Gerald H. Pollack

The Fourth Phase of Water

④

Beyond

① Solid
② Liquid
③ Vapor

"The most significant scientific discovery of this century."

"**The most interesting science book I've ever read**. It has shown me that it's still possible to establish something genuinely new in science." *Zhiliang Gong, University of Chicago.*

"**The most significant scientific discovery of this century.** What strikes me above all is the elegant simplicity of [Pollack's] experimental approach. Many of the experiments can be done on the kitchen table, and you don't even need a microscope to see the results." *Mae-Wan Ho, Author, Living Rainbow* H_2O*; Director, Institute of Science and Society, London.*

"**Dr. Pollack is one of the pioneers in this field**, and his discoveries can be expected to have important implications." *Brian Josephson,* ***Nobel Laureate****, Cambridge University.*

"**Fantastic material with revolutionary insights.** What impresses me most is that the experiments are visually instantly accessible." *Helmut Roniger, Consulting physician*

"**I blame Pollack for my chronic loss of sleep** during the past week. Devouring his book has inspired in me a whole new burst of enthusiasm for science." *Jason Gillen, Massage therapist, Sydney Australia.*

"**The most original thinker I have ever met.**" *Csaba Galambos, University of Colorado*

"**Einstein has got nothing on Pollack.** Pollack has the uncanny ability to pinpoint the right questions and grasp the simple ideas." *Capt. T.C. Randall, Author, Forbidden Healing*

"**This is like getting new glasses! The clarity is astounding.**" *Charles Cushing, Independent Scientist*

"**Unputdownable.**" *Nigel Dyer, University of Warwick, UK.*

"**As good a page-turner as a Dan Brown novel.** … this book has a folksy style that I know will be very popular." *David Anick, Harvard University*

"**By Chapter 5 I was spellbound.** By the end I was so captivated by the implications that I wished I could begin again in science and follow the new path this work has shaped." *Kathryn Devereaux, Science writer, UC Davis*

With balance and grace, Pollack seems to have come closest to presenting a 'unified field' vision of matter through the lens of water." *John Fellows, Independent Scientist*

"**This amazing book has changed my understanding of all the processes going on in water** which I was confident I knew about — the understanding that dictated my many years of teaching and organized my research. I must now come to terms with the demonstration that water is not just a medium in which physics and chemistry happen, but a machine that powers and manages physics and chemistry." *Martin Canny, Australian National University*

"**Brilliant!** Read the last chapter first." *Molly McGee, University of Washington*

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Ever wonder…

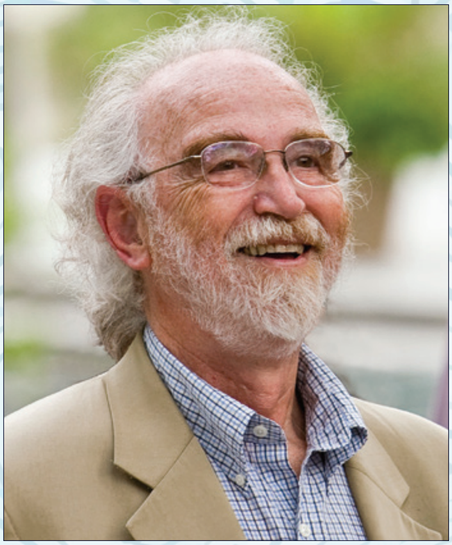
What mysteries lurk in the depths of a glass of water? What makes the wispy clouds of vapor rising from your cup of hot coffee? Or the puffy white clouds hovering in the sky? Why do the bubbles in your pop get bigger the longer you wait? What keeps Jell-O's water from oozing out? Why does your tongue stick to something frozen? And why don't your joints squeak?

Questions such as those have remained unanswered not only because they have seemed complex, but also because they require that scientists pursue a politically risky domain of science: water research. Scientists trying to understand the "social behavior" of H_20 do so at grave risk to their reputations and livelihoods because water science has suffered repeated fiascos. Water scientists have been virtually tarred and feathered.

Undaunted, one scientist has navigated the perils of water science by conducting dozens of simple, carefully controlled experiments and piecing together the first coherent account of water's three dimensional structure and behavior.

Professor Pollack takes us on a fantastic voyage through water, showing us a hidden universe teeming with physical activity that provides answers so simple that any curious person can understand. In conversational prose, Pollack relentlessly documents just where some scientists may have gone wrong with their Byzantine theories, and instead lays a simple foundation for understanding how changes of water structure underlie most energetic transitions of form and motion on Earth.

Pollack invites us to open our eyes and re-experience our natural world, to take nothing for granted, and to reawaken our childhood dream of having things make sense.



Professor Gerald Pollack is Founding Editor-in-Chief of the scientific journal, *WATER* and is recognized as an international leader in science and engineering.

The University of Washington Faculty chose Pollack, in 2008, to receive their highest annual distinction: the Faculty Lecturer Award. He was the 2012 recipient of the coveted Prigogine Medal for thermodynamics of dissipative systems. He has received an honorary doctorate from Ural State University in Ekaterinburg, Russia, and was more recently named an Honorary Professor of the Russian Academy of Sciences, and Foreign Member of the Srpska Academy. Pollack is a Founding Fellow of the American Institute of Medical and Biological Engineering and a Fellow of both the American Heart Association and the Biomedical Engineering Society. He recently received an NIH Director's Transformative R01 Award for his work on water, and maintains an active laboratory in Seattle.

Pollack's interests have ranged broadly, from biological motion and cell biology to the interaction of biological surfaces with aqueous solutions. His 1990 book, *Muscles and Molecules: Uncovering the Principles of Biological Motion,* won an "Excellence Award" from the Society for Technical Communication; his subsequent book, *Cells, Gels and the Engines of Life,* won that Society's "Distinguished Award."

Pollack is recognized worldwide as a dynamic speaker and a scientist willing to challenge any long-held dogma that does not fit the facts.

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The Fourth Phase of Water

Beyond Solid, Liquid, and Vapor

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to Gilbert Ling

who taught me that water in the cell
is nothing like water in a glass;

whose courage has been a
continuing inspiration.

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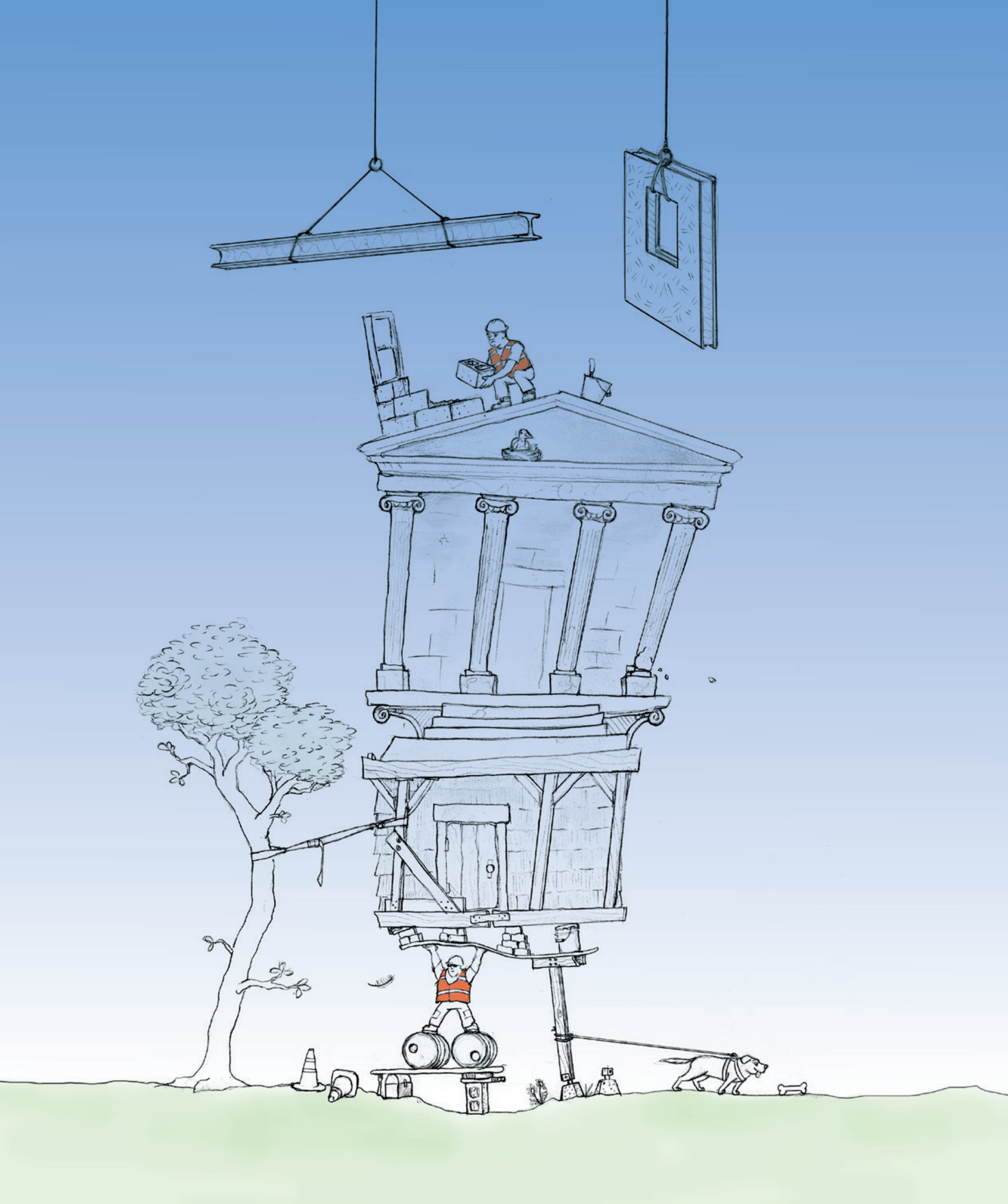


Preface

There in my living room sat the Nobel laureate. He was shy and I was intimidated, a combination certain to generate awkwardness. It was like trying to make small talk with Einstein. What do you say?

Sir Andrew Huxley was a Nobelist among Nobelists. He had already done classical work on cell membranes, and by the time of our meeting he'd become the leader in the field of muscle contraction. His many accolades included President of the Royal Society; Master of Trinity College, Cambridge; and recipient of the Order of Merit from the Queen of England. He was also a member of the distinguished Huxley family, a lineage that produced the legendary biologist Thomas Henry Huxley ("Darwin's bulldog") and the prescient writer Aldous Huxley. Here in my humble living room sat this towering scientific aristocrat.

During those awkward moments, nobody dared mention the elephant in the room: experimental results from our laboratory demonstrating that my guest's theory might be wrong. He'd come to check out our evidence, which took place earlier, within the confines of my laboratory. But, in my living room, we avoided that thorny subject altogether, focusing instead on such compelling issues as the weather. Even with a few rounds of sherry for social lubrication, it was a struggle to let it hang out; after all, Huxley was a scientific oracle — practically a deity.

Towering figures like Huxley appear awesome; however, we tend to forget that even the most renowned scientists are human. They eat the same foods we eat, share the same passions, and are subject to the same human foibles. So, while we may marvel at their insights and respect their contributions, we need not feel obliged to treat those contributions as faultless or absolute; scientific formulations are hardly sacred.

Treating any scientific formulation as sacred is a serious error. Any framework of understanding that we build needs to rest on solid foundations of experimental evidence rather than on sacred formulations; otherwise, the finished product may resemble one of M.C. Escher's renderings of subtle impossibility — a result worth avoiding. Even long-standing models remain vulnerable if they have not managed to bring simple, satisfying understandings. Galileo's story teaches us that when an established foundation requires the support of elaborate "epicycles" to agree with empirical observations, it's time to begin searching for simpler foundations.

This book attempts to build reliable foundations for a new science of water. The foundation derives from recent discoveries. Upon this new foundation, we will build a framework of understanding with considerable predictive power: everyday phenomena become plainly explainable without the need for mind-bending twists and jumps. Then comes the bonus: the process of building this new framework will yield four new scientific principles — principles that may prove applicable beyond water and throughout all of nature.

Thus, the approach I take is unconventional. It does not build on the "prevailing wisdom"; nor does it reflexively accept all current foundational principles as inherently valid. Instead, it returns to the root method of doing science — relying on common observation, simple logic, and the most elementary principles of chemistry and physics to build understanding. Example: in observing the vapor rising from your cup of hot coffee, you can actually *see* the clouds of vapor. What must that tell you about the nature of the evaporative process? Do prevailing foundational principles sufficiently explain what you see? Or must we begin looking elsewhere? (You'll know what I mean if you read Chapter 15.)

This old-fashioned approach may come across as mildly irreverent because it pays little homage to the "gods" of science. On the other hand, I believe the approach may provide the best route toward an intuitive understanding of nature — an understanding that even laymen can appreciate.

I certainly did not begin my life as a revolutionary. In fact, I was pretty conventional. As an undergraduate electrical engineering student, I came to class properly dressed and duly respectful. At parties, I wore a tie and jacket just like my peers. We looked about as revolutionary as members of an old ladies' sewing circle.

