Previous studies of bombardier beetles have shown that some species have a continuous discharge while others exhibit a pulsed discharge. Here, a mathematical model of the defence mechanism of the bombardier beetle is developed and the hypothesis that almost all bombardiers’ defences have some sort of cyclic behaviour at frequencies much higher than previously thought is put forward. The observation of pulses arises from secondary lower frequency cycles that appear for some parameter values. For realistic parameter values, the model can exhibit all the characteristics seen in the various species of bombardier. The possibility that all bombardiers have the same underlying defence mechanism gives weight to the theory that all bombardiers’ explosive secretory mechanisms have diversified from a common ancestral mechanism.

1. Background

Bombardier beetles are ground beetles (Carabidae) whose defence mechanism has earned them a special place in entomology. They spray their attackers with a noxious and often hot spray that is ejected with force from their abdomen, in some cases with great accuracy [1]. There are many species of bombardier from the tribes Brachinini, Crepidogastrini, Metriini, Mystropomini, Paussini and Ozaenini [2], and their collective name derives from the audible pop that often accompanies the ejection [3] (table 1).

A bombardier beetle stores reactant chemical compounds in a reservoir and, when attacked, contracts muscle that forces these reactants into a rigid-walled reaction chamber containing catalytic enzymes. In this chamber, the compound starts to react exothermically, increasing the chamber pressure and ultimately forcing the reactants out of glands in the beetle’s abdomen at temperatures of up to 100°C, in what has been termed an explosive secretory discharge (ESD) [6]. A system of valves stops these reactants from entering the beetle’s greater anatomy. The total ejection lasts for only a fraction of a second but is easily enough to ward off most predators.

The defence mechanism of the bombardier beetle has fascinated entomologists for close to two centuries since they were first discovered by the naturalist J. O. Westwood in 1839. Individuals of the Brachinus genus (species unknown) were amongst the first to be examined [6], and it was found that the reservoir solution contained 10 per cent hydroquinone and 25 per cent hydrogen peroxide with heat of reaction of 48.5 kcal per mol hydroquinone [5]. Although the range of chemicals found in the secretions of different bombardiers is remarkably similar, there is a marked difference between species in the proportions of the different constituent parts [7].

While the outlet temperature of the discharge is often quoted as being 100°C (the maximum outlet temperature calculated by Aneshansley et al. [6]), it has also been seen to vary over a considerable range depending on species. For instance, Coniotropis nicaraguensis has an outlet flow with a much lower temperature (average 65°C, maximum observed temperature 81°C) [1]. Similarly, the discharge temperature of some individuals of the tribe Crepidogastrini (Carabidae) is 65°C [2], secretions of Metrius contractus have been measured at 55°C on average [8] and Mystropomus regularis has a relatively cold discharge of only 34–47°C [9]. The duration of the ESD varies across studies but in general the
### Table 1. Variables and parameters.

<table>
<thead>
<tr>
<th>independent variables</th>
<th>time</th>
<th>s</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>dependent variables</th>
<th>volumetric flow rate of substance in and out</th>
<th>m³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>specific enthalpy of oxygen and water vapour</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>enthalpy of the chamber wall</td>
<td>J</td>
</tr>
<tr>
<td></td>
<td>enthalpy of the components inside the reaction chamber</td>
<td>J</td>
</tr>
<tr>
<td></td>
<td>quantity of benzoquinone in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of hydrogen peroxide in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of hydroquinone in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of oxygen in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of water in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of liquid water in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>quantity of water vapour in the reaction chamber</td>
<td>mol</td>
</tr>
<tr>
<td></td>
<td>chamber pressure</td>
<td>Pa</td>
</tr>
<tr>
<td></td>
<td>partial pressures of oxygen and water in the gas phase</td>
<td>Pa</td>
</tr>
<tr>
<td></td>
<td>rate of energy flow into and out of the chamber</td>
<td>J s⁻¹</td>
</tr>
<tr>
<td></td>
<td>reaction rates 1 and 2</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>temperature of the chamber contents and chamber wall</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>saturation temperature of water at chamber pressure</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>outlet velocity</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td></td>
<td>volume of benzoquinone in the chamber</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>volume of hydrogen peroxide in the chamber</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>volume of hydroquinone in the chamber</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>volume of gas and liquid in the chamber</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>volume of liquid water in the chamber</td>
<td>m³</td>
</tr>
<tr>
<td></td>
<td>molar volume of gas, inlet mixture, mixture</td>
<td>m³ mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of benzoquinone exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of hydrogen peroxide entering chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of hydrogen peroxide exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of hydroquinone entering chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of hydroquinone exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of oxygen exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of water entering chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of liquid water exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>molar flow rate of water vapour exiting chamber</td>
<td>mol s⁻¹</td>
</tr>
<tr>
<td></td>
<td>mole fraction of benzoquinone in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mole fraction of hydrogen peroxide in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mole fraction of hydroquinone in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mole fraction of oxygen in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mole fraction of liquid water in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mole fraction of water vapour in the chamber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mixture density</td>
<td>kg m⁻³</td>
</tr>
<tr>
<td></td>
<td>inlet flow constriction factor</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>adjustable model parameters</th>
<th>Arrhenius factor for reaction 1 and 2</th>
<th>5 × 10⁶ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>chamber internal surface area = πD²</td>
<td>m²</td>
</tr>
</tbody>
</table>
discharge has either finished (in the case of jet discharges) or peaked (for secretory/mist discharges) after 30 ms [2,6,10].

