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Life at low Reynolds Number Re-visited: The apparent activation energy of viscous flow in sea water

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A B S T R A C T

In a 1976 lecture entitled "Life at low Reynolds Number," Edward Purcell examined constraints on mobility of small aquatic animals defining the energetic challenge as "to move far enough to beat diffusion." We show that the essential requirement is the need to do sufficient work to overcome the activation energy of viscous flow. Raman spectroscopy shows that sea water is dominated (78–85%) by the hydrogen bonded forms, primarily as the large $(H_2O)_5$ tetrahedral pentamer form. Two hydrogen bonds must be broken to disrupt this structure. The strength of the hydrogen bond in water is ~8.4 kJ/mol and the experimentally determined activation energy of viscous flow (~16.7 kJ/mol) is approximately equal to that required to break two hydrogen bonds in water. For viscous flow to occur a molecular vacancy must form for a flowing molecule to move into; the smaller the vacancy needed the less energy required. The heat created by a small animal swimming breaks hydrogen bonds thus forming a layer of small non-hydrogen bonded H_2O molecules around the animal. These "lubricate" the surface yielding far more efficient viscous flow. The activation energy of the viscous flow of water decreases with pressure most likely due to the weaker strength of the hydrogen bond under pressure – lab and field data support this observation. The dissipation of tidal energy as heat, often attributed to "intermolecular forces," is directly related to the breaking of hydrogen bonds.

1. Introduction

In June 1976 Edward Purcell presented a widely celebrated and entertaining lecture entitled "Life at low Reynolds Number" on the challenges faced by small animals and microbes in propelling themselves through what for them is the viscous medium of water. The lecture was so much in demand that it was later published as Purcell (1977) and it has been widely cited. Ingeniously illustrated by hand-drawn sketches the lecture drew attention to the various organism propulsion types that are essentially tied to the local physics of the fluid: bent legs, rotating flagella, the motions of cilia, and the forces they must create to propel the organism. Purcell (1977) described the energetic challenge for an organism swimming at very low Reynolds number as "to move far enough to outrun diffusion … if you don't swim that far you haven't gone anywhere."

An aquatic animal exists within the molecular structure of water but no hint of this appears in the account by Purcell; here water is simply assumed to be a continuum. This is unfortunate for fundamental publications describing the essential hydrogen bonded structure of water

and the dominant molecular species present had been published some 10 years earlier (Walrafen, 1964, 1967) and as we will see these water species play a key but little understood role in determining viscosity and in enabling efficient animal mobility.

A reader of Purcell's paper would be forgiven for seeing here a description of the life of small organisms in the deep sea. But similar to the absence of a discussion of the molecular structure of water, there is no reference to the ocean at all; no temperature was specified, there are no temperature or pressure gradients, and no salts. Over the last 40+ years there has been a great deal of progress in understanding the molecular machinery of flagellae (Kojima and Blair, 2004; Lauga and Goldstein, 2012) and in gaining the ability to observe with high resolution the exact motions of small marine species (Gemmell et al., 2013) and to image the flow fields they create (Malkiel et al., 2003).

Meanwhile, little progress has been made in the relationship of these motions to the physical structure of water, and that is the focus of this paper. Purcell noted in an aside that "the reason viscosity changes is that it's got one of these activation energy things" and he declined to pursue the problem further. One can see why for the problem of the structure of

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water and sea water and the molecular basis for the activation energy of viscous flow in water has proved elusive for over 50 years. It should be understood that the term "activation energy" as applied to viscous flow has a fundamentally different meaning than the Arrhenius activation energy derived from collision theory, or the Gibbs activation energy related to the formation of an activated complex; both these forms have a critical role to play in ocean science (Brewer and Peltzer, 2017). But here the term refers to the energy required to create a molecular vacancy in a flowing fluid that an adjacent molecule can move into (Eyring, 1936; Tabor, 1991).

The standard description is that liquid viscosity arises from intermolecular forces and the ability of thermal fluctuations to combine with the applied shear to produce flow. On applying pressure the viscosity and the activation energy of viscous flow increase since the molecules are pushed closer together and more work must be done to create a vacancy in the flow. The challenge here is that water does not simply follow these rules.

We must provide a note of caution as to why Purcell was so wise to be wary of tackling this challenge. It is widely noted that the Eyring model and its descendants "are most suitable for unassociated molecules with van der Waals attractions between the molecules. Highly polar molecules do not fit so well" (Tabor, 1991). This is due to the fact that polar molecules have a strong tendency to self-associate into larger structures, and water is a prime example of this (Brewer et al., 2019). Thus the need to create a molecular vacancy to permit efficient viscous flow is intimately related to the work done to dissociate the larger water molecular structures into smaller single H_2O molecules and this will become the dominant term.

Water is essentially a bi-molecular fluid with the single H_2O species, and the complex of hydrogen bonded $(H_2O)n$ species, existing in a temperature dependent equilibrium state. Thus the molecular weight distribution will be strongly bi-modal (Brewer and Peltzer, 2019). For this reason we use here the term "apparent activation energy" to distinguish the observed effect from that of a simple liquid.

Early work by Walrafen (1964, 1967) made use of Raman spectroscopy to identify the structures by which the polar H_2O molecules could achieve their minimum energy configuration and he determined this to be the tetrahedral pentamer form. A copy of the original depiction (Walrafen, 1964) is shown here in Fig. 1. Essentially all published work since that time has recognized this form as the dominant species in water (Guardia et al., 2015) and it is widely known as the "Walrafen pentamer."

The molecular structure of water has been the subject of intense study for over 50 years: Brewer et al., 2019 report that a web search for "scholarly articles on the structure of water" yields some 19 million hits. But few to none of these articles refer to sea water and the state of the oceans. With the development of highly stable sea going Raman spectrometers (Brewer et al., 2004; Zhang et al., 2012) it became possible to examine ocean processes. Today careful laboratory and field quantitative analyses of the principal molecular species present as a function of temperature are available (Brewer et al., 2019).