Only in graduate school at the University of Pennsylvania did someone implant in me the seeds of revolution. My field of study at the time was bioengineering. I found the engineering component rather staid, whereas the biological component brought some welcome measure of leavening. Biology seemed the happening place; it was full of dynamism and promise for the future. Nevertheless, none of my biology professors even hinted that students like us might one day create scientific breakthroughs. Our job was to add flesh to existing skeletal frameworks.

I thought that incrementally adding bits of flesh was the way of science until a colleague turned on the flashing red lights. Tatsuo Iwazumi arrived at Penn when I was close to finishing my PhD. I had built a primitive computer simulation of cardiac contraction based on the Huxley model, and Iwazumi was to follow in my footsteps. "Impossible!" he asserted. Lacking the deferential demeanor characteristic of most Japanese I'd known, Iwazumi stated in no uncertain terms that my simulation was worthless: it rested on the accepted theory of muscle contraction, and that theoretical mechanism couldn't possibly work. "The mechanism is intrinsically unstable," he continued. "If muscle really worked that way, then it would fly apart during its very first contraction."

Whoa! A frontal challenge to Huxley's muscle theory? No way.

Although (the late) Iwazumi exuded brilliance at every turn and came with impeccable educational credentials from the University of Tokyo and MIT, he seemed no match for the legendary Sir Andrew Huxley. How could such a distinguished Nobel laureate have so seriously erred? We understood that the scientific mechanisms announced by such sages constituted ground truth and textbook fact, yet here came this brash young Japanese engineering student telling me that this particular truth was not just wrong, but impossible.

Reluctantly, I had to admit that Iwazumi's argument was persuasive — clear, logical, and simple. As far as I know, it stands unchallenged to this very day. Those who hear the argument for the first time quickly see the logic, and most are flabbergasted by its simplicity.

For me, this marked a turning point. It taught me that sound logical arguments could trump even long-standing belief systems buttressed by armies of followers. Once disproved, a theory was done — finished.

The belief system was gone forever. Clinging endlessly was tantamount to religious adherence, not science. The Iwazumi encounter also taught me that thinking independently was more than just a cliché; it was a necessary ingredient in the search for truth. In fact, this very ingredient led to my muscle-contraction dispute with Sir Andrew Huxley (which never did resolve).

Challenging convention is not a bed of roses, I assure you. You might think that members of the scientific establishment would warmly embrace fresh approaches that throw new light on old thinking, but mostly they do not. Fresh approaches challenge the prevailing wisdom. Scientists carrying the flag are apt to react defensively, for any such challenge threatens their standing. Consequently, the challenger's path can be treacherous — replete with dangerous turns and littered with formidable obstacles.

Obstacles notwithstanding, I did somehow manage to survive during those early years. By delicately balancing irreverence with solid conventional science and even a measure of obeisance, I could press on largely unscathed. Our challenges were plainly evident, but we pioneered techniques impressive enough that my students could land good jobs worldwide, some rising to academia's highest levels. Earning that badge of respectability saved me from the terminal fate common to most challengers.

During the middle of my career, my interests began expanding. I sniffed more broadly around the array of scientific domains, and as I did I began smelling rats all over. Contradictions abounded. Some of the challenges I saw others raise to their fields' prevailing wisdom seemed just as profound as the ones raised in the muscle-contraction field.

One of those challenges centered on the field of water — the subject of this book. The challenger of highest prominence at the time was Gilbert Ling. Ling had invented the glass microelectrode, which revolutionized cellular electrophysiology. That contribution should have earned him a Nobel Prize, but Ling got into trouble because his results began telling him that water molecules inside the cell lined up in an orderly fashion. Such orderliness was anathema to most biological and physical scientists. Ling was not shy about broadcasting his conclusions, especially to those who might have thought otherwise.

So, for that and other loudly trumpeted heresies, Ling eventually fell from favor. Scientists holding more traditional views reviled him as a provocateur. I thought otherwise. I found his views on cell water to be just as sound as Iwazumi's views on muscle contraction. Unresolved issues remained, but on the whole his proposal seemed evidence-based, logical, and potentially far-reaching in its scope. I recall inviting Ling to present a lecture at my university. A senior colleague admonished me to reconsider. In an ostensibly fatherly way, he warned that my sponsorship of so controversial a figure could irrevocably compromise my own reputation. I took the risk — but the implications of his warning lingered.

Ling's case opened my eyes wider. I began to understand why challengers suffered the fates they did: always, the challenges provoked discomfort among the orthodox believers. That stirred trouble for the challengers. I also came to realize that challenges were common, more so than generally appreciated. Not only were the water and muscle fields under siege, but voices of dissent could also be heard in fields ranging from nerve transmission to cosmic gravitation. The more I looked, the more I found. I don't mean flaky challenges coming from attention-seeking wackos; I'm referring to the meaningful challenges coming from thoughtful, professional scientists.

Serious challenges abound throughout science. You may be unaware of these challenges, just as I had been until fairly recently, because the challenges are often kept beneath the radar. The respective establishments see little gain in exposing the chinks in their armor, so the challenges are not broadcast. Even young scientists entering their various fields may not know that their particular field's orthodoxy is under siege.

The challenges follow a predictable pattern. Troubled by a theory's mounting complexity and its discord with observation, a scientist will stand up and announce a problem; often that announcement will come with a replacement theory. The establishment typically responds by ignoring the challenge. This dooms most challenges to rot in the basement of obscurity. Those few challenges that do gain a following are often dealt with aggressively: the establishment dismisses the challenger with scorn and disdain, often charging the poor soul with multiple counts of lunacy.

The consequence is predictable: science maintains the *status quo*. Not much happens. Cancer is not cured. The edifices of science continue to grow on weathered and sometimes even crumbling foundations, leading to cumbersome models and ever-fatter textbooks filled with myriad, sometimes inconsequential details. Some fields have grown so complex as to become practically incomprehensible. Often, we cannot relate. Many scientists maintain that that's just the way modern science must be — complicated, remote, separated from human experience. To them, cause-and-effect simplicity is a quaint feature of the past, tossed out in favor of the complex statistical correlations of modernity.

I learned a good deal more about our acquiescence to scientific complexity by looking into Richard Feynman's book on quantum electrodynamics, aptly titled *QED*. Many consider Feynman, a legendary figure in physics, the Einstein of the late 20th century. In the Introduction to the 2006 edition of Feynman's book, a prominent physicist states that you'll probably not understand the material, but you should read the book anyway because it's important. I found this sentiment mildly off-putting. However, it was hardly as off-putting as what Feynman himself goes on to state in his own Introduction: "It is my task to convince you *not* to turn away because you don't understand it. You see, my physics students don't understand it either. That's because *I* don't understand it. Nobody does."

The book you hold takes an approach that challenges the notion that modern science must lie beyond human comprehension. We strive for simplicity. If the currently accepted orthodox principles of science cannot readily explain everyday observations, then I am prepared to declare that the emperor has no clothes: these principles might be inadequate. While those foundational principles may have come from towering scientific giants, we cannot discount the possibility that new foundations might work better.

Our specific goal is to understand water. Water now *seems* complicated. The understanding of everyday phenomena often requires complex twists and non-intuitive turns — and still we fail to reach satisfying understandings. A possible cause of this unsatisfying complexity is the present foundational underpinning: an *ad hoc* collection of long-standing principles drawn from diverse fields. Perhaps a more suitable foundation — built directly from studying water — might yield simpler understandings. That's the direction we're headed.

To read this book, you needn't be a scientist; the book is designed for anyone with even the most primitive knowledge of science. If you understand that positive attracts negative and have heard of the periodic table, then you should be able to get the message. On the other hand, those who might thumb their noses at anything that seriously questions current dogma will certainly find the approach distasteful, for threads of challenge weave through the book's very fabric. This book is unconventional —a saga filled with steamy scenes and unexpected twists, all of which resolve into something I hope you will find satisfying, and perhaps even fun to read.

I have restricted formal references to those instances in which citations seemed absolutely necessary. Where the point is generally known or easily accessible, I've omitted them. The overarching goal was to streamline the text for readability.

Finally, let me admit to having no delusion that all of the ideas offered here will necessarily turn out to be ground truth. Some are speculative. I have certainly aimed at producing science fact, not science fiction. However, as you know, even a single ugly fact can demolish the most beautiful of theories. The material in this book represents my best and most earnest attempt to assemble the available evidence into a cohesive interpretational framework. The framework is unconventional, and I already know that some scientists do not agree with all aspects. Nevertheless, it is a sincere attempt to create understanding where little exists.

So, as we plunge into these murky waters, let us see if we can achieve some needed clarity.

GHP

Seattle, September 2012

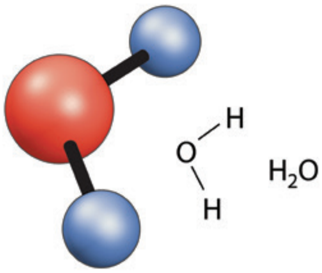
Discovery consists of seeing what everybody has seen and thinking what nobody has thought.

Albert Szent-Györgyi,
Nobel laureate (1893-1986)

A BESTIARY

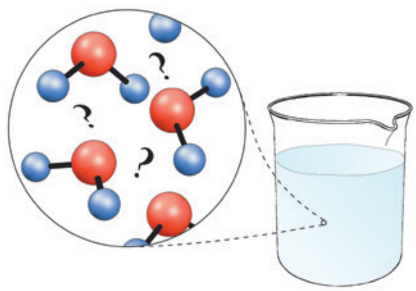
A READER'S GUIDE TO THE SPECIES THAT LURK WITHIN THE MYSTERIOUS AQUEOUS DOMAIN

WATER MOLECULE



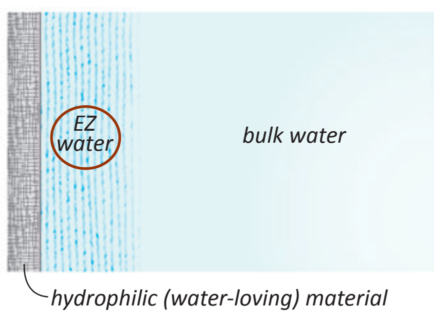
The familiar water molecule, composed of two hydrogen atoms and one oxygen atom.

BULK WATER



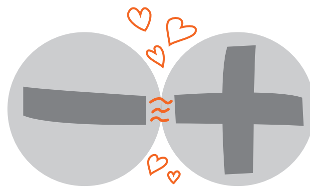
The standard collection of water molecules, whose arrangement is still debated.

EXCLUSION ZONE (EZ)



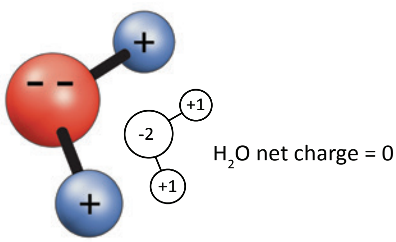
The "exclusion zone" (EZ), the unexpectedly large zone of water that forms next to many submersed materials, got its name because it excludes practically everything. The EZ contains a lot of charge, and its character differs from that of bulk water. Sometimes it is referred to as water's fourth phase.

Electron and Proton



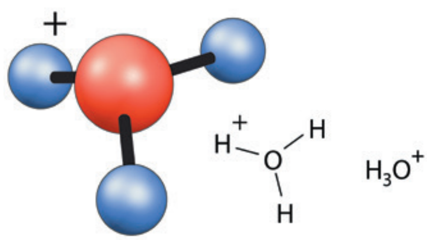
Electrons and protons are the elementary units of charge. They attract one another because one is positive and the other is negative. Electrons and protons play central roles in water's behavior — more than you might think.

Water Molecule Charge



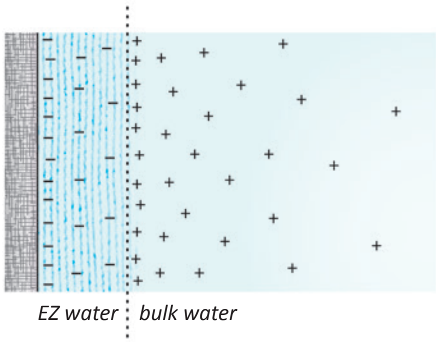
The water molecule is neutral. Oxygen has a charge of minus two, while each of the hydrogen atoms has a plus one charge.

Hydronium Ion



Protons latch onto water molecules to form hydronium ions. Imagine a positively charged water molecule and you've got a hydronium ion. Charged species like hydronium ions are highly mobile and can wreak much havoc.

Interfacial Battery

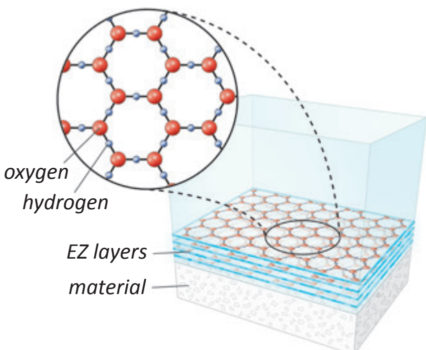


This battery comprises the exclusion zone and the bulk water zone beyond. The respective zones are oppositely charged, and the separation is sustained, as in an ordinary battery.

Radiant Energy

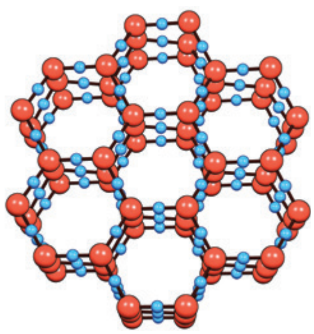
Radiant energy charges the battery. The energy comes from the sun and other radiant sources. The water absorbs these energies and uses them to charge the battery.