Additionally, the manner in which beetles discharge varies between species. Many species, e.g. those of the genus Brachinus and Stenaptus insignus, eject their discharge as a spray or jet which can often be aimed with very high accuracy [11]. Other species, e.g. M. contractus, have a more diffuse, mist-like secretion and in some cases also produce a froth that can build-up on the individual’s body. Of particular interest is the outlet flow of S. insignus, which is not continuous but pulsed [10]. Again, the duration of the entire discharge is short (2.6–24.1 ms), but each discharge contains between 2 and 12 pulses (average 7) at a frequency of between 400 and 800 Hz [10]. The discharge velocities of
this pulsed flow are, in general, an order of magnitude higher than those of non-pulsed flow in other beetles, averaging $12 \text{ m/s}^{-1}$ with a range between 3.25 and $19.5 \text{ m/s}^{-1}$ [10]. Despite the diversity of ESD behaviour, the prevailing literature [1, 2, 12], with only a single exception [13] states that the internal mechanism is remarkably similar between species, consisting of a thin and flexible reservoir and separate rigid-walled reaction chamber. Figure 1 shows schematic of the bombardier gland system.

Although it is clear that the ESD mechanism of the bombardier beetle can be seen in many forms from pulsed jet sprays to frothing mists and at many temperatures, many questions about them remain unanswered. In particular, the evolutionary pathway and the phylectic relationships between the different species and tribes is still unknown. Some [14] believe that bombardiers have a monophyletic lineage (i.e. the mechanism evolved only once) and that the paussoids and brachinoids are sister groups. Others [15] believe the mechanism evolved separately in the two families of paussoids and brachinoids.

Previous modelling work [4] used methods from computational fluid dynamics to build a model of the beetle’s anatomy. This approach neglected the chemistry and injection phase and instead considered a body of water and some method of heating. The model gave accurate answers by including high-resolution spatial variables and allowing the flow and temperature to vary across the reaction chamber. Such success enabled the authors to build a working experimental rig in which water is heated electrically in a combustion chamber approximately 2 cm long and fired up to 4 m with varying spray temperatures and droplet sizes [16]. This spray technology, called μMist, is envisaged to have important applications in fire extinguishers, drug delivery devices such as nebulizers and inhalers, and fuel-injection systems in cars and other vehicles, as well as large environmental advantages. By excluding chemical reactions, the authors were able to show that the discharge velocities seen in bombardiers can be recreated using only flash evaporation.

The model presented here includes the terms necessary to exhibit flash evaporation but also includes terms to describe the chemical reactions within the beetle. This addition allows us to elucidate the dynamics of beetles with lower temperature ejections where flash evaporation is not available. The importance of chemically released oxygen in the mechanism driving the ESD was originally posited by Aneshansley in 1969 [6] and, by including both mechanisms, the model presented here allows comparison between these two potential driving forces.

In this study, we construct a simple, dynamic mathematical model of the beetles’ defence mechanism. The model assumes that the reaction chamber is spatially homogeneous and the dynamics are only time-dependent; this simplification has the advantage of allowing key features such as reaction chemistry to be included. We show that this simplified model can exhibit all the modes of behaviour previously described. On the basis of this model, we put forward the hypothesis that many more individuals than previously thought are undergoing a cyclic flow, but at a very high frequency. The model demonstrates that observed pulses are actually secondary cycles and can also be used to predict which traits of individuals may lead to the different types of observed behaviour.

