account of the fact that the long dimension length of the molecule let alone the dB wavelength is  
317  $\ll$  the diameter of the pore in particular which should give room to high degree of random motion while  
318 moving through the tube or pipe. But it must be pointed out that there are ways of gas flow such as  
319 pure molecular diffusion (in this case there is no contact with the walls of the pore), Knudsen +  
320 molecular diffusion (in which there are contacting and non-contacting molecules with the walls of the  
321 pore), pure Knudsen diffusion (in which there is total contact or collision with the wall of the pore), and  
322 diffusion through “tortuous paths” which occurs in compacted solids [19, 20]. A gas molecule will  
323 always deviate from its formerly course, as a consequence of randomness which is reduced  
324 according to Eq. (27) or Eq. (28). The issue arising from these various ways or mechanism is the  
325 negation of one or two of the postulates of the kinetic theory of gases in particular; the fact that gas

326 molecules in the absence of potential chemical gradient or pressure gradient is always in constant  
327 random motion colliding elastically with each other, and the walls of the vessel cannot be overlooked.

328 One may wish to know the significance of Eq. (27b) or Eq. (28) given Eq. (1). Equation (27b)  
329 or Eq. (28) unlike Eq. (1) directly illustrates likely effect of diameter on the rate of diffusion in volume  
330 per unit cross-sectional area per unit time. The question is there any capillary whose diameter is of  
331 the nano-scale length needs to be answered. This may not be impossible if suitable technology to do  
332 so has been contrived similar to suggestion elsewhere [12]. But if in nature, human pulmonary system  
333 for instance where the terminal bronchiole diameter may not be as small as nano-scale length, it  
334 shows that randomness may not be totally eliminated in bio – and non – biophysical process such as  
335 diffusion. As shown in Table 1, there are different values of  $u$  for different values of the diameter of the  
336 pores if it is assumed that the diameter of the pores is equal to  $D_0$ . Indeed the magnitude of  $u$  for the  
337 same gas is inversely proportional to the cube root of  $D_0$  or diameter,  $d$  (which may be  $= n_p \lambda_{dB}$  where  
338  $n_p$  may be number of times the molecules moved in different directions or degree of randomness.).  
339 Thus the values of  $u$  decrease as  $D_0$  or  $d$  increases, while according Eq. (31) The entropy decreases  
340 with decrease in the length of the diameter of the pores (Table 1). Determination of  $u$  values and  
341 entropy implicit in random motion seem not to have any parallel in literature as in this research which  
342 should motivate further research experimentally. But a lot of concern has been expressed in literature  
343 without equations that may quantify the parameter as in this research. According to Marten [5] and  
344 references therein, there are large variety of natural and artificial confined geometries in which the  
345 geometric restriction to the particles' dynamics result in confined diffusion and what is referred to as  
346 entropic barrier. While a typical man-made confined geometry may be the perforated double cylinders of  
347 kerosene stove [18] there are natural confined geometries such as biological cells, membrane ion  
348 channels *etc* [5], the bronchioles in lungs, the stomata in plants *etc*. There is a call for the recognition  
349 of both Brownian motion and entropic effects whenever study of transport of gases at the macro – and  
350 nano – scales through confined geometries is carried out [21] such as stomata, for instance. In gas  
351 phase the reduction of randomness or entropy, promotes higher volume of gas flow per cross-  
352 sectional area of pore per unit time which is more likely with pore of shorter diameter than pore of  
353 longer diameter as shown by the work of Brown and Escombe [2]. The basis of this is illustrated with  
354 Eq. (27b) and Eq. (28) In this research and the entropic values are shown in Table 1 – 3. Initially or at  
355 earliest stage of diffusion the parameter expressed by Eq. (27b) or Eq. (28) are higher (Table 2) than

356 latter values but much less than latter values with respect to entropic values calculated with Eq. (31).  
 357 Several authors (researchers to be specific) after Brown Escombe [2] namely Raschk [22], Wong *et al*  
 358 [23], McElwain and Chaloner [24], Hetherington and Woodward [25], Franks and Beerling [26],  
 359 MacElwain *et al* [27] cited by Elliott – Kingston *et al* [28] confirms the effect of smaller stomata and  
 360 consequently small apertures in general. Smaller stomata have > surface area to volume ratio than  
 361 larger stomata [28]. Before proceeding further, it is necessary to state that this research is not about  
 362 plant physiology; rather stoma is a good example that exemplifies the effect of the diameter of  
 363 apertures.

364 It is relevant to point out that within mass movement of molecules, a single molecule  
 365 translational motion is the focus of model formulation; this is no longer strange as unique – particle  
 366 tracking method with hi-tech instrumentation are used for the study of microscopic behaviour and  
 367 interactions of individual molecules, tiny objects in soft matter or biological environment [10].

### 368 5. CONCLUSION

369 The equations that explain the effect of different diameters of conduit pipes which may be  
 370 natural or non – biological were derived. The reduced velocity is inversely proportional to the cube  
 371 root of the width of the pore. The entropic value arising from the effect of diameter is directly  
 372 proportional to a natural logarithm of the square of half of the diameter. If the diameter of the pore is  
 373 equal to the dB wavelength, the gas molecule may continue its motion at root mean square velocity.