Honeycomb Sheet



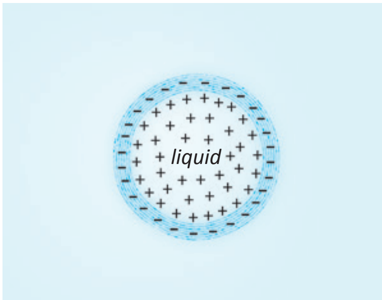
The honeycomb sheet is the EZ's unitary structure. Sheets stack parallel to the material surface to build the EZ.

Ice



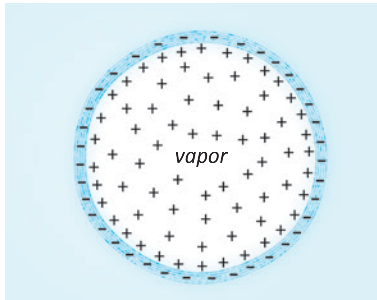
The atomic structure of ice closely resembles the atomic structure of the exclusion zone. This similarity is beyond coincidence: one transforms readily into the other.

Droplet



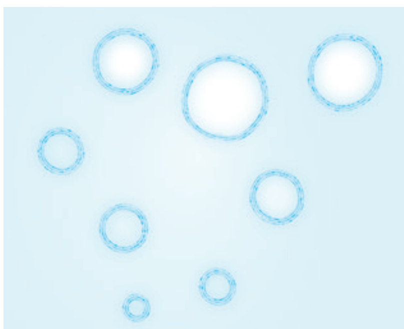
The water droplet consists of an EZ shell that envelops bulk water. The two components have opposite charges.

Bubble



The bubble is structured like the droplet, except that it has a gaseous interior. Commonly, that gas is water vapor.

Vesicle



Since droplets and bubbles are similarly constructed, we introduce the generic label: *vesicle*. A vesicle can be a droplet or a bubble, depending on the phase of the water inside. When a droplet absorbs enough energy, it can become a bubble.

Section I

Water Riddles:
Forging the Pathway

1 Surrounded by Mysteries

Beaker in hand, two students rushed down the hall to show me something unexpected. Unfortunately, their result vanished before I could take a look. But it was no fluke. The next day the phenomenon reappeared, and it became clear why the students had reacted with such excitement: they had witnessed a water-based phenomenon that defied explanation.

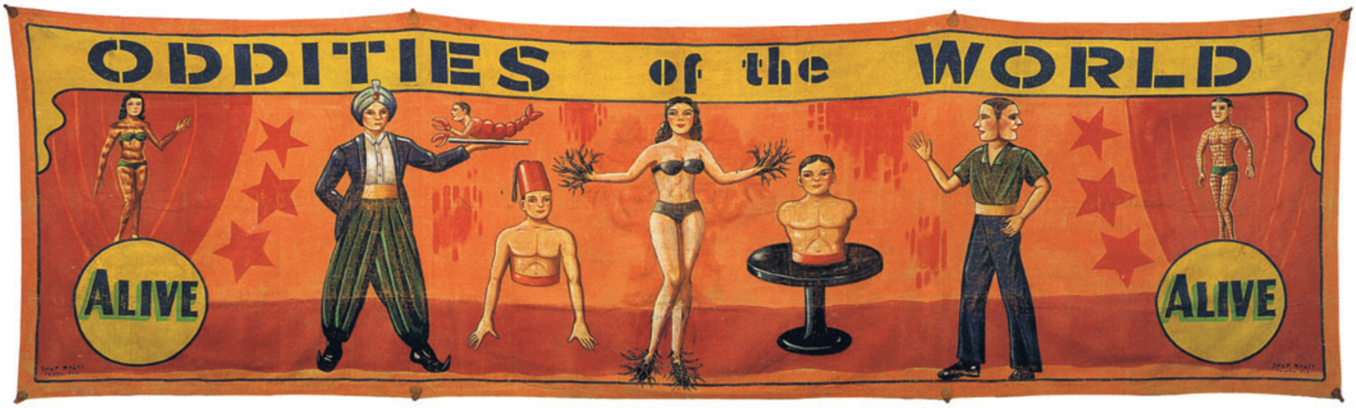
Water covers much of the earth. It pervades the skies. It fills your cells — to a greater extent than you might be aware. Your cells are two-thirds water by volume; however, the water molecule is so small that if you were to count every single molecule in your body, 99% of them would be water molecules. That many water molecules are needed to make up the two-thirds volume. Your feet tote around a huge sack of mostly water molecules.

What do we know about those water molecules? Scientists study them, but rarely do they concern themselves with the large ensembles of water molecules that one finds in beakers. Rather, most scientists focus on the single molecule and its immediate neighbors, hoping to extrapolate what they learn to larger-scale phenomena that we can see. Everyone seeks to understand the observable behavior of water, i.e., how its molecules act "socially."

Do we really understand water's social behavior?

Since water is everywhere, you might reasonably conclude that we understand it completely. I challenge you to confirm that common presumption. Below, I present a collection of everyday observations, along with a handful of simple laboratory observations. See if you can explain them. If you can, then I lose; you may stop reading this book. If the explanations remain elusive even after consulting the abundant available sources, then I ask you to reconsider the presumption that we know everything there is to know about water.

I think we don't. Let's see how you fare.



Everyday Mysteries

Here are fifteen everyday observations. Can you explain them?

• *Wet sand vs. dry sand.* When stepping into dry sand, you sink deeply, but you hardly sink into the wet sand near the water's edge. Wet sand is so firm that you can use it for building sturdy castles or large sand sculptures. The water evidently serves as an adhesive. But how exactly does water glue those sand particles together? (The answer is revealed in Chapter 8.)

• *Ocean waves.* Waves ordinarily dissipate after traveling a relatively short distance. However, tsunami waves can circumnavigate the Earth several times before finally petering out. Why do they persist for such immense distances? (See Chapter 16.)

• *Gelatin desserts.* Gelatin desserts are mostly water. With all that water inside, you'd expect a lot of leakage (**Fig. 1.1**). However, none occurs. Even from gels that are as much as 99.95% water,[1] we see no dribbling. Why doesn't all that water leak out? (Read Chapters 4 and 11.)

Fig. 1.1 *What keeps the water from dribbling out of the Jell-O?*

• *Diapers.* Similar to gels, diapers can hold lots of water: more than 50 times their weight of urine and 800 times their weight of pure water. How can they hold so much water? (Look at Chapter 11.)

• *Slipperiness of ice.* Solid materials don't usually slide past one another so easily: think of your shoes planted on a hilly street. Friction keeps you from sliding. If the hill is icy, however, then you must exercise great care to keep from falling on your face. Why does ice behave so differently from most solids? (Chapter 12 explains.)

- *Swelling*. Your friend breaks her ankle during a tennis match. Her ankle swells to twice its normal size within a couple of minutes. Why does water rush so quickly into the wound? (Chapter 11 offers an answer.)

- *Freezing warm water.* A precocious middle-school student once observed something odd in his cooking class. From a powdered ice cream mix he could produce his frozen treat faster by adding warm water instead of cold water. This paradoxical observation has become famous. How is it that warm water can freeze more rapidly than cold water? (See Chapter 17.)

- *Rising water.* Leaves are thirsty. In order to replace the water lost through evaporation in plants and trees, water flows upward from the roots through narrow columns. The commonly offered explanation asserts that the tops of the columns exert an upward drawing force on the water suspended beneath. In 100-meter-tall redwood trees, however, this is problematic: the weight of the water amassed in each capillary would suffice to break the column. Once broken, a column can no longer draw water from the roots. How does nature avert this debacle? (Check out Chapter 15.)

- *Breaking concrete*. Concrete sidewalks can be cracked open by upwelling tree roots. The roots consist mainly of water. How is it possible that water-containing roots can exert enough pressure to break slabs of concrete? (Look through Chapter 12.)

- *Droplets on surfaces*. Water droplets bead up on some surfaces and spread out on others. The degree of spread serves, in fact, as a basis for classifying diverse surfaces. Assigning a classification, however, doesn't explain *why* the droplets spread, or *how far* they spread. What forces cause a water droplet to spread? (Go to Chapter 14.)

- *Walking on water.* Perhaps you've seen videos of "Jesus Christ" lizards walking on pond surfaces. The lizards scamper from one end to the other. Water's high surface tension comes to mind as a plausible explanation, but if surface tension derives from the top few molecular layers only, then that tension should be feeble. What is it about the water (or about the lizard) that makes possible this seemingly biblical feat? (Read Chapter 16.)

Fig. 1.2 *What directs the rising water vapor to specific locations?*

- *Isolated clouds.* Water vapor rises from vast uninterrupted reaches of the ocean's water. That vapor should be everywhere. Yet puffy white clouds will often form as discrete entities, punctuating an otherwise clear blue sky (**Fig. 1.2**). What force directs the diffuse rising vapor towards those specific sites? (Chapters 8 and 15 consider this issue.)

- *Squeaky joints.* Deep knee bends don't generally elicit squeaks. That's because water provides excellent lubrication between bones (actually, between cartilage layers that line the bones). What feature of water creates that vanishingly small friction? (Take a look at Chapter 12.)

- *Ice floats.* Most substances contract when cooled. Water contracts as well — until 4 °C. Below that critical temperature water begins expanding, and very much so as it transitions to ice. That's why ice floats. What's special about 4 °C; and, why is ice so much less dense than water? (Chapter 17 answers these questions.)

- *Yoghurt's consistency.* Why does yoghurt hold together as firmly as it does? (See Chapter 8.)

Mysteries from the Laboratory

I next consider some simple laboratory observations, beginning with the one seen by those students rushing down the hall to show me what they'd found.

(i) The Mystery of the Migrating Microspheres

The students had done a simple experiment. They dumped a bunch of tiny spheres, known as "microspheres," into a beaker of water. They shook the suspension to ensure proper mixing, covered the beaker to minimize evaporation, and then went home for a good night's sleep. The next morning, they returned to examine the result.

By conventional thinking, nothing much should have happened, besides possibly some settling at the bottom of the beaker. The suspension should have looked uniformly cloudy, as if you'd poured some droplets of milk into water and shaken it vigorously.

The suspension did look uniformly cloudy — for the most part. However, near the center of the beaker (looking down from the top), a clear cylinder running from top to bottom had inexplicably formed (**Fig. 1.3**). Clarity meant that the cylinder contained no microspheres. Some mysterious force had driven the microspheres out of a central core and toward the beaker's periphery. If you've ever seen *2001: A Space Odyssey*, and the astonishment of the ape-humans upon first seeing the perfect monolith, you have some sense of just how our jaws dropped. This was something to behold.

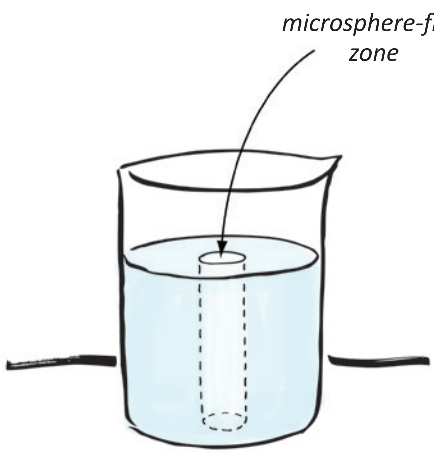


Fig. 1.3 *Near-central clear zone in microsphere suspension. Why does the microsphere-free cylinder appear spontaneously?*

So long as the initial conditions remained within a well-defined window, these clear cylinders showed up consistently; we could produce them again and again.[2] The question: what drives the counter-intuitive migration of the spheres away from the center? (Chapter 9 explains.)

(ii) The Bridge Made of Water

Another curious laboratory phenomenon, the so-called "water bridge," connects water across a gap between two glass beakers — if you can imagine. Although the water bridge is a century-old curiosity, Elmar Fuchs and his colleagues pioneered a modern incarnation that has aroused interest worldwide.

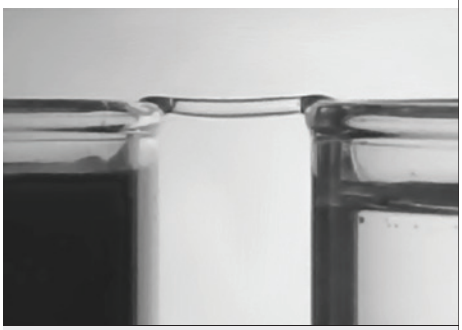


Fig. 1.4 *The water-bridge. A bridge made of water spans the gap between two water-filled beakers. What sustains the bridge?*

The demonstration starts by filling the two beakers almost to their brims with water and then placing them side-by-side, lips touching. An electrode immersed in each beaker imposes a potential difference on the order of 10 kV. Immediately, water in one beaker jumps to the rim and bridges across to the other beaker. Once the bridge forms, the two beakers may be slowly separated. The bridge doesn't break; it continues to elongate, spanning the gap between beakers even when the lips separate by as much as several centimeters (**Fig. 1.4**).

Astonishingly, the water-bridge hardly droops; it exhibits an almost ice-like rigidity, even though the experiment is carried out at room temperature.