2. Mathematical model

The defence apparatus is modelled as a non-rigid reservoir and a rigid-walled cylindrical reaction chamber joined by a tube with a zero friction non-return valve, the closing of which is driven by an increase in the chamber pressure. Further details of the beetles’ valve system can be found in McIntosh & Beheshti [16]. The reaction chamber also has an outlet with a sticky valve. An aqueous solution of hydrogen peroxide and hydroquinone is forced under pressure $P_{\text{res}}$ from the reservoir into the reaction chamber, on the walls of which there are catalysts for the decomposition of both. The hydrogen peroxide decomposes and the hydroquinone reacts to form benzoquinone ($C_6H_4O_2$).

\[
\text{H}_2\text{O}_2 \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \quad \text{with rate } R_1 \text{ and heat of reaction } \Delta H_1
\]

\[
C_6\text{H}_6\text{O}_2 \rightarrow C_6\text{H}_4\text{O}_2 + \text{C}_6\text{H}_4\text{O}_2 \quad \text{with rate } R_2
\]

The resultant hydrogen reacts with the oxygen to produce water.

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{(which is likely to be high)}
\]

If, as expected, hydrogen peroxide is more abundant than hydroquinone and reacts at least as fast, then oxygen will be in excess and the second and third reactions can be combined as

\[
C_6\text{H}_4\text{O}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + C_6\text{H}_4\text{O}_2
\]

with rate $R_2$ and heat of reaction $\Delta H_2$.

The combined reaction is

\[
\text{H}_2\text{O}_2 + \nu C_6\text{H}_6\text{O}_2 \rightarrow (1 + \nu) \text{H}_2\text{O} + \frac{1}{2}(1 - \nu)\text{O}_2 + \nu C_6\text{H}_4\text{O}_2
\]

where $\nu$ is the molar ratio of hydroquinone to hydrogen peroxide. Schuldnecht [5] measured the inlet to be 10 per cent hydroquinone and 25 per cent hydrogen peroxide. Assuming this to be by mass, the mole fractions of the feed would be 2.0 per cent hydroquinone, 17 per cent hydrogen peroxide and 81 per cent water. The solubility of hydroquinone in water is 5.9 g 100 ml$^{-1}$ at 15°C (and 7 g 100 ml$^{-1}$ at 25°C) [17], which is lower than the
concentration given, indicating that the solubility is higher in a hydrogen peroxide solution [18].

The reaction generates oxygen as a gas, and the heat from the exothermic reaction can also evaporate some water. Both of these cause a pressure build-up, which, if higher than some critical value, \( P_{\text{open}} \), will open a flexible outlet that acts as a valve and eject a gas/liquid mixture. When the pressure drops to a critical closing value, \( P_{\text{close}} \), the valve closes.

The model uses molar balances for the quantities of hydrogen peroxide (\( N_{\text{hp}} \)), water (\( N_w \)), comprising both liquid (\( N_{wL} \)) and vapour (\( N_{wV} \)) states, oxygen (\( N_{O2} \)), hydroquinone (\( N_{HQ} \)), and benzoquinone (\( N_{BQ} \)) in the reaction chamber (for full symbol details, see table 1).

\[
\frac{dN_{\text{hp}}}{dt} = W_{\text{hp,in}} - W_{\text{hp,out}} - R_1
\]
\[
\frac{dN_w}{dt} = W_{w,in} - W_{w,L,out} - W_{w,V,out} + R_1 + R_2,
\]

where \( N_w = N_{wL} + N_{wV} \).

\[
\frac{dN_{O2}}{dt} = -W_{\text{hp,out}} + \frac{(R_1 - R_2)}{2}
\]
\[
\frac{dN_{HQ}}{dt} = W_{HQ,in} - W_{HQ,out} - R_2
\]
\[
\frac{dN_{BQ}}{dt} = -W_{BQ,out} + R_2
\]

\( W_i \) denotes the flow rate in moles per second, either in or out of the chamber, for constituent \( i \); \( R_1 \) and \( R_2 \) are the rates of the two reactions. Enthalpy balances are used for the reaction chamber contents (\( H_R \), including both reactants and products) and for the reaction chamber wall (\( H_C \))

\[
\frac{dH_R}{dt} = -Q_{\text{out}} - \Delta H_R R_1 - \Delta H_R R_2 - h_A C(T - T_C)
\]
\[
\frac{dH_C}{dt} = h_A C(T - T_C).
\]

The chamber enthalpy is

\[
H_R = (N_{\text{hp}} C_{p,\text{hp}} + N_{HQ} C_{p,\text{HQ}} + N_{BQ} C_{p,\text{BQ}} + N_{wL} C_{p,\text{wl}} + N_{O2} C_{p,O2} + N_{HQ} C_{p,HQ})(T - T_{ref}) + h_{wV} N_{wV}
\]

and the wall enthalpy is

\[
H_C = m_{C} C_{p,C}(T_C - T_{ref}).
\]

This dynamical formulation of mass and enthalpy balances allows the modelling of the system in various states and phase transitions, including full and partial (also known as flash) evaporation and condensation [19].