Viscosity is highly temperature dependent and some better knowledge of the basis for this could be helpful for predicting the consequences of ocean warming on marine life. Viscosity is well known as a key factor in the energetics of marine species (Fuiman and Batty, 1997) and a warmer ocean may be expected to reduce the energy demands of swimming.

Purcell derived the energetic requirements for propulsion solely from estimates of the viscous drag. The work drew much attention, but when direct experimental manipulations of viscosity were investigated the picture that emerged was more complex. For example Gemmell et al. (2013) carried out elegant studies of the escape strategies of a small copepod where viscosity was varied independently of temperature by addition of methylcellulose. Their finding was that "copepod nauplii have natural adaptive mechanisms to compensate for viscosity variations with temperature but not in situations in which viscosity varies
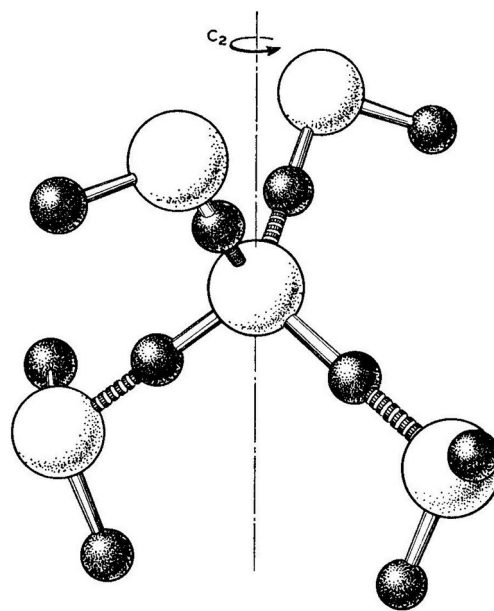

Fig. 1. The original depiction of the tetrahedral pentamer water molecule as determined by Walrafen (1964). This species is the most abundant form of the hydrogen bonded water molecules which comprise some 78–85% of the mass of the oceans (Brewer et al., 2019). It exists in thermal equilibrium with the far smaller population of single H_2O molecules and a collection of very short lived intermediate species (dimers, trimers etc.) This pentamer is unique in that two hydrogen bonds must be broken to break apart the molecule; breakage of only a single hydrogen bond can disrupt the other species.

independent of temperature." Their conclusion was that this was regulated by the temperature dependence of the swimming appendage muscle groups.

Put bluntly if water is made less viscous by adding methylcellulose, thereby changing the molecular structure of the fluid, it is harder for animals to swim. The implication for this analysis is that it would be wise to investigate the molecular basis for propulsion in water as well as for viscous drag for many of the same principles based upon the temperature and pressure dependent structures of water apply.

In this paper we review what is known of the viscosity of sea water and the estimates of the activation energy of viscous flow. We relate these to recent advances in determining the molecular structure of water (Brewer et al., 2019) with the aim of improved knowledge of the energetic requirements for motion of small deep sea animals in a warming ocean. The vast majority of deep-sea animals operate within the low Reynolds number regime and thus the problem has wide generality. When animals do work to swim they inevitably produce heat, and the production of heat will break hydrogen bonds. The interplay of these forces lies at the heart of the problem.

The challenge here is to probe the chemical physics of the regime where the macroscopic rules of fluid dynamics no longer apply, and molecular processes dominate. It will not be possible to provide exact solutions and this paper is very much in the spirit of inquiry of the original publication where approximations must be made and challenges identified, for as Purcell wisely noted "the viscosity of a liquid is a very tough nut to crack."

In order to propel themselves animals must overcome an energy barrier, defined by the activation energy of viscous flow. The problem has two interlocking parts: the mechanism by which the swimming appendage of the animal can generate thrust by pushing against the molecular structure of water, and the mechanism by which viscous flow–the motion of one layer relative to another over the surface of the animal–can occur.

There is a vast literature in the physical sciences on the molecular

properties of water: but very little attention has been paid as to how this might apply to the oceans, the largest body of water on Earth. The challenge here is to extract those parts that are applicable, and to examine how they might contribute to better understanding of ocean processes and life in the sea. The problem has wide applicability for viscous flow – the Newtonian process of one layer of a fluid sliding by another – at all scales is a ubiquitous feature of fluid flow in the ocean.

The earliest ideas on the properties of matter as indivisible particles ($\alpha\tau o\mu o\varsigma$) differentiated by the position and arrangement of the voids ($\kappa\varepsilon\nu o\nu$) are generally attributed to the ancient Greek Democritus (*c.* 460–370 BC). The property of viscosity is highly dependent on the size of the molecular structures, and the ability of animals to swim depends also on size of the voids/spaces between them. In tackling this problem we need to juxtapose the analysis of two independent forces: the role played by the force of the hydrogen bond in water that determines the size of the structures, and that of the coulombic forces that control the spacing between molecules.

2. Background

The dimensionless Reynolds number R_e (Reynolds, 1883) represents the ratio of the inertial forces to the viscous forces within a fluid; for small plankton $R_e < 1$ is typical, and for most zooplankton and microbes R_e is far less. Although the inertial forces can be well described, the "viscous forces" representing the interactions between water molecules are difficult to calculate due to the complex hydrogen-bonded structures of water, yet it is these that determine viscosity and also determine the efficiency of propulsion. This is not an easy problem.

Water is a complex system of different chemical species based on the H_2O unit and existing in temperature- and pressure-dependent equilibrium. All ocean chemists are familiar with the complexities of the CO_2 system where the properties of dissolved CO_2, HCO_3^-, CO_3^{2-}, and a host of metallic ion pairs must be accounted for. The structure of water is far more complex with species such as the simple H_2O molecule co-existing in a rapidly changing temperature-dependent equilibrium with the dominant tetrahedral pentamer and an assemblage of quasi-planar ring molecules: dimers, trimers, pentamers, octamers and decamers (Keutsch and Saykally, 2001; Smith et al., 2005; Kumar et al., 2007) which may associate into far larger structures (Ludwig, 2001).