I caution you to resist the temptation to repeat this high-voltage experiment unless you consider yourself immune to electrocution. Better to watch a video of this eye-popping phenomenon.[w1] The question: what sustains the bridge made of water? (See Chapter 17.)

(iii) The Floating Water Droplet

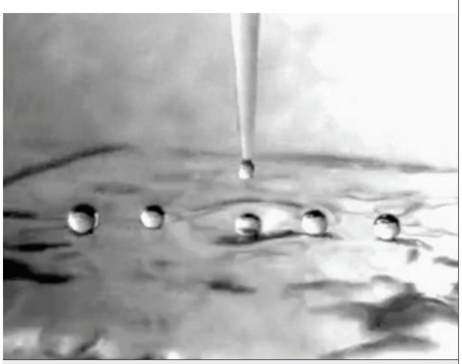


Fig. 1.5 *Water droplets persist on water surface for some time. Why?*

Water should mix instantly with water. However, if you release water droplets from a narrow tube positioned just above a dish of water, those droplets will often float on the water surface for a period of time before dissolving (**Fig. 1.5**). Sometimes the droplets may sustain themselves for up to tens of seconds. Even more paradoxically, droplets don't dissolve as single unitary events; they dissolve in a succession of squirts into the pool beneath.[3] Their dissolution resembles a programmed dance.

Floating water droplets can be seen in nature if you know where to look. A good time is just after a rainfall, when water drips from a ledge onto a puddle or from a sailboat's gunwales onto the lake beneath. Even raindrops will sometimes float as they hit ground water directly. The obvious question: if water mixes naturally with water, then what feature might delay the natural coalescence? (Look at Chapters 13 and 16)

(iv) Lord Kelvin's Discharge

Finally, **Fig. 1.6** depicts another head-scratching observation. Water drawn from an upside-down bottle or an ordinary tap is split into two branches. Droplets fall from each branch, passing through metal rings as they descend into metallic containers. The rings and containers are cross-connected with electrical wires, as shown. Metal spheres project toward one another from each container through metallic posts, leaving an air gap of several millimeters between the spheres.

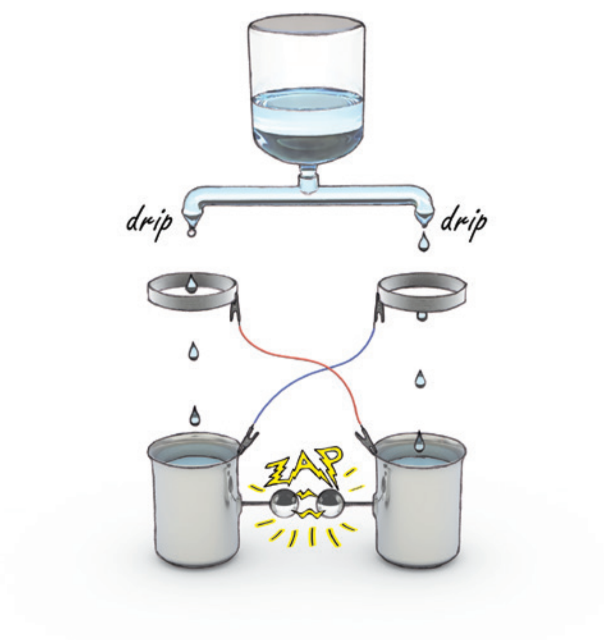


Fig. 1.6 *The Kelvin water-dropper demonstration. Rising water levels create a high-voltage discharge. Why does this happen?*

Originally conceived by Lord Kelvin, this experiment produces a surprising result. Once enough droplets have descended, you begin hearing a crackling sound. Then, soon after, a flash of lightning discharges across the gap, accompanied by an audible crack.

Electrical discharge can occur only if a large difference in electrical potential builds between the two containers. That potential difference can easily reach 100,000 volts, depending on gap size. Yet, the massive separation of charge needed to create that potential difference builds from a *single source of water.*

Constructing one of these exotic devices at home is possible[w2]; however, observing the discharge on video is a lot simpler. A fine example is the one produced by Professor Walter Lewin,[w3] who demonstrates the discharge to a classroom full of awe-struck MIT freshmen. He then invites the students to explain the phenomenon as their homework assignment. Can you explain how a single source of water can yield this massive charge separation? (Read about it in Chapter 15.)

Lessons Learned from These Mysteries

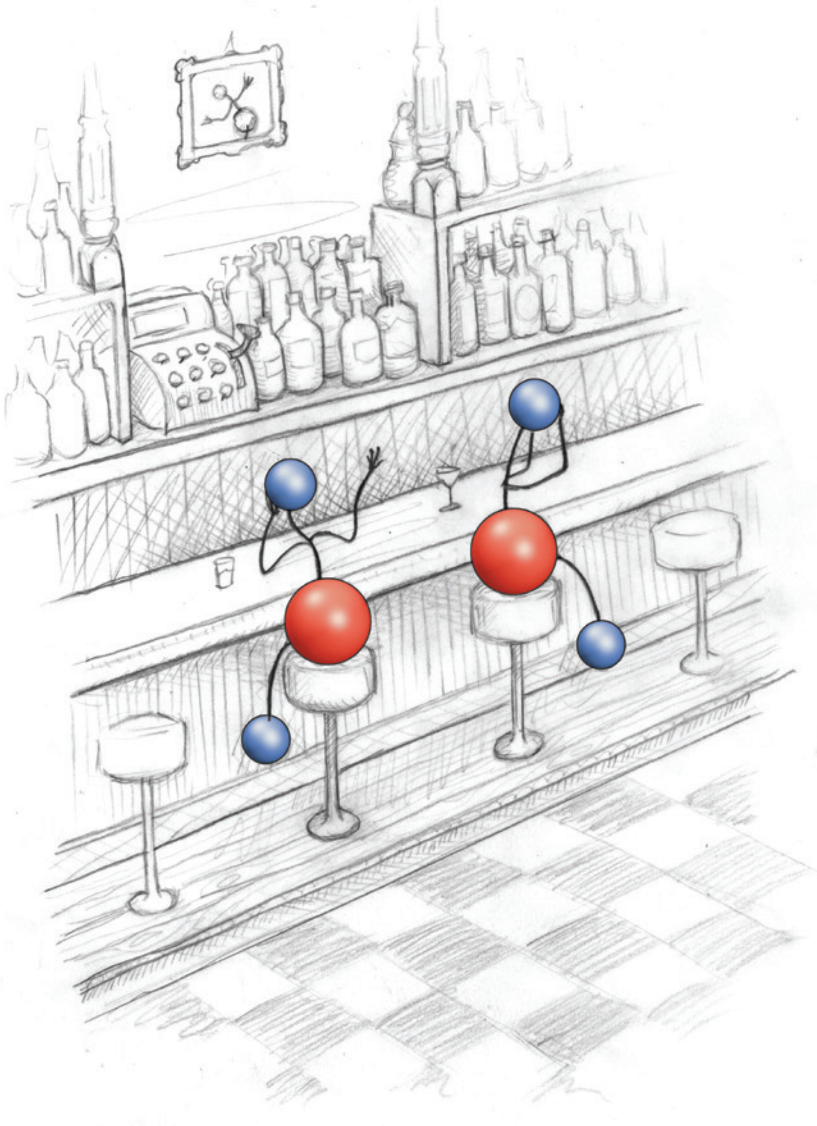
The phenomena presented in the foregoing sections defy easy explanation. Even prominent water scientists I know cannot come up with satisfying answers; most cannot get beyond the most superficial explanations. Something is evidently missing from our framework of understanding; otherwise, the phenomena should be readily explainable — but they are not.

I want to reemphasize that we're not dealing with water at the molecular level; we're dealing with crowds of water molecules. We don't yet understand water molecules' interaction with other water molecules — water's "social" behavior.

Social behavior is the purview of social scientists and clinicians, from whom we might learn. A friend of mine, a psychiatrist, once told me that, in order to understand human behavior, you should focus on oddballs and weirdos. Their behavioral extremes, the psychiatrist opined, provide clues for understanding the subtler behaviors of the rest of the population. That same reasoning can apply here: the foregoing cases describe some situations where water exhibits extreme "social" behaviors; as such, they provide clues for understanding the more ordinary behaviors of water molecules.

Thus, rather than brushing aside our inability to explain the phenomena above, we exploit them for the clues they provide. We turn ignorance to advantage. You'll see many examples of this process once we reach the book's middle chapters.

The next chapter provides some helpful background. It considers what we already know about water's social behavior and what we don't, but it focuses mainly on the surprising reasons why we know so little about Earth's most common substance.



2 The Social Behavior of H_2O

Water is central to life — so central that Albert Szent-Györgyi, the father of modern biochemistry, once opined: "Life is water dancing to the tune of solids." Without that dance, there could be no life.

Given that centrality, you might assume that we in the 21st century know pretty much all there is to know about water. All answers should be in by now. Yet the previous chapter confirmed otherwise, showing how little we really know about this familiar and pervasive substance.

Consider what Philip Ball has to say on that issue. Ball is one of the premier science writers of our time, author of *H_2O: A Biography of Water*, and a long-time science consultant for the journal *Nature*. Ball puts it this way[1]: "No one really understands water. It's embarrassing to admit it, but the stuff that covers two-thirds of our planet is still a mystery. Worse, the more we look, the more the problems accumulate: new techniques probing deeper into the molecular architecture of liquid water are throwing up more puzzles."

The water molecule itself is pretty well understood. Gay-Lussac and von Humboldt defined its essential nature just over two centuries ago; by now, fine details of its architecture are known. Essentially, the water molecule consists of two hydrogen atoms and one oxygen atom, arranged in a configuration that you might have seen in textbooks (**Fig. 2.1**).

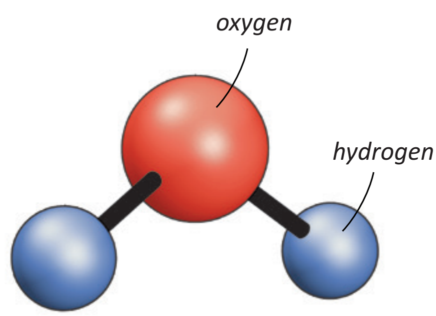


Fig. 2.1 *Artist's sketch of the water molecule.*

We still know too little about how that molecule interacts with other water molecules or with molecules of different kind. Non-experts rarely raise questions of this nature. For most, it suffices to know that water molecules somehow link up with other water molecules. That's it. Biologists, for example, often regard water as the vast molecular sea that bathes the important molecules of life. We do not picture water molecules as seriously interacting with anything.

But water molecules must interact. Think of the simple water droplet: at least some of the gazillions of water molecules that make up the droplet must stick to others, for without cohesion there could be no droplet. Those cohesive interactions cannot be static. They must change as two droplets coalesce, and they must change as a droplet spreads on a surface. Even the simple droplet can't be understood without understanding water-water interactions.

So we ask, what is the nature of those interactions?

The Current Status of Understanding

Although a hodgepodge of ideas, the following list provides a short description of recent attempts to account for water's behavior. The theories of water-water interactions are complex, and even water scientists occasionally have difficulty understanding one another's theories. So, I will keep it brief. Readers seeking a more comprehensive understanding might find it useful to read a detailed review by Philip Ball.[2] Here I merely outline how seven prominent scientific groups think water molecules interact with one another (**Fig. 2.2**).

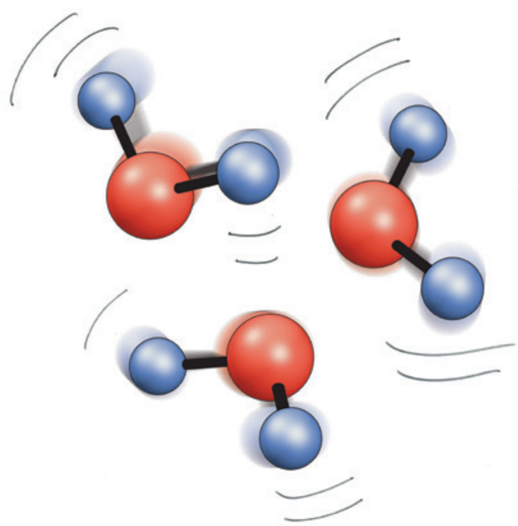


Fig. 2.2 *Interaction among water molecules. The nature of the interaction is not well understood.*

• The classical view of water-water interaction is the "flickering cluster" model introduced in 1957 by Frank and Wen. In this model, clusters of water molecules build from surrounding water. Positive feedback makes the clusters grow to a critical size and then spontaneously disperse. All of this happens on a time scale of 10^{-10} to 10^{-11} seconds; hence, the clusters “flicker.” Although outdated, this model still appears in many textbooks.

• Martin Chaplin of London South Bank University, England, presents a model with slightly more organization. Chaplin suggests that liquid water consists of two types of intermixed nanoclusters. One type is empty, shell-like, and more-or-less collapsed, while the other is rather solid and more regularly structured. Molecules of water switch their allegiance rapidly between these two phases, but under a given set of conditions, the average number of molecules in each category remains the same. Those interested in this model can find details, and much more about water, on Chaplin’s famously informative website.[w1]

• Quite a different picture emerges from the work of Anders Nilsson of Stanford University and Lars Petterson of Stockholm University. Their model also posits two coexisting types of water: ice-like clumps or chains containing up to about 100 molecules; and a disordered type of organization that surrounds those clumps. The authors envisage a kind of disordered sea, containing rings and chains of hydrogen and oxygen atoms.