The volume \( V \) occupied by each of the liquid components in the chamber is expressed in terms of the molar volume, \( \bar{V} \)

\[
V_{\text{hp}} = N_{\text{hp}} \bar{V}_{\text{hp}}, \quad V_{HQ} = N_{HQ} \bar{V}_{HQ}, \quad V_{BQ} = N_{BQ} \bar{V}_{BQ},
\]
\[
V_{wL} = N_{wL} \bar{V}_{wL}.
\]

Hence, the total volume of liquid in the chamber is \( V_L = V_{wL} + V_{\text{hp}} + V_{HQ} + V_{BQ} \), and the total volume of gas is \( V_G = V - V_L \). Provided there is some liquid water in the chamber, the partial pressure of the water can be calculated using Antoine’s equation [20] fitted over the range 20–100°C:

\[
p_{wV} = \exp \left( \frac{23,423 - 3955.6}{T - 40.65} \right);
\]

otherwise, the water vapour follows the ideal gas law,

\[
p_{wV} V_G = N_{wV} RT.
\]

The partial pressure of the released oxygen is

\[
p_{O2} V_G = N_{O2} RT,
\]

and the total pressure in the chamber is

\[
P = p_{wV} + p_{O2}.
\]

The reaction rates are modelled with an Arrhenius term and determined by the quantity of reactant and the temperature.

\[
R_1 = N_{\text{hp}} A_{1} e^{-E_{A1}/RT} \]
\[
R_2 = N_{HQ} A_{2} e^{-E_{A2}/RT}.
\]

The overall volumetric inlet flow rate is governed by a constricted Poiseuille flow

\[
F_{in} = \left( \frac{P_{inclose} - P_{inclose}^0}{P_{inclose}^0 - P} \right) \pi \frac{8L_{\mu in}}{\xi}.
\]

The constriction is provided by the \( \xi \) parameter, which varies between 0 (no inlet flow) and 1 (full flow). It is known that an increase in the chamber pressure will cause a decrease in flow as the inlet tube is constricted [16] and it is assumed that this constriction is the primary cause of the inlet flow decrease (i.e. \( P_{inclose} > P_{inclose}^0 \)) and results in a linear decrease in the flow rate, with full flow at ambient pressure, \( P_0 \), and no flow when a critical pressure, \( P_{inclose}^0 \), is reached.

\[
\xi = \frac{P_{inclose} - P}{P_{inclose}^0 - P_0}.
\]

The individual inlet components have flow rates

\[
W_{\text{hp,in}} = \frac{\phi_{\text{hp,in}} F_{in}}{V_{in}}
\]
\[
W_{HQ,in} = \frac{\phi_{HQ,in} F_{in}}{V_{in}}
\]
\[
W_{w,in} = \frac{(1 - \phi_{\text{hp,in}} - \phi_{HQ,in}) F_{in}}{V_{in}},
\]

and the molar volume of the inlet flow is

\[
V_{in} = V_{wL,x_{wL,in}} + V_{\text{hp}} x_{\text{hp,in}} + V_{HQ} x_{HQ,in} + V_{BQ} x_{BQ,in} + V_G.
\]

When the outlet valve is open, the outlet flow is two-phase liquid and gas; so the volumetric flow rate is determined by Bernoulli’s equation. Assuming that the outlet acts as an orifice with a rounded entrance, this outflow rate is then given by

\[
F_{out} = C_4 \sqrt{\frac{2(P - P_0)}{\rho_{mix} r_{out}^2}}.
\]

The outlet mixture has molar volume

\[
V_{mix} = V_{wL,x_{wL,in}} + V_{\text{hp}} x_{\text{hp,in}} + V_{HQ} x_{HQ,in} + V_{BQ} x_{BQ,in} + V_G;
\]

and density

\[
\rho_{mix} = \frac{\sum x_i M_i}{V_{mix}},
\]

where \( x_i \) is the molar fraction of component \( i \),

\[
x_i = \frac{N_i}{\sum N_i},
\]

and the molar volume of the gas is

\[
V_G = RT \frac{P}{P}.
\]
The enthalpy of water vapour in the range 20–100°C (when referenced to 20°C) can be described by the following empirical equation [21]:

\[ h_{wV} = M_w \cdot \left( -1.568182(T_{sat} - 273.15)^2 + 1916.348(T_{sat} - 273.15) + 2416597 + 1904(T - T_{sat}) \right). \]

The inlet flow is at ambient reference temperature and hence provides no incoming heat energy. The outlet heat flow is

\[ Q_{out} = (W_{wL,in}C_{p, wL} + W_{hp, out}C_{hp} + W_{HQ, out}C_{HQ} + W_{HQ, out}C_{O2})/(T - T_{ref}) + W_{hv,hv} + W_{O2}h_{O2}. \]

The molar outflow rate of each of the six components (liquid water, water vapour, hydrogen peroxide, hydroquinone, benzoquinone and oxygen) is

\[ W_{i, out} = \frac{x_i F_{out}}{V_{mix}}. \]

The model does not predict the duration of a discharge; rather, the model is run for 30 ms with the reservoir pressure kept constant throughout this time. While, during a real discharge, one would expect the reservoir pressure to rise to some maximum value and then decrease after the conclusion of the attack, the aim of this study was to show the types of solution available under a more simple set of assumptions. Brief explorations of different reservoir pressure time profiles showed that this addition to the model made very little difference to the results shown here. During the model explorations, longer simulations were frequently carried out and where an extended run would significantly change the model’s output, this has been described. Details of all model parameters, values and units can be found in table 1.