Recent work with laser Raman spectroscopy (Brewer et al., 2019) has shown that it is possible to measure within ±1% precision the molar quantities of the single H_2O molecule, and the combined hydrogen-bonded forms, in both water and sea water as a function of temperature. The intermolecular forces that determine viscosity arise from attractive forces between these multiple water species. These are not precisely known although very good approximations may now be made (Stillinger and Rahman, 1974).

2.1. Viscosity

It is not within the scope of this paper to offer a comprehensive review of the molecular basis for viscous flow in liquids.

The early theory of Eyring (1936) based on the formation of molecular–sized holes in the liquid into which the adjacent chemical species can flow is a basic departure point and derivations from this are widely used in industrial chemistry. A lucid account is given in the text by Tabor (1991) and we draw on that here. In this theory in order to transpose a molecule (a jump) from one position to another against the attractive forces of neighbors we have to surmount a potential energy barrier E. The rate (f_L) at which this is possible as a result of thermal fluctuations (molecules in a liquid experience librations (hindered rotations) with a frequency of 10^{10}–10^{12} per second) is given by

$$f_L = C \, exp \, (- E \, / \, kT) \tag{1}$$

where C is a frequency term related to the vibrational/librational

frequency of the molecule, E is the potential energy barrier, k is Boltzman's constant and T is temperature in Kelvins. From the above it should be understood that any one molecule, such as the dominant pentamer, has only a fleeting existence and is best considered as a time-averaged assemblage.

When shear stress is applied the potential energy curve is distorted and the direction of the jump is facilitated by the direction of the macroscopic flow; there is a formulation for this process. The energy barrier—the activation energy of viscous flow—may be regarded as the work needed to create a hole in the liquid big enough to receive the transposed molecule. Although this theory has found widespread applicability it is often noted that it "does not work well for polar molecules" strongly suggesting that researchers have found interpretation of viscous flow and the viscosity of water to be challenging.

3. Observations of the viscosity of sea water

3.1. Experimental data

The measured viscosity of water and sea water is well known. Early classic measurements of viscosity of sea water at 1 atm were reported by Miyake and Koizumi (1948), but measurement over the oceanic range of pressure proved far more difficult. The viscosity of water decreases with rising temperature.

The viscosity of water and sea water can be experimentally determined by use of a rolling ball viscometer. This represents a bulk fluid property; parsing this into discrete molecular steps is challenging. If we imagine a solid object moving through water then a force is required to move adjacent layers of the fluid relative to each other and the force (*f*) is directly proportional to viscosity (η), the area (*A*), the velocity difference between layers (*v*), and is inversely proportional to the distance between the layers (*d*). This yields an equation of the form:

$$f = \eta \frac{Av}{d} \tag{2}$$

Liquid viscosities are typically reported as the centipoise (0.01 g cm^{-1} sec^{-1}); the viscosity of pure water at 20 °C is nearly 1 cP.

Measurements of the viscosity of sea water for a range of temperatures have been reported by Horne et al. (1965) and over a range of pressures by Horne and Johnson (1966), and with high precision by Stanley and Batten (1969). The results reported by Stanley and Batten (1969) cover the range from 0 to 30 °C, and the pressure range from atmospheric to 1406 kg/cm^2 (gage pressure, equivalent to 1378.8 bar or ~13,300 m depth, and deeper than the Mariana Trench).

Stanley and Batten (1969) reported their sea water viscosity measurements as relative viscosity. Each set of viscosity measurements made at increasing pressure and constant temperature were normalized to the viscosity of sea water measured at 1 atm (total pressure) and that temperature. Unfortunately, they did not report the absolute viscosity of the samples measured at 1 atm making it difficult to back calculate the absolute dynamic viscosities. Additionally, the fact that each temperature group was normalized to a different viscosity compounds the problem. We chose to use the excellent set of measurements made by Miyake and Koizumi (1948) at 7 temperatures and 11 chlorinities as the 1 atm reference data set. Using their 0 °C viscosities, it was a simple matter to interpolate the viscosity at the appropriate salinity and 1 atm pressure in order to back calculate the dynamic viscosity at the temperatures and pressures used by Stanley and Batten (1969).

In Fig. 2 we show this absolute dynamic viscosity data plotted versus temperature at various pressures (Fig. 2A), and as a series of isothermal lines at different pressures (Fig. 2B). The viscosity of warm water (*T* > 15 °C) increases with increasing pressure, but the viscosity of cold water (*T* ≤ 10 °C) decreases with increasing pressure. However, these effects are small within the realm of oceanic pressures. The viscosity of sea water is higher than that of pure water.
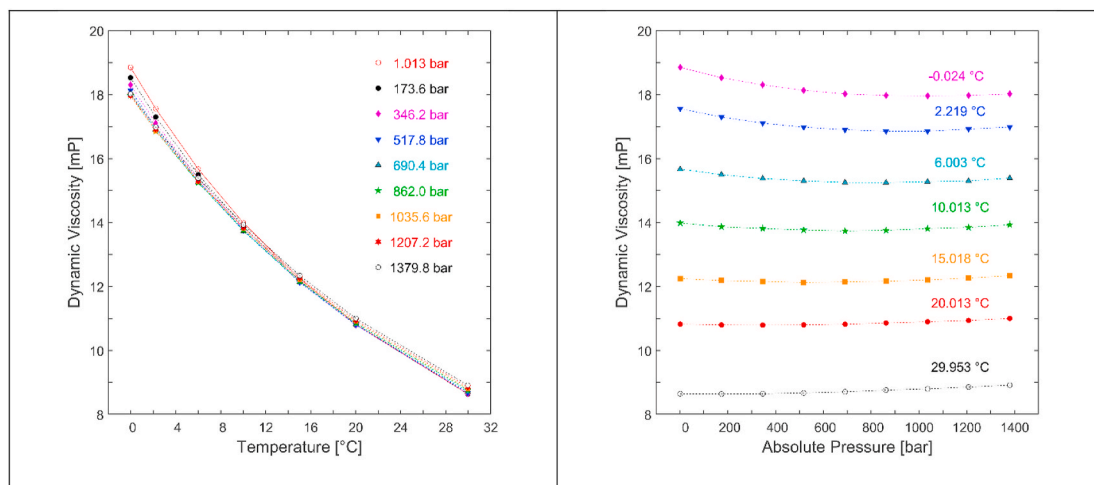
Fig. 2. (A) The dynamic viscosity of sea water as function of temperature at different pressures. (B) The dynamic viscosity of sea water plotted as a series of isothermal lines as a function of pressure. Data are from Stanley and Batten (1969) corrected to absolute dynamic viscosity using the 1 atm viscosity data from Miyake and Koizumi (1948). See the text for a complete description of the data conversion.