• The model of of the University of Milan is characterized by a much larger scale of clustering. Based on quantum-field theory, del Giudice posits submicron-sized coherence domains of water, each of which may contain many millions of molecules. The bonds between the water molecules within those domains may be thought of as antennae that receive electromagnetic energy from outside. With such energy, the water molecules can release electrons, making them available for chemical reactions.

• A popular model that builds on the associations inherent in all of the foregoing models comes from Gene Stanley of Boston University. Stanley suggests that water has two distinct states, low density and high density. The distinction appears most clearly in supercooled water. Low-density water has an open tetrahedral structure, while high-density water has a more compact structure. The two states dynamically interchange with one another.

• Another two-state model emphasizes that water molecules can exist as mirror images. That is, one fraction of water molecules is left-handed, while the other is right-handed. Major proponents of this kind of model include Sergey Pershin from Russia and Meir Shinitzky and Yosi Scolnik from Israel. They argue that the relative proportions of these two species can explain diverse features of water.

• The most structurally complex model, put forth by the late materials-science pioneer Rustum Roy, emphasizes the heterogeneity of water structure, as well as the ease of water-molecule interchange. Interchanges require very little energy. **Figure 2.3** shows a cartoon schematizing some representative structures.

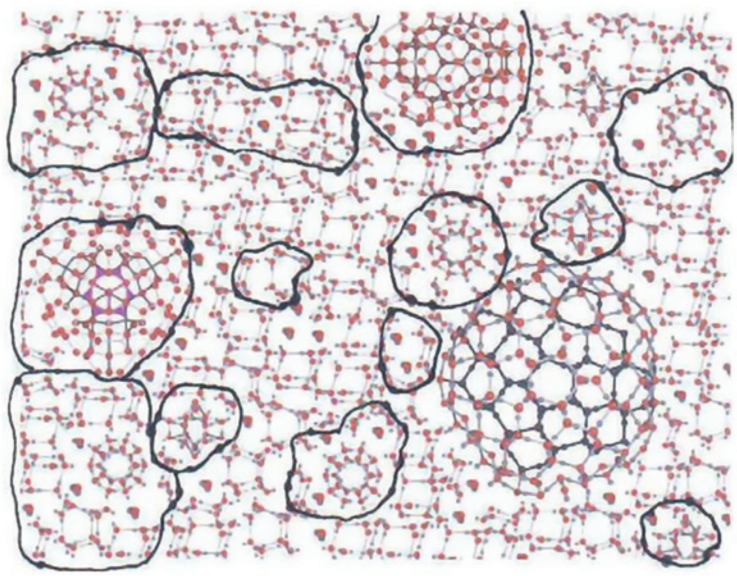


Fig. 2.3 *Proposed structure of liquid water, from Rustum Roy and colleagues.[3] Clusters are outlined in black.*

By now, you may feel you have heard enough about structural models. Yet this sampling is merely representative of a larger group of models that are continually argued and debated. Our understanding of water remains unresolved or, as Ball puts it, "a mystery."

On the other hand, most of these models share a common feature: multiple states. The common view is that liquid water has but one state; yet these models theorize some additional state. Later, we will see concrete evidence for a robust state of water that is visually detectable and endowed with well-defined features.

Why We Understand So Little

You might find it hard to believe, but few scientists study water. Most scientists presume, as do lay people, that everything about this common substance must already be known — so where's the scientific challenge? Better to pursue some trendy area like molecular biology or nanoscience rather than plunge into boring water.

Scientists shun water for a second reason. Water seems to have acquired a rather mystical character. Ancient religious gurus felt certain that water was endowed with exotic healing powers. Think of "holy water." This mystical tinge makes water research a potentially risky business: an exotic finding may be viewed as the work of the devil, rather than as the work of science. Better to avoid the risk of condemnation.

Despite those two disincentives, water once occupied a central position in scientific research. During the first half of the 20th century, science had a different emphasis than it does now. Rather than adding detailed knowledge to narrowly focused areas, scientists sought to uncover general principles that might apply throughout nature. The whole seemed more important than its molecular parts. That whole had to include water because water was virtually everywhere.

It was also a time when colloids, submicroscopic particles suspended in a liquid, seemed important. Believing that a colloidal foundation was the basis of life, many scientists assumed that knowledge about colloid-water interaction would elucidate life's underlying chemistry. The focus on colloids, combined with the holistic approach, put water at the center of scientific research.

But, by the middle of the 20th century, two things blighted the promising water harvest. First was the shift toward specialization. That shift drew scientists toward more molecular approaches that assigned water a secondary role. Molecules became the rage. The more you understood a molecule, it seemed, the closer you approached scientific truth. Inevitably, water research became old-fashioned and gradually lost its prominence.

The second thing that made scientists shy away from water involved two sociopolitical incidents, each of which had a terrible dampening effect on progress in understanding water.

The first incident, the so-called “polywater debacle,” began during the Cold War, in the late 1960s, with a provocative Russian discovery. Water confined within narrow capillary tubes seemed to behave differently than ordinary water: its molecules vibrated differently; its density was anomalously high; and it was difficult to freeze or to vaporize. Clearly, this was some exotic brand of water. Because its properties implied the high stability common to many polymers, chemists thought of it as polymer-water and coined the ultimately fateful descriptor, “polywater.”

The discovery of polywater triggered excitement among many scientists — imagine, a new phase of water. But the discovery also met with skepticism, and the Russians eventually wound up embarrassed when Western scientists identified an insidious problem: impurities. The supposedly pure water situated inside those capillary tubes was shown to contain salts and silica leached from the surrounding glass tubes. Those impurities had apparently given rise to the exotic features that were reported. Even Boris Derjaguin, the legendary physical chemist responsible for most of the initial studies, eventually admitted publicly that the impurities had been present. The skeptics could find justification in their initial reaction that polywater was “hard to swallow.”

I’ll have more to say later on polywater. I will just mention here that “contaminants” are bugaboos that plague all scientific fields. A scientist hopes for something pure, but absolute purity is often difficult to attain. In the case of water, achieving purity is virtually impossible because water has a propensity to absorb all kinds of foreign molecules; it’s a natural solvent for almost everything. In this sense, contaminants are natural features of water, and their presence in limited quantities does not necessarily imply that any observed feature needs to be reflexively discarded.

However, the damage was done. By the early 1970s, the Russians were deemed guilty of careless experimentation. The injury to the field grew far out of proportion to the indictment’s significance, mainly because of the sensational publicity given to polywater when the press caught hold of the story. Imagine, they suggested: a drop of polywater thrown into the sea could act like any polymeric catalyst — that single drop could polymerize the earth's entire water supply into a single blobby mass, which would end all life. Dangerous stuff, for sure (**Fig. 2.4**).

The public was therefore relieved by the reports of the contamination error. Other, less paranoid folks felt disappointed that this exciting new scientific finding turned out to be nothing more than an experimental flub. Either way, water scientists were considered incompetent.

The ensuing catastrophic impact on all water research is not difficult to imagine. If Russia's premier physical chemist could go so easily astray, then what about ordinary scientists? The risk of embarrassment seemed high. Talented scientists who might have pursued water research chose to work on safer subjects to avoid any possible taint of polywater.

So, largely out of fear, water research screeched to a halt. A few brave diehards persisted, mainly in the area of biological water, but the momentum was killed. The lingering mystery of water was left for others to resolve — sometime in the vaguely distant future.

The Water Memory Debacle

Two decades later, water science showed signs of incipient recovery — until an even deadlier blow struck: the so-called "water memory" debacle. Here, the central figure was the late French scientist and renowned immunologist, Jacques Benveniste. Almost by accident, Benveniste and colleagues obtained evidence that water could retain information from the molecules with which it interacted. Water, you might say, could "remember."

The evidence for water memory came from experiments involving successive dilutions of biologically active substances. Take such a substance dissolved in water, and dilute it. Then take a bit of this dilute solution and dilute it again; repeat this process again and again. After you have diluted it enough times, all you have left is water;

Fig. 2.4 *The specter of polywater.*

statistically, none of the original substance remains. Benveniste and colleagues would continue to dilute it even well beyond that stage of nothing remaining and still found that the solution could have as much biological impact as the original. Pouring either the concentrated substance or the serially diluted substance onto cells could trigger the same molecular dance. It appeared that the diluted water retained a "memory" of the molecules with which it had been in contact, for only those molecules were specific enough to initiate that dance.

Preposterous, thought the editor of *Nature*, Sir John Maddox. How on earth could water retain information? But not everyone shared that seemingly obvious response. Homeopaths use a similar procedure when preparing their remedies, and some members of the homeopathic community felt that a distinguished scientist had finally vindicated their approach. Benveniste, on the other hand, was less interested in homeopathy than in science. Reacting to the summary rejection of his findings by *Nature*, Benveniste asked colleagues in three other laboratories to repeat his experimental protocols to see if they could obtain the same results.

Remarkably, they did. And, once again, Benveniste submitted a report of the findings to *Nature*. The journal responded the same as before. Evidently, no matter how many laboratories could reproduce the result, the findings looked so improbable that some experimental gremlin clearly must have been lurking in that diluted water. With the polywater incident still very much in mind, *Nature* smelled a rat.

Under pressure to act fairly, the journal finally agreed to publish the results, albeit with one condition: the editor reserved the right to summon a committee to look over the shoulders of the French scientists as they performed their experiments; then the committee would report back to the readers of *Nature*. The French group accepted the stipulation. The paper quickly appeared, along with an appended disclaimer of skepticism. The editor indicated that he would launch an investigation: a committee of peers would determine just what those French scientists were really up to.

The committee of peers was, in fact, a committee of sleuths. Editor Maddox headed the committee. Maddox recruited two additional people. The first was Walter Stewart, who worked at the US National Institutes of Health in a special division dedicated to uncovering scientific fraud. Stewart was a professional sleuth. The other was James Randi, otherwise known as "The Amazing Randi." A world-class stage magician, Randi earned his fame by debunking the tricks of other magicians, such as Uri Geller's claim that he could levitate. Judging from the makeup of this committee of "peers," it was clear that Maddox suspected more than just an innocent error.

The committee came to Paris and carefully watched the experiments. The first sets of experiments went pretty much as claimed, and the French seemed to prevail in the early rounds. But when one of the visitors himself performed the dilutions, the results did not go as well. The visitors then huddled. They quickly concluded that, since the French could produce the claimed result but the visitors could not, therefore a trick must be at play. The nature of the trick remained unclear to the professional debunkers. Nevertheless, their report to the world of science boldly declared that water memory was "a delusion."

This colorful story is rich with detail, and for more of that I recommend two books. The first is the above-cited book by Philip Ball,[1] who worked for *Nature* at the time and was close to Maddox. The second book, entitled *The Memory of Water*,[4] was written by the late physicist Michel Schiff. Schiff had been working in the French laboratory at the time of the incident. As you may imagine, these authors have rather different sympathies. To get the full picture, you should read both books.

As a result of this fiasco, Benveniste suffered widespread humiliation. That humiliation included the loss of grant support, the collapse of a large and productive laboratory, difficulty publishing any further scientific work, and — the ultimate ignominy — twice winning the "Ig-Nobel" Prize, awarded by Harvard students for improbable research. It was not a happy time for French science (**Fig. 2.5**).

The main point, however, is neither the ugliness of the incident nor the instant demise of an illustrious scientific career; the main point is the impact this had on the field of water research. Barely having recovered from the polywater debacle, the field suffered this second, even more devastating setback. Water memory became the laughingstock of the entire scientific community. Finding it hard to remember names? Try drinking more water. (Ha, ha!)

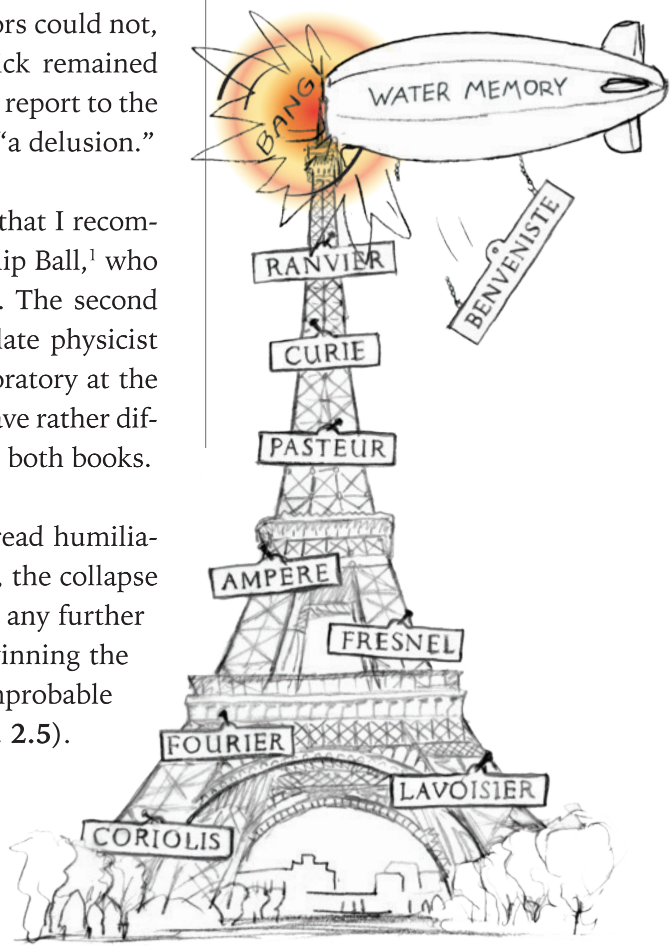


Fig. 2.5 *An embarrassment to French science?*

Given this troubled history, you can imagine the consequence for water research. How many scientists of sound mind would dare enter a field first tainted by polywater and then debased as the butt of scientific jokes? Very few indeed. Yet there is some irony, for others would later confirm Benveniste's result,[5] and still others, including Nobel laureate Luc Montagnier, would build on water memory to claim transmission of information stored in water.[6] Despite all that, water memory remains largely a joking matter rather than a subject of serious scientific investigation.