The set of stiff, algebraic-differential equations given by the model was solved using the Matlab ode15s function, a variable order solver based on the numerical differentiation formulae and Gear’s method. The system was explored for a wide range of parameter values and initial conditions, and the only behaviour types seen were those given here. The stability of many solutions over a longer time period was also tested. Unless stated otherwise, all parameters for the solution figures are as in table 1. Many of the parameters are known chemical constants and the internal dimensions of the beetle are available for some species (for references, see table 1). For the remaining parameters whose values are not widely known (e.g. reaction rates and activation energies), a range of values were tested and the results are discussed.

3. Results
When solved, the equations above result in a three-phase process illustrated in figure 2. Initially, the pressure is low \(P < P_{inclose}\); so the inlet valve is open and the outlet valve is closed: this is the refilling phase. Reactants enter the chamber, contact the enzyme catalyst contained there and start to heat up. This temperature rise has an associated pressure increase that forces the extremities of the chamber to constrict the inlet pipe. The pipe is completely closed when the pressure reaches \(P_{inclose}\), triggering the second (closed) phase. As the reaction continues, the pressure increases further owing to the release of oxygen from the decomposition of the hydrogen peroxide and to the water vapourizing at the increased temperature. At some point, the pressure is enough to open the outlet valve \(P \geq P_{outopen}\) and the third phase, exhaust, is initiated. The high pressure in the chamber forces the contents out through the outlet pipe and the pressure decreases. Owing to this pressure drop, the inlet valve reopens and the chamber is once more placed in the refilling phase. At the start of the exhaust
phase, the system is under pressure and the temperature may be above 100°C. If this is the case, then the opening of the outlet valve and resultant pressure drop may cause a significant increase in the steam quality of the water vapour in the chamber owing to partial or flash evaporation. The speed of the partial evaporation event is controlled by the size of the outlet [4].

In all cases, the system was tested for a range of inlet closing pressures and inlet tube radii. Together, these two parameters control the flow of reactant entering the chamber. The other adjustable model parameters were also tested within reasonable ranges both in turn and, wherever possible, in groups. Where adjustment of a parameter or a group of parameters changed the model behaviour significantly, the results have been detailed below. However, in many cases, the behaviour of the system was highly robust to parameter changes and, while it showed some small quantitative changes, there were no qualitative changes. While a parameter space of such high dimension can never be fully explored, we are confident that, qualitatively, the system can show only four different modes of behaviour, which can be described as follows.

3.1. Inert—no reaction

If either the inlet closing pressure or the inlet pipe radius is very small, the fluid enters the chamber so slowly that the heat generated by the reaction is lost to the walls and there is no subsequent build-up of pressure during the first 30 ms. For higher inflow rates, this model is not stable, i.e. if the model were run for a longer time period, the system would move to one of the other possible modes.

3.2. Continuous cycles

In this mode, while the inlet valve is open, enough fuel is entering the chamber to allow the reaction to proceed and the chamber pressure to increase. The system undergoes the three phases outlined above and the cycle repeats, putting the system in a steady oscillating state. While the frequency of the cycles is usually very high (over 1000 Hz), there is a small range of parameter space (low inlet closing pressure and small inlet radius) where these cycles can be observed at a much lower frequency. As with the inert case, there are some regions of parameter space where this behaviour is not stable in the long-term; if the model was run for a longer time period, the continuous cycles may result in pulsed cycles.

3.3. Pulsed cycles

Here, the system initially follows the behaviour seen in the continuous cycles case. However, in this case, the inlet flow rate is low, either due to a narrow inlet tube or small inlet closing pressure. Without the additional cooling effect caused by the incoming fluid at ambient temperature in each cycle, the maximum temperature reached is a little higher and the reaction starts sooner. This causes the inlet valve to stay open for a shorter length of time, allowing less fuel to enter the chamber; so there is less cooling provided by the incoming fluid. At some point, this positive feedback loop results in a lack of fuel entering the chamber and causes the reaction to stop, the chamber temperature and pressure both to drop dramatically, and, consequently, no discharge to be observed for a brief period of time. However, the drop in pressure causes the inlet valve to open, and, slowly, the incoming fuel reacts and the sequence starts again. Ultimately, this results in a series of pulsed cycles. Pulsed cycles generally have a higher maximum temperature than ordinary cycles and the frequency of the pulsing is usually around 200 Hz, with the primary cycles occurring at approximately 2000 Hz. Even in this state, the water in the chamber remains predominantly in a liquid state, with only a small fraction of the available water in the chamber turning to steam. Once the system reaches this state, it appears to be stable indefinitely, provided there is fuel in the reservoir.