3.2. Activation energy of viscous flow

The activation energy of viscous flow is an important property. It represents the mechanical work done in carrying a molecule to the top of the potential energy barrier, after which the molecule gives up its energy as heat. The temperature dependence is normally written out as an "Arrhenius-like" equation of form

$$\eta = A e^{\left(\frac{Ea}{RT}\right)} \qquad (3)$$

And this can be re-written in logarithmic form as

$$ln\eta = lnA + \left(\frac{Ea}{R}\right)\frac{1}{T} \qquad (4)$$

Thus a plot of ln(viscosity) versus the reciprocal absolute temperature should be linear and the slope can be used to determine the activation energy for viscous flow.

It should be noted that although the term "Arrhenius-like" is commonly used this refers only to the basic numerical formulation. There is no derivation from collision theory as in the Arrhenius activation energy, nor from formation of an activated complex as in the Gibbs activation energy widely used for enzymatic systems (Eyring, 1935). Thus the term A in equation (3) is not the equivalent of the pre-exponential factor in the standard Arrhenius equation. Rather, A is simply a conversion factor to yield units of viscosity and not enthalpy or entropy.

In Fig. 3 we re-plot the relative viscosity data from Stanley and Batten (1969), as modified to absolute viscosity using the data from Miyake and Koizumi (1948) as was done previously, in this form. We emphasize the need to regard these calculated properties as "apparent activation energies" to reflect that they are determined within an essentially bi-molecular fluid.

Fig. 4 illustrates one important difference in the concept of the activation energy of viscous flow. The Arrhenius activation energy is a constant for a particular chemical reaction where it accurately represents the activated complex (Eyring, 1935) that forms; the Arrhenius and Eyring activation energy for the microbial decomposition of organic matter in sea water is now well known (Brewer and Peltzer, 2017). But the evidence here shows that the activation energy of viscous flow in water decreases with increasing pressure; no explanation for this phenomenon has yet been given.

Our calculated activation energies (Figs. 3 and 4) are in broad agreement with the values reported by Stanley and Batten (1969). They report that "the activation energies of viscous flow decrease in a uniform
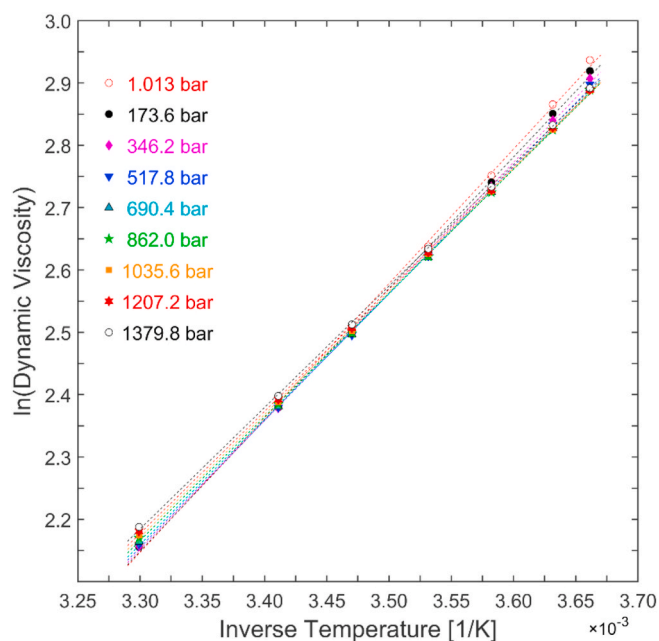

Fig. 3. The dynamic viscosity of sea water as an Arrhenius plot at a series of pressures as required to determine the activation energy of viscous flow. Note the linear form, and also that the activation energy (calculated from the slope of the regression line) decreases as a function of pressure. The calculated activation energies ranged from 3.86 to 4.26 kcal/mol (16.2–17.9 kJ/mol). See Fig. 4A.

manner with increasing pressure and temperature" but provide no details as to how this property was calculated and thus we cannot repeat this work. We do observe here the dependence on pressure but their claim of significant temperature dependence for the activation energy will seem unusual to those familiar with the classic Arrhenius activation energy which must be independent of temperature. Indeed, we find no evidence for such a temperature dependency here with our re-plotting of their data.