The Mystery Lingers

I think you can now appreciate the paradox: why we have come to know so little about something so familiar. Two successive debacles have turned a once-dynamic field into a treacherous domain into which few scientists have the temerity to enter.

Rising from the ashes of those two debacles is the current field of water research. The field may be best described as schizophrenic. On the one side, mainstream scientists employ computer simulations and technologically sophisticated approaches to learn more about water molecules and their immediate neighbors. Their results more or less define the field. Taking relatively risk-free approaches, they have provided incremental advances that help refine and embellish the various models outlined earlier in this chapter.

On the other side are the scientists who explore the more provocative phenomena, such as those described in the previous chapter. The very mention of those phenomena often provokes a chuckle from mainstreamers, who consider the phenomena odd and less than scientific. Some mainstreamers like to dismiss those phenomena as a species of "weird water."

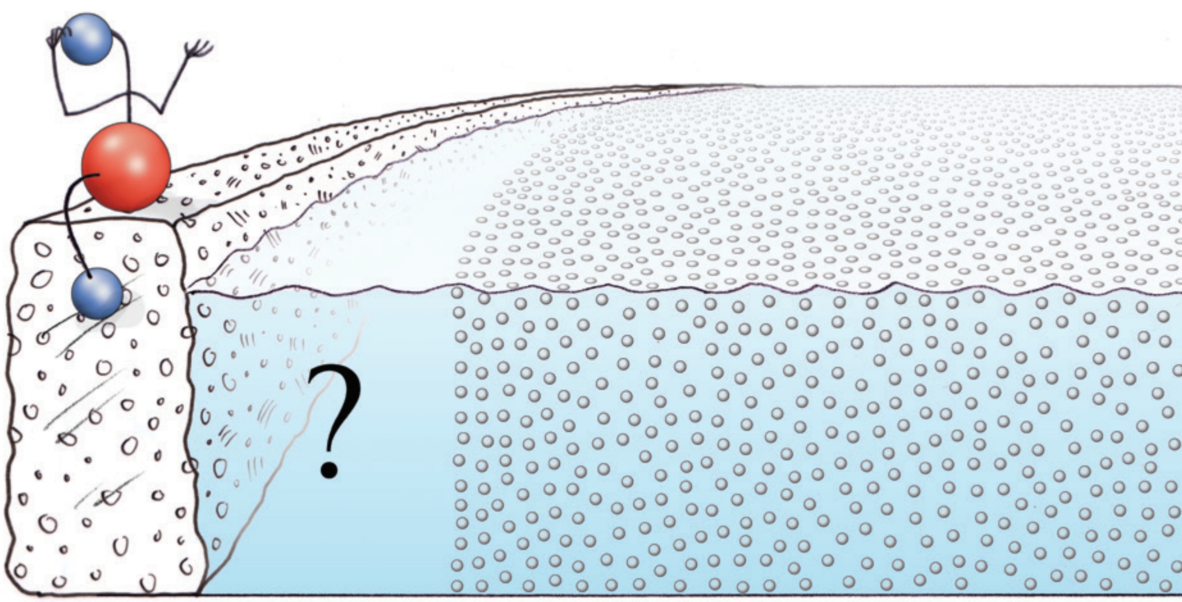
Rarely do the two sides mix. The weird water folks admire the mainstreamers' sophistication but often find their approaches dense and impenetrable; hence, they keep their distance. Mainstreamers, in turn, avoid the weird water folks like the plague. Some mainstreamers cringe at the prospect of yet another water debacle. Weird-water phenomena are thus consigned to fringe science — placed in the same category as cold fusion, UFOs, and subtle energies. You'd better keep your distance if you hope to retain your scientific respectability.

Given this atmosphere of suspicion, you can appreciate why building understanding has become a challenge. Conducting fundamental research on water is something like searching for gold nuggets in the mud. A few can be found here and there, but this slow, arduous gathering process occurs in an atmosphere of suspicion that makes it impractical to lay even a primitive foundation of understanding.

• • •

The chapters that follow will bypass this muddy, well-trodden pathway. We will forge an entirely fresh trail built on clues that others have ignored, and use this path to progress toward a better understanding. We take the position that the social behavior of water should not be as incomprehensible as now conceived: if nature itself is simple and intuitive as many scientists think, then we'd hope that its most ubiquitous component might be equally simple and intuitive.

It is this simple understanding that we strive to uncover.



3 The Enigma of Interfacial Water

In a glass, all of the water looks the same. Peering intently into the glass provides no hint that molecules in one region might arrange themselves differently from molecules in another region. After all, water is water.

On the other hand, superficial appearances can deceive. I learned only during the past decade that material surfaces can profoundly impact nearby water molecules — so profoundly and extensively that most everything about that water radically changes. Practically any surface that touches the water will have such effects: the container, suspended particles, or even dissolved molecules. Surfaces of all kind profoundly affect nearby water molecules.

Had I bothered to read the literature, I would have been fully aware of this surface impact: a half-century-old review article by JC Henniker[1] cites more than a hundred published studies confirming the long-range effect of varied surfaces on many liquids, including water. The evidence has been widely available.

For me, however, such long-range effects were a fresh revelation. I had been aware of surfaces affecting water out to perhaps tens of water molecule layers; I had even written a book on the biological relevance of such ordered water.[2] However, a truly long-range impact extending up to thousands or even millions of molecular layers was rather jarring. If true, this strong influence seemed inescapably central for all water-based phenomena.

I'll describe how we first stumbled upon evidence for this long-range ordering, and what we did to check that the evidence was sound. The alert came from a chance encounter at a scientific conference.

Lunch with Hirai

On a blisteringly hot summer day in the late 1990s, while darting from one building to another to attend a seminar, I had the good

Toshihiro Hirai, Shinshu University.

fortune to run into Professor Toshihiro Hirai from Japan's Shinshu University. We chatted at length. I described the book I was then writing on the role of water in cell function (*Cells, Gels, and the Engines of Life*). The subject evidently caught his attention, for as we proceeded to lunch to escape the heat, Hirai informed me of a seemingly relevant observation that his students had made — one that ultimately proved pivotal for understanding water.

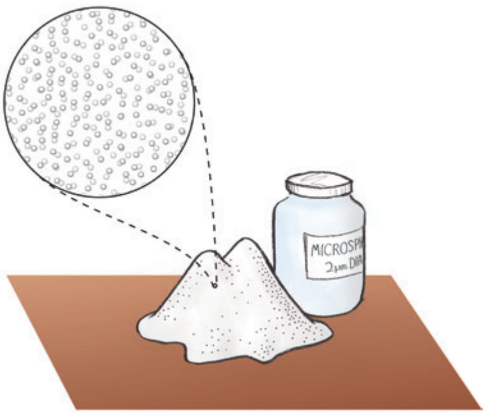


Fig. 3.1 *Microspheres are common tools for scientists.*

Hirai and his students had been studying blood flow in vessels. In lieu of actual vessels, they used cylindrical tunnels bored through gels; for blood, they used suspensions of microspheres (**Fig. 3.1**). Thus, water suspensions of tiny spheres pumped through gel tunnels mimicked the blood flowing through vessels. The investigators could track the flowing "blood" because the gel was transparent; all they needed was a simple microscope.

Hirai eagerly shared their observations with me. I found his results on the patterns of blood flow illuminating, but what really caught my attention was his description of the odd behavior of the microspheres. He told me that the flowing microspheres avoided the annular zone just inside the gel surface; they restricted themselves to the tunnel's central core (**Fig. 3.2**). Hirai indicated that he did not pay particular

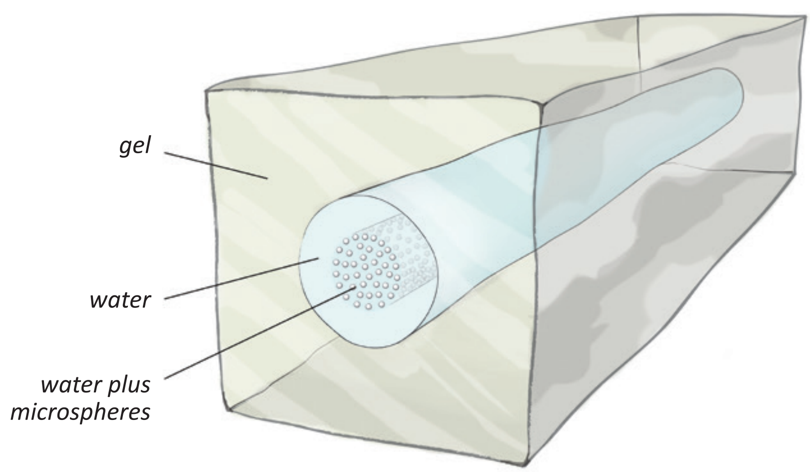


Fig. 3.2 *Schematic diagram illustrating the microsphere-free zone just inside the gel tunnel.*

attention to this feature, assuming it was a secondary effect. The possible centrality of this near-surface exclusion apparently had not occurred to him.

Following that encounter, Hirai and I exchanged many emails. Exercising care to avoid overstepping the boundaries of polite Japanese communication, I tried to persuade Hirai to publish his findings, as I had hoped to cite them in my then-forthcoming book. That was not to happen. Hirai grew justifiably impatient with my incessant emails and finally offered to include me as coauthor of any forthcoming publication while allowing him to proceed at his own pace.

To the best of my knowledge, Hirai's observations remain unpublished. However, quite serendipitously, a former postdoctoral research fellow of his moved to Seattle and walked into my lab looking for work. I instantly hired Jian-ming Zheng (**Fig. 3.3**), and we proceeded to follow up on Hirai's observations.

Fig. 3.3 *Jian-ming "Jim" Zheng.*

I had reason to suspect that the microspheres' inclination to avoid the zone near the gel surface might indicate something significant. It seemed possible that the gel surface might order contiguous water molecules; the growing order would then push out microspheres in the same way as growing ice crystals push out suspended debris. This hypothesis was unorthodox; however, my 2001 book detailed a substantial body of evidence pointing to that very notion.

The most astonishing aspect of Hirai's observations, however, was the scale. The microsphere-free zone extended about a tenth of a millimeter inward from the gel surface, implying that the ordered lineup might include hundreds of thousands of water molecules. That's akin to a lineup of marbles extending over several dozen US football fields. Even as an author championing the idea of water ordering in the cell,[2] I had trouble with that colossal magnitude; the span seemed too long.

I might have been a tad less skeptical had I been properly aware of the older scientific literature. Published over sixty years ago and based on numerous published papers, the review article that I mentioned[1] drew a similar conclusion: surfaces exert long-range influence on contiguous liquids; they bring substantial molecular reordering. Unaware of this evidence, we naïvely went on to reinvent the wheel.

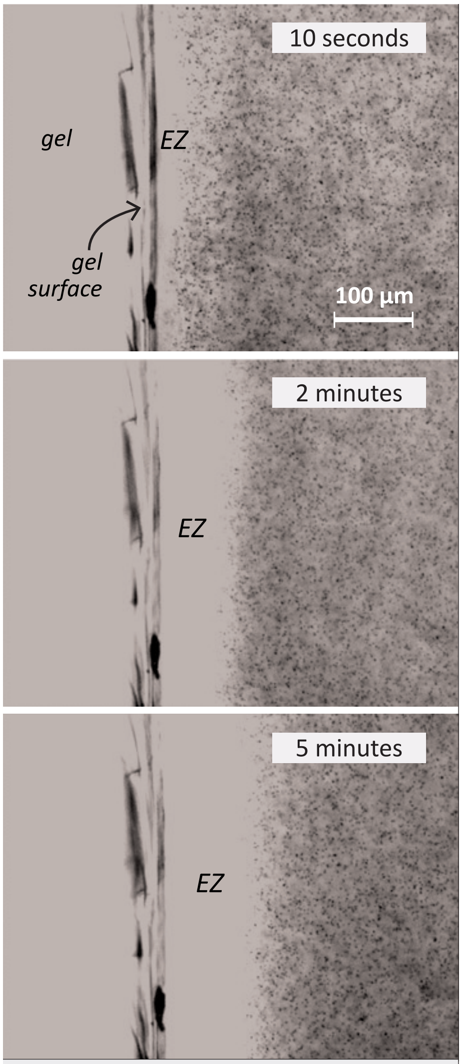


Fig. 3.4 *Microsphere-exclusion zone (EZ) next to a gel surface. The zone grows with time and then remains relatively stable after about five minutes.*

We started with simpler initial experiments than Hirai's. Using the same type of gel, we plunked a piece into a chamber and suffused it with an aqueous suspension of microspheres. We then looked into the microscope to see what might happen. As soon as the liquid suspension met the gel, the microspheres began moving away from the gel's surface, leaving a microsphere-free zone just under 100 μm (0.1 mm) wide. Water remained in that zone, but microspheres did not. Once formed, the zone remained intact: even after several hours of examination, the microspheres resisted invasion. **Figure 3.4** shows the development of this microsphere "exclusion zone."