374 **Table 1. Entropic parameters, the conductance of aperture and long cylindrical tube from**  
 375 **theoretical and experimental approaches.**

$\Delta S = R \ln \left( \frac{\pi r^2}{R_v} \sqrt{\frac{3k_B \theta}{m}} \right)$ (J/mol.K)(in this research and [2])	$C_a = A \cdot \sqrt{\frac{R_0 T}{2\pi M_m}}$ for aperture (Theoretical) Exp (-3) (m <sup>3</sup> /s)[20]	B & E $C_a$ for aperture (Experimental) Exp (-11) (m <sup>3</sup> /s) [2]	$C_{mL} = \frac{d^3}{3l} \sqrt{\frac{\pi R_0 T}{2M_m}}$ for long tube (Theoretical) Exp (-3)(m <sup>3</sup> /s) [20]	B & E $C_{mL}$ for long tube (Experimental result) Exp (-11) (m <sup>3</sup> /s) [2]
179.90	36.69	6.39	11.41	1.325
176.93	17.94	2.58	2.74	0.35

108.07	17.94	2.83	11.41	1.158
101.10	4.23	1.54	9.70	1.079
100.60	4.48	1.74	10.05	1.121
162.06	1.29	1.11	4.98	0.636
142.86	1.21	1.10	4.69	0.569

376  $C_a$  is the Conductance of aperture;  $C_{ml}$  is the conductance of long tube. B&E is Brown & Escombe  
377 result from experiment;  $R_0$ ,  $\Delta S$ ,  $r$ ,  $R_v$  (from reference number 2) and  $k_B$  are the gas constant, entropy,  
378 radius of pore, rate of flow of gas in volume per unit time, and Boltzmann constant;  $A$ ,  $M_m$ ,  $\theta$  (in this  
379 research),  $T$  (in literature) are area of pore, molar mass of the gas and thermodynamic temperature  
380 respectively;  $d$  and  $l$  are the diameter and length of tube or duct.  
381

382 **Table 2. Entropic parameter, reduced velocity, and conductance of aperture of a long tube.**

Earlier entropy, $\Delta S = R \ln \left( \left( \sqrt[6]{3mk_B\theta} \right) \cdot \sqrt[3]{\frac{d_{ia}}{h}} \right)$ for a long tube in this research and [2] (J/mol.K)	$L = \sqrt[3]{\pi r^2 l}$ (m)[2]	Earlier B & E Theoretical $u$ for a long tube in this research and [2] (m/s)	Earlier B & E Theoretical $C_a =$ $\pi r^2 u$ for a tube in this research and [2] (exp (-5) $m^3$ )
57.50	0.0424	0.3211	13.5794
"	0.0682	0.2741	13.4465
"	0.0424	0.3211	13.5794
57.45	0.0435	0.3184	13.0049
57.47	0.0436	0.3182	13.2258
57.39	0.0538	0.2966	11.5890
57.35	0.0522	0.2996	11.3934

383  $C_a = \pi r^2 u = \pi r^2 \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}}$ ;  $u = \sqrt[3]{\frac{3k_B\theta h}{m^2 D_0}}$ ; Earlier B&E theoretical  $u$  means the reduced velocity and other  
384 lower parameters at the earlier stage of diffusion through the long tube. Here,  $D_0$  is taken as  $L$ . The  
385 same is applicable to entropy.  $\Delta S$ ;  $C_a$ ,  $r$ ,  $l$ , and  $d_a$  (which is in literature [2]) are the entropy,  
386 conductance of aperture of a long tube, radius of aperture, length of tube, and diameter of tube;  $m$ ,  $R$ ,  
387  $k_B$ ,  $h$ , and  $\theta$  are mass of the molecule, gas constant, Boltzmann constant, Planck's constant and  
388 thermodynamic temperature. Some parameters are theoretically determined in this research.  
389

390 **Table 3. The earlier entropic parameter, reduced velocity, and conductance of aperture.**

Earlier entropy, $\Delta S = R \ln \left( \left( \sqrt[6]{3mk_B\theta} \right) \cdot \sqrt[3]{\frac{d_{ia}}{h}} \right)$ for aperture in this research and [2] (J/mol.K)	Diameter [2] (mm)	Earlier B & E theoretical $u$ for aperture in this research and [2]. (m/s)	Earlier B & E theoretical $C_a =$ $\pi r^2 u$ in this research and [2] for aperture exp (- 4) $m^3/s$
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~60.05	22.7	0.440	1.78
58.21	12.06	0.543	0.62
"	"	"	"
56.10	5.86	0.691	0.19
56.18	6.03	0.684	0.20
54.31	3.233	0.842	0.07
54.34	3.216	0.844	~ 0.69

392

393  $C_a = \pi r^2 u = \pi r^2 \sqrt{\frac{3k_B \theta h}{m^2 D_0}}$ ;  $u = \sqrt[3]{\frac{3k_B \theta h}{m^2 D_0}}$ ; Earlier B&E theoretical you mean the reduced velocity and other  
394 lower parameters at the earlier stage of diffusion through the aperture. Here,  $D_0$  is taken as the  
395 diameter shown in Table 3. The same applies to entropy.  $\Delta S$ ;  $C_a$ ,  $r$ ,  $l$ , and  $d_{ia}$  are the entropy,  
396 conductance of aperture of a long tube, the radius of opening, and diameter of opening;  $m$ ,  $R$ ,  $k_B$ ,  $h$ ,  
397 and  $\theta$  are mass of the molecule, gas constant, Boltzmann constant, Planck's constant and  
398 thermodynamic temperature. All parameters are theoretically determined in this research.

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400

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