3.3. Interpretation of the viscometer experimental data

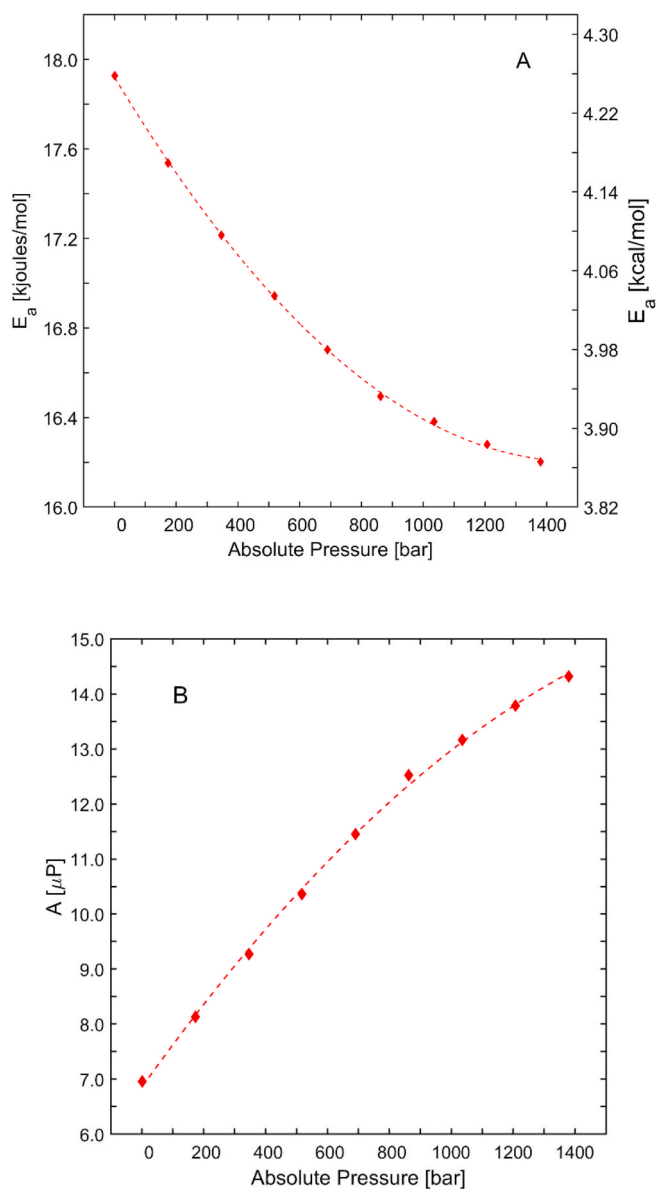We must now examine the physical meaning of the experimental

Fig. 4. A. The change in activation energy of viscous flow of sea water as a function of pressure. The reduction in activation energy with increasing pressure is highly unusual for a liquid and it reflects some of the unique properties of the molecular structure of water and a weakening of the strength of the hydrogen bond under pressure. **B** The change in the A term of equation (3) as a function of pressure. A is calculated from the y-intercept of the isobaric linear regressions (Fig. 3) and is unrelated to the pre-exponential factor of the classic Arrhenius equation.

evidence of the activation energy of viscous flow of water. The range of values reported by Stanley and Batten (1969) is strongly suggestive that the dominant term is the energy required to break two hydrogen bonds—that which is required to break apart the tetrahedral pentamer (Walrafen, 1964). In fact the hydrogen bond has no absolute value and varies to some degree with the local molecular environment. Silverstein et al. (2000) have carefully reviewed many of the estimates of H bond enthalpy and reported a range from 1.5 to 2.9 kcal/mol, with their preferred value being 1.9 kcal/mol. Thus in order to break two bonds the range is 3–5.8 kcal/mol (12.5–24.2 kJ/mol) and the range of values reported in Fig. 4 is well within these bounds. In Appendix 1 of Brewer et al. (2019), we reported a simple and robust estimate of the hydrogen bond enthalpy in water and sea water at 1 atm of 2.624 kcal/mol (10.98 kJ/mol).

The question must be examined as to why it is necessary for a rolling ball – or as implied, a small organism – to break on average two hydrogen bonds and convert the large hydrogen-bonded species into smaller monomer H_2O species in order to create efficient flow over its surface. So far as we are aware there is as yet no description of this available. There is evidence for confusion: Horne et al. (1965) report that "H-bond rupture and *not* vacancy formation is rate determining." We show here that H-bond rupture is necessary for efficient vacancy formation.

In Brewer et al. (2019) we reviewed the status of water structures and noted that: "The hydrogen-bonded tetrahedral pentamer is the only fully three–dimensional structure and it is highly favored as a local energy minimum state (Walrafen, 1964). It is represented by the ~3 times greater length of the hydrogen bond (280 p.m.) versus the covalent O–H bond (96 p.m.). Based upon a very simple spherical approximation the pentamer has approximately 50 times the volume of a single H_2O molecule, and is 10 times larger than the five individual molecules that comprise the pentamer."

This would be a very large structure to accommodate in any "Eyring hole": recall that the formula weight of the pentamer is 90. The ensemble average molecular weight of water in sea water is a function of temperature and ranges from 89.4 to 84.5 (Brewer and Peltzer, 2019). For a specific example of the size of the molecular cavity that must be created to accommodate a Walrafen pentamer we can refer to Wang et al. (2012) who constructed such a host molecule and showed that it could stably contain a water pentamer guest.

What then happens? In our hypothesis as work is done on the liquid by the rolling ball, or the animal propelling itself, heat is generated and at a critical point sufficient work is done to break two hydrogen bonds—and this point occurs well before a hole big enough to accommodate the pentamer is created. Smaller water fragments, primarily the single H_2O form, are created and these can far more easily populate the nascent "Eyring hole" formed by overcoming the weaker intermolecular forces (Section 4.1) and thus allow efficient viscous flow to be created. The breaking of hydrogen bonds therefore forms a safety valve, or path of least resistance, and allows flow to occur over the surface of the animal with minimal effort. Were it not for this the viscous drag would be far greater.

The decrease in activation energy with increase of pressure is highly unusual for in almost all liquids the reverse is true, and this must be related to the hydrogen-bonded nature of water. The simplest explanation would be that the hydrogen bond is weaker at higher pressure and thus less work would be required to break apart the water pentamer. There is experimental evidence for this.

In Brewer et al. (2019), following techniques pioneered by Carey and Korenowski (1998), we reported on a series of heated cell Raman spectroscopy experiments both in the laboratory, and at sea at up to 4000 m depth, to examine the change in sea water enthalpy (ΔH) as a function of pressure as a first order indicator of the strength of the hydrogen bond.