3.4. Steady flow

When fuel is entering the chamber sufficiently fast, it is possible for the inlet flow combined with the reaction speed to ‘match’ the outlet flow and thus for the system to reach a steady state with both valves open and a continuous discharge. This fourth phase (not included in figure 2) usually occurs after a small number of cycles when the drop in pressure during the exhaust phase is not enough to close the outlet valve. In this mode, the residence time for the reactants within the chamber is very low and the discharge is predominantly made up of chemicals contained in the reservoir (hydrogen peroxide and hydroquinones), rather than the reaction products (water, oxygen and benzoquinones). This mode is usually much cooler than the cycling mode due to the fuel having a lower residence time in the chamber, giving less time for the reaction to take place and for heat to build-up; typical temperatures are between 20°C and 30°C. The final outlet flow rate is also significantly lower than the maximum seen during cyclic flow.

Figure 3 shows example time series for the four different behaviour modes. All system parameters are held constant (at the values given in table 1, with the inlet closing pressure fixed at 102 kPa), except the inlet radius. One would not expect an individual beetle to be able to vary this parameter; so the variations shown here represent differences between species or genera. As the inlet radius parameter is varied, the system undergoes the four modes of behaviour described above.

— Inert (no reaction) (figure 3a). For an inlet radius smaller than 6 μm, there is not enough inlet flow to sustain a reaction and the chamber temperature does not exceed 30°C.

— Continuous cycles (figure 3b). For an inlet radius between 7 and 11 μm, the chamber starts to undergo slow cycles and the temperature reaches approximately 80°C, with the cycle frequency ranging from 200 to 750 Hz. For many cases in this region, if the model was run for a longer time period, the frequency of these cycles would increase and lead to pulsed cycles.

— Pulsed cycles (figure 3c). For an inlet radius between 12 and 35 μm, the system shows pulsed behaviour, with the cycle frequency now between 900 and 1300 Hz and the pulses occurring much slower at approximately 100 Hz. The temperature is still very high, between 70°C and 80°C.

— Continuous cycles (figure 3d). As the inlet radius is increased further (26–58 μm), the cycles get faster (1400–2000 Hz), though the temperature drops (70–35°C). This behaviour will continue indefinitely.

— Steady flow (figure 3e). Finally, for the largest inlet radii (above 58 μm), the cycles are only transient and lead to cooler (around 30°C) steady outlet flow.

Figure 4 shows the different behavioural modes and the corresponding maximum chamber temperature seen for a range of inlet radii and inlet closing pressures. For larger
pressures, the pulsed flow behaviour is not seen, and for large inlet radii, the cycles simply speed up without showing pulsed behaviour during the first 30 ms of the discharge. The hottest modes are always the pulsed and cyclic modes and the steady flow mode is the coolest (except the mode with no reaction). The greatest total discharge during the first 30 ms is, as expected, always seen for the largest inlet radii and highest inlet closing pressure pressures (up to 80 mg discharge during the first 30 ms of ejection at pressure of 108 kPa and inlet radius 50 µm). However, the greatest outlet rate (of 40 mg s⁻¹) is observed during the cyclic flow (be it pulsed or not); the outlet flow rate during steady flow is approximately an order of magnitude smaller. The maximum rate is governed by the state of the reaction chamber (in particular the pressure) and is thus not dependent on the inlet closing pressure or the inlet radius. The total mass discharged is more strongly dependent on the frequency of the cycles, which is significantly higher for larger pressures (up to 5000 Hz). The mass flow rates seen here are very similar to those seen by the detailed model of Beheshti & McIntosh [4], which used spatial information to convert these rates to outlet velocities of between 2 and 30 ms⁻¹, fitting well with reported observations. Without detailed spatial information, the observed outlet velocity of a discharge is best predicted by the average velocity of the outlet. During cyclic flow, this is approximately 5 ms⁻¹; however, during pulsed flow,
were all decreased by a factor of 0.5. This results in a change increased by a factor of 2, and on the bottom row, they top row, all the beetle's internal length measurements were behavioural modes to the beetles internal measurements: on the