Our observations revealed that the microsphere-free zone seen by Hirai did not arise from the hydrodynamics of "blood" flow; our setup had no flow, yet we obtained a similar zone of exclusion. Something about the gel surface appeared to drive the microspheres into hasty retreat — with or without imposed flow. Both scenarios produced the same result: a distinct exclusion zone, or "EZ," as we came to call it.

The Conventional Expectation

The exclusion phenomenon seems to fly in the face of the tenets of modern chemistry. The phenomenon should not exist. Surfaces may certainly affect the adjacent liquid, but it is widely presumed that the impact does not project into the liquid beyond a few molecular layers (despite the evidence cited in Henniker's review article).

Why so limited an impact? The prevailing view derives from the theorized presence of an electrical "double layer" of charge. Thus, a charged surface placed in water will attract oppositely charged ions dissolved in that water (**Fig. 3.5,** *opposite page*). Beyond that ion layer lies a second layer whose polarity is opposite the first, extending diffusely into the liquid. And beyond that double layer must lie additional diffuse charges, etc. Eventually, neutrality prevails. To an observer situated beyond those neutralizing layers, the surface should be unnoticeable — as though the surface were absent.

That minimum distance for insensitivity is labeled the "Debye length," after the Dutch physicist Peter Debye. The value of the Debye length reflects the extensiveness of the counter-ion clouds. Although the exact value depends on many factors, typical values are on the nanometer (10^{-9} meter) scale. Beyond those several nanometers, according to theory, any solute or particle situated in the liquid should be insensitive to the presence of the material surface.

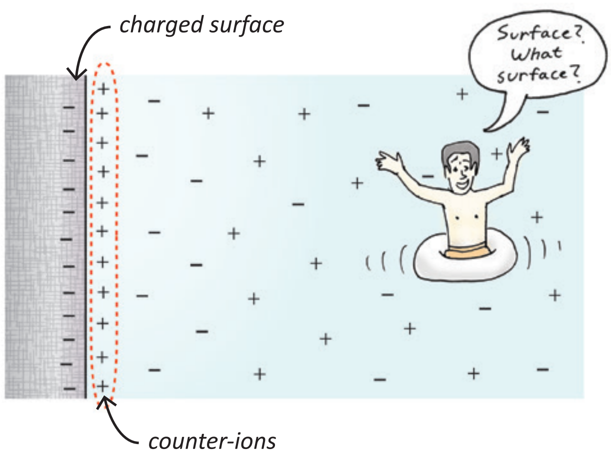


Fig. 3.5 *Standard double-layer theory. Charged surface (left) is expected to attract counter-ions of opposite polarity, as shown. Those counter-ions then attract a diffuse cloud of opposite charges, etc. An observer sitting in the water at a site far from the interface should not sense the neutralized surface.*

That is not what we observed (**Fig. 3.4**). Particles were *markedly* sensitive to the material surface — distancing themselves from the surface by some 100,000 times the Debye length.

That observation spelled trouble, because the Debye length and double-layer theory are bedrock concepts of surface chemistry. Challenging that theory with conflicting experimental observation meant that we had to make certain; we had to be sure that no trivial explanation or underlying artifact (scientific jargon for error) might have confounded our observations.

Trivial Explanation?

Zheng and I dedicated a full year to probing every conceivable error.[3,4] We got lots of input from others, who were not shy about suggesting gremlins that might lurk insidiously beneath the interpretational surface. Of the many issues we addressed, four seemed particularly problematic.

• The first issue involved convectional flow that might arise from slightly different temperatures in different regions. Such temperature gradients might create fluidic swirls that could draw microspheres away from the surface. In many experiments, we did observe convectional flows; in other experiments, however, flow was altogether absent, and yet the exclusion zone persisted. We concluded that convectional flows could not provide a general explanation for the observed exclusion zones.

• A second issue was the polymer-brush effect. Gels are made of polymers (large molecules consisting of repeating structural units), whose strands might project beyond the gel proper and into the surrounding solution — like the bristles of a brush. Sparse, thin bristles might escape microscopic detection while excluding microspheres. However, running an ultrasensitive nanoprobe parallel to the gel surface revealed no evidence for any such bristles. The invisible bristle argument seemed bogus.

Subsequent experiments confirmed that conclusion. One of those experiments used self-assembled monolayers, i.e., single molecular layers functionalized with charge groups. Monolayers have no projecting polymers. Yet they could produce exclusion zones of ample size.[4] We also saw substantial exclusion zones next to certain n-type silicon wafers, as well as next to metal surfaces,[5] which, again, contain no projecting bristles. **Figure 3.6** shows an example.

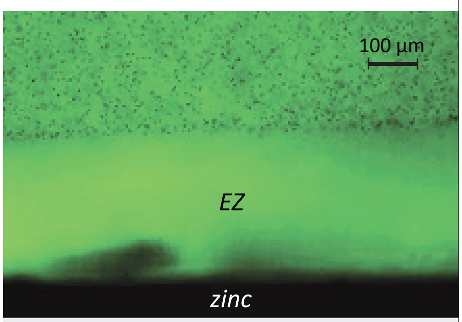


Fig. 3.6 *Exclusion zone next to zinc, from reference 5. Green color results from using a green filter in the microscope.*

• A third trivial explanation for microsphere exclusion invoked long-range electrostatic repulsion. If both the material surface and the microspheres are negatively charged, then the two entities should repel; strong enough repulsion should drive away the microspheres, creating a zone of exclusion. We considered this hypothesis even though double-layer theory predicts that any such repulsion ought to vanish at separations beyond a few nanometers, a distance some 100,000 times smaller than what we regularly observed.

The simplest test of the repulsion hypothesis was to substitute positive microspheres for negative microspheres. According to the electrostatic hypothesis, the positive microspheres should be drawn toward the negative surface. We found that the positively charged microspheres did sometimes collapse the exclusion zone; in other instances, the exclusion zone not only remained, but also remained the same size as seen with the negative microspheres.[3,4]

We got a similar result when we reversed the charge of the excluding surface. For those experiments, we used gel beads, whose spherical surfaces create shell-like exclusion zones (**Fig. 3.7**). Negatively charged microspheres were consistently excluded. It didn't matter whether the beads' surface contained negatively charged or positively charged polymers.[6] Simple electrostatic repulsion cannot explain these results.

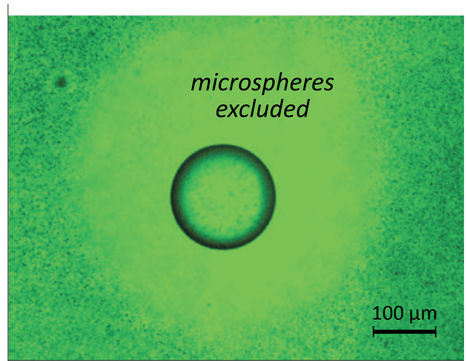


Fig. 3.7 *Microspheres excluded from the vicinity of a charged gel bead, as seen in an optical microscope. (Color arises because of microscope filter.) We positioned the bead on a glass surface and added the microsphere suspension. The EZ grew with time to the extent shown.*

• A fourth possibility involved some material diffusing from the gel. Leaking contaminants might conceivably push away the microspheres, leaving an apparent zone of exclusion. However, monolayer results contradict that hypothesis: those single molecular layers produced substantial exclusion zones,[4] yet they are so thin that virtually nothing is available to leak out.

• We also tried another approach: washing away any putative leaking contaminants. Vigorous flow parallel to the EZ-nucleating surface, no matter how swift, could not eliminate the EZ.[7]

• Finally, we could find exclusion zones too extensive to be explained away by leaking materials. Such extensive EZs were found in long, horizontally oriented cylindrical chambers. At one end of the cylinder, we mounted a disc-like gel held by clips. We then filled the chamber with a microsphere suspension and watched. A pancake-like exclusion zone grew, as expected, from the gel surface to a thickness of several hundred micrometers. But the growth didn't stop there (**Fig. 3.8**); the EZ continued to grow by wedging down to pole-like projections. Sometimes branching, those pole-like EZs typically extended to the very ends of meter-long chambers.[8] Clearly, a diffusing contaminant could not account for these ultralong exclusion zones.

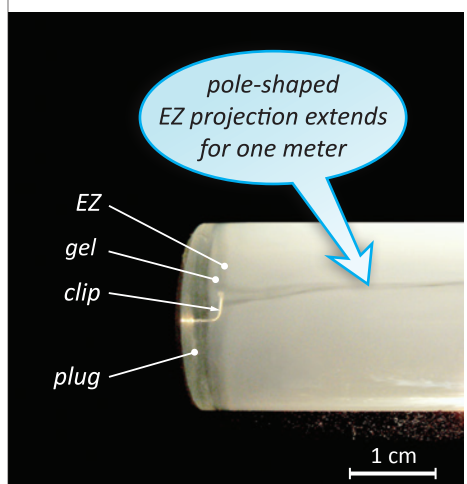


Fig. 3.8 *Long EZ projection. The disc-like gel creates a disc-like EZ that wedges into a long pole-like projection. The projection can extend at least one meter.*

Our yearlong studies lent confidence that the observed exclusion zones do not arise from trivial explanations. At this writing, several dozen laboratories have confirmed the existence of EZs. Furthermore (and to our chagrin), a recently uncovered paper published in 1970 showed largely the same results: microsphere-excluding zones several hundred micrometers thick, found adjacent to polymeric and biological gel surfaces.[9] Hence, microsphere exclusion is not a fluke. Something unpredicted is happening that drives microspheres from certain material surfaces.

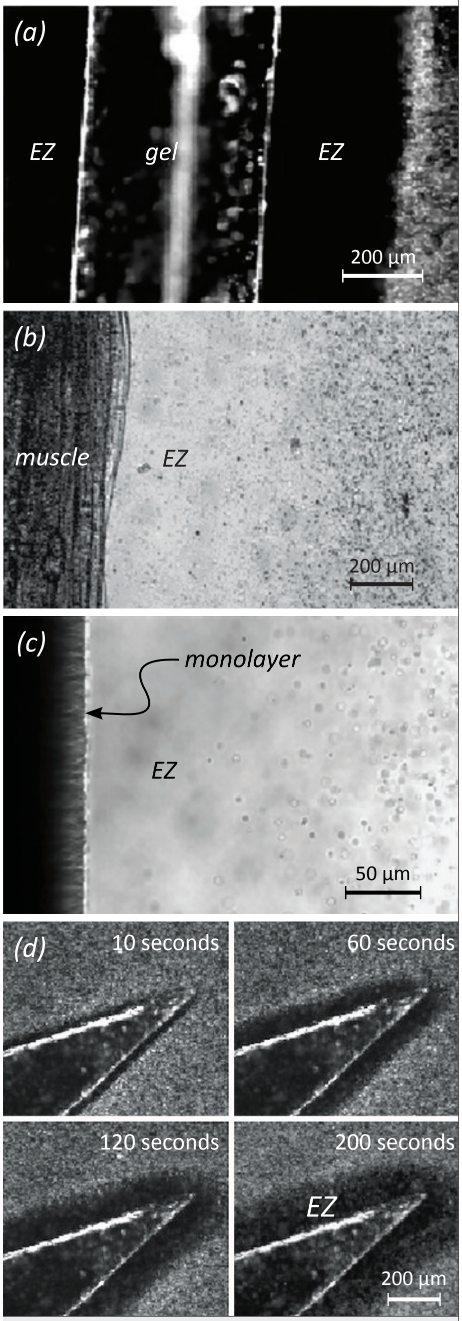


Fig. 3.9 *Examples of microsphere-excluding zones, viewed in an optical microscope. (a) polyacrylic acid gel; (b) muscle; (c) a self-assembled monolayer on gold. (d) Nafion polymer, time series.*

Although our artifact-seeking experiments consumed a good deal of our energy, they brought an unexpected clue. Those meter-long exclusion zones struck us as implying some kind of crystal-like structure, for crystals easily grow to such lengths: think of an icicle. Crystals also exclude particles as they grow. The prospect that the EZ might be some kind of crystal-like material intrigued us.

Crystals generally grow from nucleation sites, i.e., from surfaces of some kind. It seemed important therefore to determine what kinds of surfaces nucleate exclusion zones.

How General Are Exclusion Zones?