The experiment executed is a "thermal titration" akin to the familiar pH titration, but by replacing the pH electrode with a laser and observing the changing water peaks via Raman spectroscopy. The basic formulation is then (Carey and Korenowski, 1998; Brewer et al., 2017)

$$(H_2O)_{H\text{-bonded}} \leftrightarrow (H_2O)_{free}$$
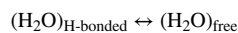
Where $K = [H_2O]_{free}/[H_2O]_{H\text{-bonded}}$, and $d(\ln K)/d(1/T) = -\Delta H/R$.

Although the experimental techniques are challenging these results did show a decrease in the observed enthalpy of the hydrogen bond strength from 2.3 to 1.6 kcal/mol for the pressure change from atmospheric to 400 bars; so the simplest explanation may well be correct.

4. The equal and opposite reaction

4.1. The normal state of water

The counterpart to the drag of viscosity is the need for the swimming appendage of the animal to generate enough force to make progress. In order to understand the molecular basis for the propulsion stroke of swimming it is necessary first to understand the normal state of water for this must provide the essential Newtonian equal and opposite reaction. This is little discussed in the Earth and Ocean sciences so a brief introduction may be useful here.

Any population of molecules is subject to two primary coulombic forces—the short-range attractive force pulling things together, and the even shorter range nuclear force opposing this. This was first described by Lennard-Jones (1924, 1925) through his analysis of the interactions of noble gases and a number of simple crystals. His formulation is the most basic rule of computational chemical physics:

$$V_{LJ} = 4\varepsilon \bullet [(\sigma/r)^{12} - (\sigma/r)^{6}] \tag{5}$$

where V_{LJ} is the Lennard-Jones potential, ε is the energy potential well, σ is the characteristic distance where the attractive force and the repulsive force are equal in magnitude but opposite in direction, and r is the intermolecular distance. The distance (r_m) where V_{LJ} is at a minimum (and equal to $-\varepsilon$) is equal to $2^{1/6} \bullet \sigma$.

In simplest terms, as an atom attached to a molecule makes a close approach to an atom attached to another molecule (for water an oxygen atom approaching another oxygen atom attached to a neighbor molecule) they experience an attractive force akin to the familiar van der Waals forces and these scale as r^{-6}. As the interatomic distance becomes small they begin to experience the opposing Pauli repulsion force (due to the overlapping of electron orbitals) which scales as r^{-12}. The attractive forces serve to hold, in this case, the liquid together. The opposing Pauli repulsion force is that which prevents the liquid from collapsing in on itself.

The net effect is to create a potential energy well—the Lennard-Jones potential—where the difference between the repulsive force and the attractive force is minimized. This is the "normal state" of water.

The critical parameter here is the distance between oxygen atoms, or more correctly the local center of mass of the molecular assemblage; oxygen atoms comprise some 85% of the mass of the oceans. The complexity of water structures does not allow for an exact solution for all attempts quickly run into the realization that it becomes a many body problem. One well-cited estimate (Stillinger and Rahman, 1974) finds the L-J potential minimum for pure water to be located at an inter-atomic distance (r_m) of 3.48 Å with an energy minimum (ε) of 0.316 kJ/mol. There is widespread agreement as to the interatomic distance at which the potential minimum occurs, but somewhat less certainty as to the depth of the potential energy well. For comparison the length of the ~462 kJ/mol covalent O–H bond in a single H_2O molecule is 1 Å, and the strength of a single ~2 Å long hydrogen bond linking H_2O molecules is 8.4 kJ/mol. The Lennard-Jones attractive force is some 26 times weaker than the hydrogen bond.

A generic (not specific to water) representation is given in Fig. 5. The purpose of this illustration is to draw the reader's attention to the marked asymmetry of the curve with the far steeper repulsion term known as the Pauli wall. It is this "resistance to compression" by water that permits thrust to occur.

The original Lennard-Jones model has been expanded upon and improved many times, and a full review is beyond the scope of this paper; but the basic "6–12" formulation remains in all versions. These molecular interactions apply generally throughout the geosciences. For example the same rules apply for the attractive forces between the atmospheric gases, although there the association is slightly looser with the N_2–O_2 potential minimum occurring at about 4 Å (Friedman, 1957).

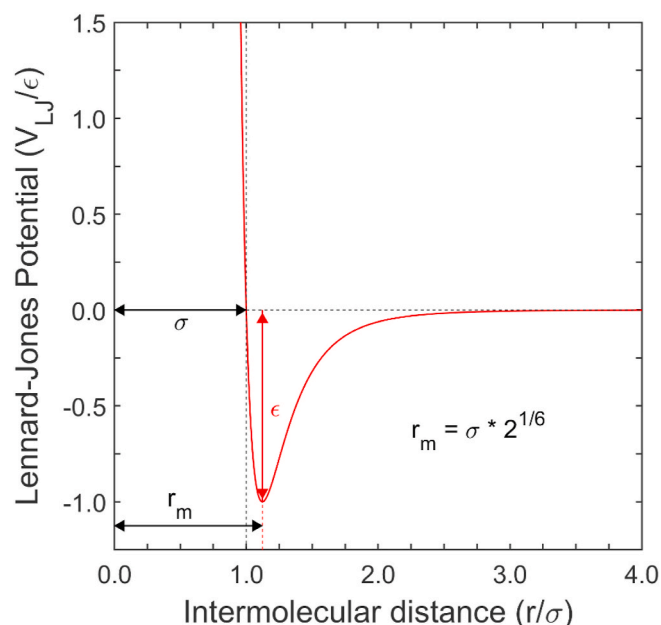Thus the general description of the work done by the rolling

Fig. 5. A general representation of the mathematically simple Lennard-Jones potential that is the basis for a huge set of computational chemistry calculations. The potential energy minimum occurs at the distance (r_m) at which the inter-particle potential is minimized. Both the distance (r_m), and the depth of the well (ε), vary for each molecular species. For water the L-J potential minimum occurs at 3.48 Å with an energy minimum of 0.316 kJ/mol (Stillinger and Rahman, 1974).

ball—and the propulsion stroke of small organisms in swimming—appears to have specific meaning. That is in order to "beat diffusion" enough work must be done by pushing against the Pauli wall to break two hydrogen bonds and break apart the Walrafen pentamer. This appears to be the minimum unit of work—it is difficult to come to any other conclusion.