spp. have a reaction chamber with length closer to 0.3 mm with length 0.7 mm [12], whereas the smaller chambers: for example, Crepidogaster spp., which correspond- ing to a wide range of parameter values. As would be expected, increasing the reactivity of the solution (either through the activation energy or the rate constants) results in individuals that are more likely to exhibit cycles and pulses rather than steady flow. Figure 6 shows two examples of beetles with different reactivity. The top row shows an individual with increased reactivity (reaction rates and heat of reaction are increased by 5% and the activation energy is decreased by 5%), which is more likely to show pulsed oscillations and a higher temperature discharge. The bottom row shows an individual with decreased reactivity (reaction rates and heat of reaction are decreased by 5% and the activation energy is increased by the same amount). An individual with this decreased reactivity shows pulsed cycles over a much smaller range of parameters and has a lower temperature discharge.

Overall, extensive explorations of the system show that the occurrence of these different modes for different parameter values is very stable. For example, an individual exerting a lower reservoir pressure or with a differently sized outlet is most likely to be able to show the range of behaviours illustrated here.

3.5. Exploring parameter space

The name bombardier beetle is used to describe many different species of beetle that all display the bombardier ESD mechanism. To explore how different species may display the mechanism, different parameter values were tested. Bombardiers come in many sizes: for example, Crepidogaster spp., which exhibit a cool (63°C) mist-like ejection, have a body length of less than 5 mm [2], and Stenaptus insignis, which exhibit pulsed discharges, are up to 20 mm long [11]. Similar ranges have been seen in SEM images of the beetle glands and reaction chambers: for example, M. contractus, with an external body length of approximately 10 mm, have a reaction chamber with length 0.7 mm [12], whereas the smaller Crepidogaster spp. have a reaction chamber with length closer to 0.3 mm [2]. Figure 5 shows an example of the sensitivity of the different behavioural modes to the beetles internal measurements: on the top row, all the beetle’s internal length measurements were increased by a factor of 2, and on the bottom row, they were all decreased by a factor of 0.5. This results in a change in the reaction chamber volume, the outlet radius and the effective thermal diffusivity in the external heat loss. Larger individuals are more likely to exhibit cycling or pulsed behaviour and will also get hotter. By contrast, the smaller individuals show more steady flow and cooler temperatures.

The chemical make-up of different bombardier species also varies widely. While there is little information available on the range of concentrations of the reactants, the products of the ESD—in particular, 1,4-benzoquinones and n-alkanes—show large variations [7], implying a potentially wide range of reactant concentrations. The chemical reaction parameter values—in particular, the reaction rate and the activation energy—are not known for any individual bombardier species, but the activation energy used here is within the range 30–60 J mol⁻¹ reported for a range of catalysts [22]. However, the results shown here are generic to a wide range of parameter values.

Figure 4. The type of behaviour seen depends on the inlet closing pressure and the dimensions of the inlet tube. (a) The different modes of behaviour for different inlet radii and inlet closing pressures. (b) The corresponding maximum temperature (°C) of the ESD.

it can increase to higher than 15 ms⁻¹ during a pulse. Variations in inlet radius and inlet closing pressure would only be expected between species or genera rather than on different occasions by the same individual. However, an individual may be able to alter other parameters in the model (e.g. reservoir pressure) and hence may be able to exhibit more than one mode of behaviour.

4. Discussion

In summary, the model shows four modes of behaviour, which include two types of oscillations, the individual cycles and the secondary pulse oscillations. The individual cycles predominantly have a very high frequency, usually above 1000 Hz; though it is possible to see slower cycles, these exist only in very small areas of parameter space. The secondary pulse oscillations are at a much lower frequency, with up to 10 pulses seen in the 30 ms of the simulation.

We hypothesize that the pulses exhibited by the model are the same as those seen in S. insignis [10], which were approximately every 1.4 ms, with roughly seven pulses seen over 12 ms. Figure 7 (top panel) shows an example of part of a pulsed solution overlaid on to the results of Dean et al. [10]. This study directed the beetles discharge onto a piezoelectric crystal and recorded the electric output. In this data, the pulse oscillations can be seen very clearly, but there are also faster oscillations within the pulses that are an excellent match with the fast oscillations seen in the model. Figure 7 shows a good agreement both qualitatively in the shape of the solutions and quantitatively in the frequency of the secondary low frequency pulses and primary high-frequency oscillations within a pulse between the data.
and the model. This simulation uses parameter values as used earlier with a slight increase (4%) in reactivity. We believe that the primary, very high frequency cycles will be exhibited by most beetles that have some form of jet spray. However, these very fast oscillations will usually be undetectable and only individuals that undergo the secondary pulses will be reported as having an oscillatory discharge.