4.2. Compression

The effect of pressure, whether the miniscule pressure exerted by a swimming appendage or the macroscopic hydrostatic pressure at ocean depth, changes the spaces between molecules. Compressibility equations for water typically contain a large number of coefficients but provide little physical understanding of the process that occurs. Water has a very low compressibility and warmer water—where the population of H-bonded forms is reduced (Brewer et al., 2019)—is less compressible than cold water.

The most direct explanation is that described by Canpolat et al. (1998) in which the "legs" of the Walrafen pentamer (the dominant molecular species in the ocean) are interleaved under pressure—all other water species are far less compressible and this appears to be the primary mechanism by which volume is reduced. A schematic representation of this taken from taken from their paper is shown in Fig. 6.

The work done in maintaining a population of pentamers in the compressed (interleaved) state at depth produces adiabatic heat. Such a process well describes most of the pressure-dependent physical properties of sea water. Paradoxically the heat created by maintaining a population of compressed pentamers breaks hydrogen bonds, producing more single H_2O species and reducing slightly the overall population of hydrogen-bonded forms.

Put simply the lower compressibility of warm water arises from the reduced quantity of pentamer forms present. At pressure a larger fraction of the pentamers are already in the interleaved state and cannot be compressed further. For a simple human analogy consider the difference between the easy interleaving of one's fingers, versus pushing together
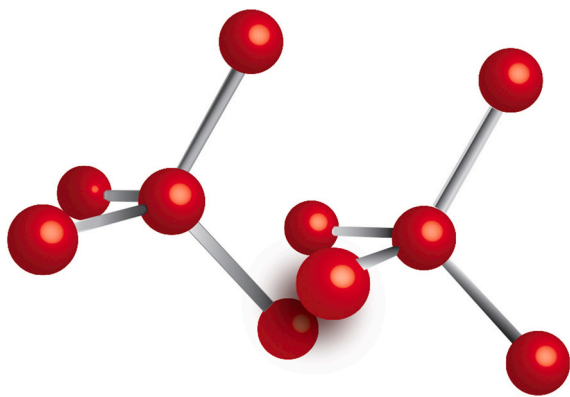
Fig. 6. From Canpolat et al. (1998) showing the manner in which the volume of water is reduced by pressure in driving the interleaving of the "legs" of adjacent pentamers. This is the dominant mechanism whereby the volume of sea water is reduced by increasing pressure in the deep sea.

two closed fists (the incompressible trimer, tetramer, pentamer etc. ring structures).

The net result is that ocean profiles of viscosity show a familiar form with a strong temperature relationship. In Fig. 7 we show a profile calculated for a Pacific Ocean hydrographic station (WOCE P17N Sta 10).

Interest in ocean viscosity was first sparked by Stokes (1845) in his paper on the attenuation of sound. This has long attracted the attention of the ocean acoustics community and the "viscous absorption of sound" is still mentioned today. But it appears to be doubtful that viscosity can be treated as an independent variable. A more correct interpretation is
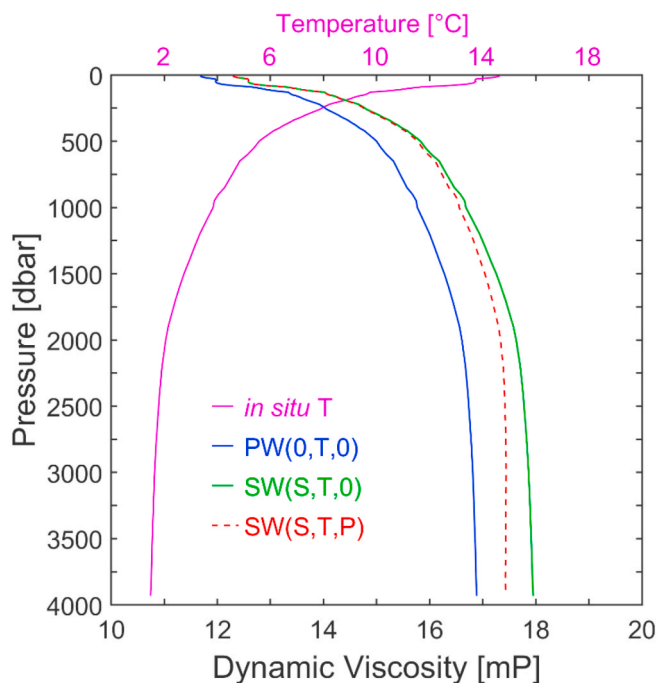

Fig. 7. A hydrographic profile of in situ viscosity (red dotted line) for a Pacific Ocean station (WOCE P17N Sta 10). The data were derived from Stanley and Batten (1969) with adjustments made to the T & S profile data based upon the one atm sea water data of Miyake and Koizumi (1948). Shown also are the equivalent pure water viscosity (blue line) at 1 atm (Miyake and Koizumi, 1948), and the sea water (green line) 1 atm pressure viscosity (Miyake and Koizumi, 1948). The effect of pressure in reducing the viscosity is seen in the difference between the red and green lines. This difference is counter intuitive and is equivalent to that created by a temperature change of about +0.8 °C.

that viscosity and the acoustic properties are both functions of the molecular structure of water. The speed of sound in sea water can be calculated with great accuracy, and with far fewer coefficients, simply by using the classic van 't Hoff-Arrhenius equations (Brewer et al., 2015). The century long influence of Stokes is still felt, and the papers on sea water viscosity by both Horne and colleagues (1965, 1966), and Stanley and Batten (1969), devote significant effort to searching for a possible mid-water minimum in viscosity, most likely as a parallel to the water column sound speed minimum. But this effort proved fruitless and we too can find no evidence for this.