Bombardier beetles are strongly associated with very high temperature discharges of 100°C. However, reports of these extreme temperatures all stem from a single study on Brachinus spp. [6]. Measuring the temperature of such a small outlet flow is not an insignificant task and usually involves back-calculations from previous calibrations of known temperature emissions [6], this could easily lead to over or under estimations of the true discharge temperature. Despite this limitation, studies have recorded a wide range of mean temperatures, all significantly lower than the original 100°C: for instance, M. contractus ejects its secretion at 55°C [12], G. nicaraguensis at 55°C [1], Crepidogastrine atrata at 65°C [2] and M. regularis at 35°C and 47°C [9]. This variability supports the model, which shows that only a very small range of beetle physiologies are able to produce very high temperature discharges and that lower temperatures are much more common. Figures 3–6 show a wide range of temperature discharges (the maximum temperature of the pulse in figure 3 is over 80°C). In addition to this, figure 8 shows a pulsed time-series that reaches the very high temperatures seen in the original work of Aneshansley. These very high temperatures can also been in cyclic flow for higher inlet closing pressures.

The model also predicts that the highest temperature discharges are most likely to be seen in individuals with pulsed flow. This hypothesis is supported by the results of Eisner et al. [2], which showed pulsed oscillations from a species thought to be Brachinus elongatus, the genus that was originally shown by Aneshansley et al. [6] to have a consistently high discharge temperature across individuals of different species. Eisner et al. [2] mention unpublished recordings of G. nicaraguensis, a beetle with a lower discharge temperature of 65°C [1], which failed to show pulsing, and reports no pulsing in the discharge of C. atrata, which also has a lower discharge temperature of 65°C, again supporting the model predictions. This hypothesis could be tested further by examining the temperature of the discharge of S. insignus, which the model predicts would be high.

A final characteristic of the bombardier beetle is the large throw ratio achieved by the ESD. A high throw ratio (the ratio of the distance travelled by the discharge and the size of the combustion chamber) is achieved by having a high mass outflow rate through a very small outlet radius. The mass outflow rates predicted by this model are of the same order (up to $4 \times 10^{-5}$ kg s$^{-1}$) as those predicted by the more detailed spatial models of Beheshi & McIntosh [4]. While the present model does not predict throw ratio, it would be expected to be of the same magnitude as that obtained by Beheshi and McIntosh because the mass outlet flow rate and the outlet radii are similar. The difference between the two models lies in the mechanism providing the force behind the two rates. Previous models have not.
included the beetle’s chemical reactions, so have concluded that the force could be provided by the chamber temperature rising above 100°C and the resulting partial evaporation of steam as the outlet valve opens and the pressure and temperature quickly fall. The present model shows that similar ejections can be achieved without the chamber temperature rising above the atmospheric boiling point of water and that the build-up of pressure needed is due mainly to released oxygen.

To summarize, the model predicts that the same underlying mechanism can result in a range of different behaviours; all the observations seen in the wide range of bombardier species can be exhibited by the model for different parameter values. Both the pulsed and continuous ejection modes that have been observed can be seen in the model for a wide range of parameter values that are consistent with the known information of individual beetles. The observed temperatures of the different beetle discharges have also

Figure 6. Insects with more reactive chemistry are more likely to show pulsed oscillations. (a,b) The results for an individual with more reactive chemistry (increased by 5%): (a) the region of parameter space exhibiting pulsed behaviour is larger, as is the region showing cycles, and (b) the individual is also more likely to have high temperature ejections. (c,d) The results for an individual with a less reactive mixture (reduced by 5%), which is more likely to exhibit behaviour in the low temperature, steady flow regime. The cyclic behaviour is also at a lower temperature.

Figure 7. A comparison of the model results with published observation data. (Top panel) The underlying time series (grey, large dots) is the original data of Dean et al. [10] (reproduced with permission). The black lines are from a model simulation \( V_R = 15 \mu \text{m}, P_{\text{close}} = 102.5 \text{kPa}, \) reactivity increased by 4%, all other parameters as in table 1). Note that the vertical axis for the observed data is the electric output for a piezoelectric crystal, while the model shows the outlet mass flow rate: the units for these quantities are not comparable in absolute terms, but one would expect them to have a similar relative size. The scaling of the horizontal axis is the same for both time series but the relative position is not fixed.
Figure 8. The bombardier first became of interest to entomologists owing to its high temperature discharge. The model also shows solutions that reach these high (in this case over 9° C) temperatures. In this case ($t_m = 10 \mu m, P_{end} = 101.3 kPa$, reactivity increased by 4%, all other parameters as in table 1), the water in the chamber is sometimes (over 60%) vapour rather than liquid.

been recreated. We believe the ability of wide-ranging behaviours to be described by a single underlying system adds weight to the theory that different bombardiers’ ESD mechanisms could have evolved from a single common mechanism.

References