5. Discussion

Translating these specific molecular processes into the general problem of "Life at low Reynolds number" is a challenge. When the swimming appendage of a small marine animal does work it is pushing against millions of water molecules of varying structures. But there are clues and without hypotheses to test we will not make progress. Consider for example a runner running on soft sand; much of the energy of the push off goes unproductively into compressing the sand. A hard track surface is far more efficient: the runner goes faster and further with less effort.

We might regard sea water as a system of mixed "granularity" where in cold water at 1 atm some of the work done by the propulsion stroke must go into unproductive compression of the water. The lower compressibility of warm water combined with the reduced viscous drag with increased temperature all combine to make the work of swimming far easier as temperature rises.

Those who see life in the deepest oceans for the first time are struck by the fact that motions are not sluggish; fish are seen to move easily with a simple flick of the tail. Although the animals are cold, under enormous pressure, and food supply is sparse and erratic they are very well oxygenated due to the interactions of pressure and partial molal volume (Hofmann et al., 2012). Although sea water in the deep ocean is more viscous this is somewhat compensated for by the reduction in the activation energy of viscous flow at depth—most likely due to the weakening of the hydrogen bond under pressure. In overcoming the activation energy barrier the work done in swimming is sufficient to break apart the large water pentamer and thus generate a population of small H_2O molecules that "lubricate" the surface and allow viscous flow to proceed far more easily.

The description of physical processes above can serve as an entry point into the problems first described by Purcell (1977), but not without difficulty. Purcell sketched out the energy requirements for a microbe moving at 0.003 cm/s with an efficiency of propulsion of 1%, and estimated this as 0.5 W/kg, or 0.5 J/s/kg. Microbes weigh far less than 1 kg, and a typical microbial mass is 10^{-12} g or 10^{-15} kg. Thus Purcell's estimate for the energy requirement for a single microbe is ∼0.5 × 10^{-15} J per sec.

There have been many other estimates of the rate at which microbes expend energy while swimming, and it is interesting to compare these. By far the most consistent approach is that based on the remarkable fidelity of the allometric scaling laws which has been shown to extend over a huge range of body sizes. The review by Mitchell (2002) provides a very clear analysis of the energetics and scaling of search strategies in bacteria and an estimate of 10^3 cal/g/km is given. By converting the very different units (10^3 cal g^{-1} km^{-1} x g/10^{12} pg × 1 J/0.2388459 cal × 30 μm/s/10^3 m = 0.125 10^{-15} J/s) we find that this is ∼25% of Purcell's estimate. Not bad considering that 45 years ago Purcell was simply presenting a novel lecture conceived of as a happy tribute to celebrate the career of a close friend.

How might this relate to the energy requirements of breaking the equivalent number of hydrogen bonds? The formula weight of water is 18.0153. Avogadro's number is 6.022 × 10^{23} molecules per mole, and the strength of the H-bond is close to 8.4 J per mol; we calculate 1.4 × 10^{-20} J for a single bond. Since the breaking of ∼2 hydrogen bonds is

required to "beat diffusion" and jump ahead by one molecular step then the minimum unit of energy (we cannot call it a "quantum") is about 2.8×10^{-20} J.

It now appears quite possible to begin to relate the bulk fluid properties and viscous motions of the ocean to more specific molecular processes even though the range of scale is enormous. Dissipation of kinetic energy (conversion to heat) is widely referred to in the ocean science literature but the mechanisms are unspoken. Munk (1966) in his adventurous "Abyssal Recipes" paper estimated "total tidal dissipation" as 24×10^{-6} erg/g/sec. A more recent estimate is that by Egbert and Ray (2000) from satellite altimeter data who find that deep ocean tidal dissipation is "10^{12} W … representing 25–30% of total dissipation"; the deep sea process is described as "bottom friction." At low Reynolds number this friction results in loss of kinetic energy from the liquid flow over the solid surface in a way very little different from the flow of a solid object through the liquid as in a rolling ball viscometer experiment. The same rules must apply.

The mighty tides that in legend even the power of kings cannot oppose eventually meet their match through the Lilliputian army of water molecules, their affinity to one another, and the strength of the hydrogen bond.

It is a puzzle as to why Purcell in 1976 was so shy of any mention of the known literature on the physical properties of water. Walrafen (1964) had published his finding that the tetrahedral pentamer structure was the dominant form 12 years earlier. Stanley and Batten (1969) had published their results on the activation energy of viscous flow some 7 years earlier, thus much of the relevant material was available. However the quantification of the molecular structure of water was still hotly debated and important advances in Raman spectroscopy and in molecular modeling had yet to be made.

Purcell presented his lecture in terms of homage to the remarkable insights of Osborne Reynolds and this cannot be ignored. The analysis stayed firmly within the low Reynolds number regime, as does this review. But the immensely challenging problem of the molecular basis for the spontaneous separation of laminar flow in a fluid as observed by Reynolds at the onset of turbulent flow remains.

6. Conclusions

We have tried to pull together here threads from two very different disciplines. A physical chemist used to modeling the molecular dynamics of a population of water molecules would find the analysis here much abbreviated. But the now huge chemical physics literature on modeling the physical properties of water makes zero reference to the largest body of water on Earth and fails to model the natural world. And while the ocean science literature makes do with a traditional and typically ad hoc approach, this offers no easy way to a better understanding of how kinetic energy is dissipated, or how life in the sea will respond to climate change. A hybrid of these two approaches appears to offer the potential for new knowledge and this was attempted here.

In reviewing this material the importance of better understanding of the activation energy of viscous flow emerges as an important topic. If the analysis we offer is correct then marine life owes much to the existence, and breaking, of the hydrogen bond. Without this weak link, or "safety valve," the work done in creating viscous flow over the animal surface would be much higher and the swimming of small animals far more difficult.

Author contributions

P. G. Brewer, concept and writing. E.T. Peltzer, calculations and figures. K. Lage, literature searches and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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