We first examined several gels over and above those mentioned. All water-containing (hydro)gels produced exclusion zones, including gels made of biological molecules and artificial polymers (**Fig. 3.9*a***). We also saw exclusion zones next to natural biological surfaces; they included vascular endothelia (the insides of blood vessels), regions of plant roots, and muscle (**Fig. 3.9*b***). I already mentioned monolayers (**Fig. 3.9*c***). Seeing substantial EZs adjacent to single molecular layers told us that material depth was not consequential: it appeared possible that *creating an exclusion zone merely required a molecular template.*

Various charged polymers also produced exclusion zones. An especially potent one was Nafion (**Fig. 3.9*d***). Nafion's Teflon-like backbone contains many negatively charged sulfonic acid groups, which make this polymer one of the more potent excluders. Because of Nafion's robust exclusion zones and ease of use, you'll see it mentioned frequently in these pages.

The only exotic features we encountered were breaches — localized surface patches devoid of EZs. Those bare patches were atypical. However, they could be found regularly next to certain metals, and also next to polymeric membranes when straddled by differing solutions, as was the case in our osmosis experiments (see Chapter 11). Those EZ breaches seemed rather like holes penetrating through the ordinary EZ dam.

The EZ-nucleating materials described in the paragraphs above fall into the category of "hydrophilic," or water loving. Their love for water seems profound enough to exclude other suitors; only the water gets to stay. "Hydrophobic" or water-hating surfaces, such as Teflon, prove inept by contrast; no exclusion zones could be found. It appears that *the exclusion phenomenon belongs to hydrophilic surfaces as a class.*

Having established the EZ's generality, we next asked: what does the EZ exclude? Does it exclude microspheres alone? Or are other substances excluded as well?

We found a wealth of excluded substances, ranging from large suspended particles down to small dissolved solutes.[3] Microspheres of all kinds were excluded. They ranged in size from 10 μm down to 0.1 μm and were fabricated from diverse substances. Even red blood cells, several strains of bacteria, and ordinary dirt particles scraped from outside our laboratory were excluded. The protein albumin was excluded, as were various dyes with molecular weights as low as 100 daltons — only a little larger than common salt molecules. The span between the largest to smallest of the excluded substances amounted to a thousand billion times (**Fig. 3.10**).

These experiments showed that the EZ rather broadly excludes substances of many sizes, from very small to very large.

We could not definitively test the tiniest of solutes — that had to wait. Nevertheless, we could conclude that the exclusion phenomenon was general: *almost any hydrophilic surface can generate an EZ, and the EZ excludes almost anything suspended or dissolved in the water.*

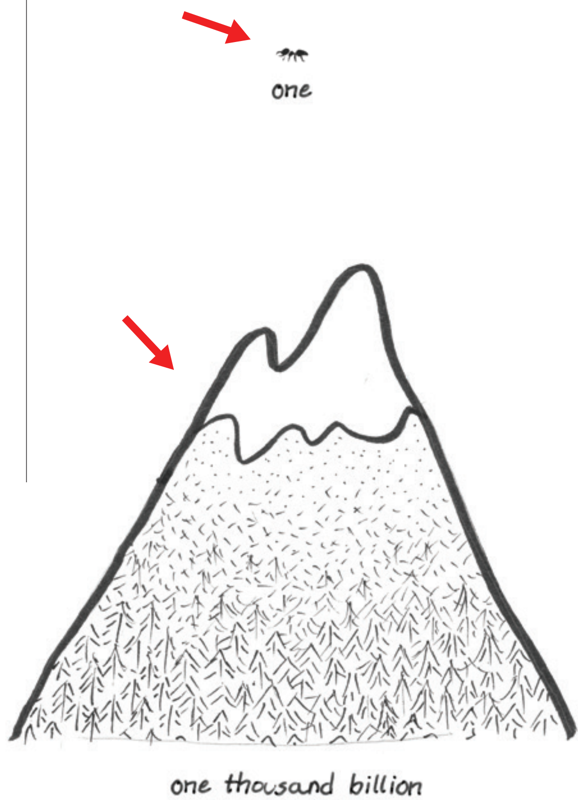


Fig. 3.10 *Range of excluded substances.*

Why Are Solutes Excluded?

This demonstrably vast exclusionary power implied yet again that we might be dealing with some kind of crystal-like substance, for crystals exclude massively. I alluded earlier to a possible crystalline structure: the hydrophilic surface could induce nearby water molecules to line up as they would in a liquid crystal. As the ordered zone grew, it would push out solutes in the same way that a growing glacier pushes out rocks.

Such molecular ordering is not a new idea. The previously referenced Henniker paper (1949) reviews many older works showing massive near-surface molecular reordering. Henniker's was not a voice lost

Fig. 3.11 *Albert Szent-Györgyi in his later years.*

Fig. 3.12 *Gilbert Ling in his earlier years.*

in the wind. Subsequently, the idea of long-range water ordering was advanced by a number of prominent scientists, including Walter Drost-Hansen, James Clegg, and especially Albert Szent-Györgyi and Gilbert Ling. Szent-Györgyi (**Fig. 3.11**) was a seminal thinker who won the Nobel Prize for discovering vitamin C. A cornerstone of his thinking was the long-range ordering of water, which he regarded as a major pillar in the edifice of life.

Gilbert Ling (**Fig. 3.12**) thought similarly. He emphasized the central role of water ordering in cell function, building a revolutionary framework for biological understanding. He wrote five books on this subject, the latest being his 2001 monograph, *Life at the Cell and Below-Cell Level*.[10] This book argues that the cell's charged surfaces order nearby water molecules, which in turn exclude most solutes. According to Ling, this ordering is the very reason why most solutes occur in low concentrations inside the cell: the cell's ordered water excludes them.

With the stage amply set by these towering figures, the idea that charged or hydrophilic surfaces might order water molecules out to appreciable distances seemed plausible; we found solid experimental precedent. It was also clear that today's mainstream chemists thought this kind of ordering unlikely because molecules tend toward disorder. Nevertheless, some mechanism had to explain the profound exclusion, and water ordering seemed a viable option. Our lab therefore set out to explore that possibility.

Additional Evidence that Surfaces Impact Nearby Water

To determine the physical nature of the exclusion zone, we pursued a variety of methods. In each, we set up an exclusion zone (always using the purest water obtainable); we tested whether the particular property under investigation in the exclusion zone differed from the water beyond the exclusion zone. By doing so, we hoped not only to test for a difference, but also, if we were lucky, to pin down the nature of EZ water. What follows is fairly technical, but I hope you will bear with me through the description of six important experimental tests.

(i) Light absorption. Substances differ in the way they absorb light. By charting the absorption of differing wavelengths ("colors"), we learn how a substance accepts electromagnetic energy; this can tell us how the molecules deal with that absorbed energy. At the very least, we hoped to see whether the wavelengths of light absorbed by the EZ differed from the wavelengths absorbed by the bulk water beyond.

To test for such differences, we set up the experiment shown in **Fig. 3.13*a***.

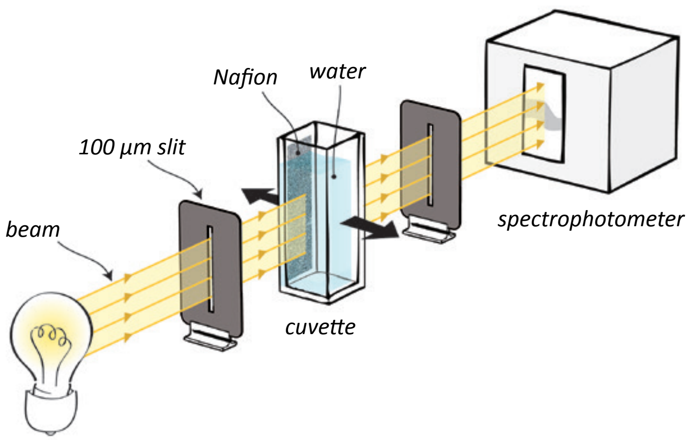


Fig. 3.13*a* *Measurement of light absorption. Moving the cuvette laterally allowed us to interrogate water at various distances from the Nafion surface.*

We bonded a sheet of Nafion to the inside face of a standard optical container, or cuvette, which we then filled with water. As the figure shows, we placed the cuvette in the path of a narrow window of light that would penetrate the water before reaching the spectrophotometer; moving the cuvette in measured increments let us investigate the light passing through regions both within and beyond the EZ.

Figure 3.13*b* shows the results. Far from the Nafion-water interface (beyond 400 μm), the spectrum was flat — i.e., the absorbed wavelengths of visible and near-visible light were no different from a blank water sample with no excluding surface present. That was anticipated. However, shifting the cuvette so that the illuminated window came closer to the Nafion-water interface and within the EZ caused a strong absorption peak to appear. Its wavelength was approximately 270 nm. The 270-nm absorption peak grew with the window's proximity to the Nafion surface and eventually dominated the absorption spectrum. Since no such peak appeared in the water beyond the EZ, it became clear that the absorption features of the EZ differ remarkably from those of the bulk-water zone.

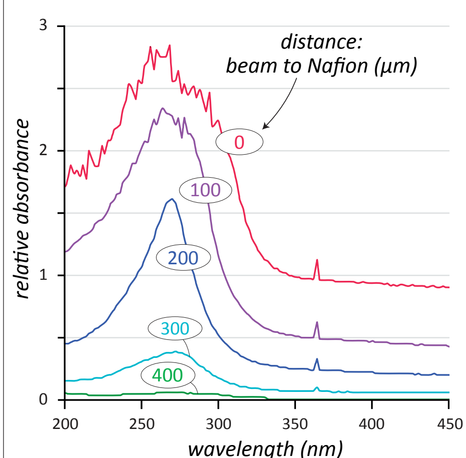


Fig. 3.13*b* *Absorption spectrum measured at various distances from the Nafion-water interface. Decreasing distances range from green to red. Numbers attached to each curve denote actual distances.*

(ii) Infrared absorption. Absorption differences can also be tested in the infrared region of the electromagnetic spectrum. Those longer wavelengths tell us something about molecular structure. **Figure 3.14** shows one result, a map of infrared absorption in and around a submerged triangular piece of Nafion. The different colors indicate different absorption magnitudes. Far from the Nafion, the uniform blue color indicates a uniformly low level of absorption. The color change closer to the Nafion (green) indicates that the EZ absorption differs from bulk water absorption.

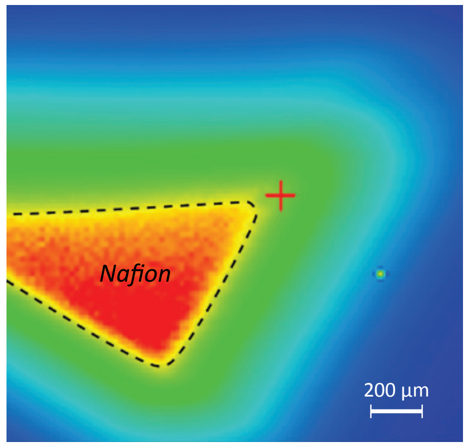


Fig. 3.14 *Triangular specimen of Nafion in water examined using infrared absorption. Color differences indicate differences of absorption. Blue is lowest.*

More detailed information may ultimately come from using thinner samples, but appropriately thin samples are challenging to produce; hence, their use may require technical advances. Nevertheless, the absorption differences seen in the current figure indicate that bulk water's structure differs from EZ water's structure.

(iii) Infrared emission. Our third approach used an infrared camera to measure the infrared radiation ("heat") emitted from a specimen. If the EZ's character differs from that of bulk water, then we might expect some difference in radiant emission.

To make the emission measurement, we placed a piece of Nafion in a shallow chamber containing water. We allowed the specimen to equilibrate for one hour. We then collected infrared radiation from the sample and averaged the radiation over multiple image frames. **Figure 3.15** shows a representative result. The dark region adjacent to the Nafion is the exclusion zone; it is dark because it radiates very little. More distant water regions radiate more brightly.

Interpreting the result requires some understanding of what determines infrared intensity. Hotter substances radiate more infrared — that's how airport thermal-image scanners can detect whether you have the flu and whether you may need to be quarantined for a week instead of lounging on the beach. Temperature, however, does not uniquely determine infrared intensity: intensity is the product of temperature and "emissivity" — the latter indicating the character of the emitting structure. Ordered, crystal-like structures emit less infrared energy than disordered structures because a crystal's molecular components move around less vigorously; those components are more stable. Thus, the generation of less infrared energy could mean either more stability or lower temperature.

Lower temperature does not explain the EZ's lower infrared emission seen in **Figure 3.15**. The records were averaged over extended periods of time during the experiment, so any temperature difference between the EZ and the bulk-water zone should have vanished. Emissivity differences seem the more plausible explanation. The darker EZ implies lower emissivity; i.e., the EZ is more ordered and crystalline than bulk water.

(iv) Magnetic resonance imaging. Magnetic resonance imaging (MRI) is a technique used for imaging tumors. Raymond Damadian, the pioneer who patented the technique, based his invention on the principle that water's character differs in different environments; this permits spatial imaging. In our MRI experiment, we placed a gel and adjacent water in the test area. The MRI imparts a pulsed magnetic field that excites water's atomic nuclei, whose protons then relax back down to their ground states. The relaxation time yields information on the degree of motional restriction relative to nearby molecules. The MRI computer then reconstructs this restriction data to create an image.

Figure 3.16 shows a map of relaxation times. Darker regions denote shorter relaxation times, which means more restriction. The map shows a dark band across the middle; this band coincides with the width and location of the EZ. Apparently, molecules within the EZ suffer more restriction than the water molecules beyond that zone.

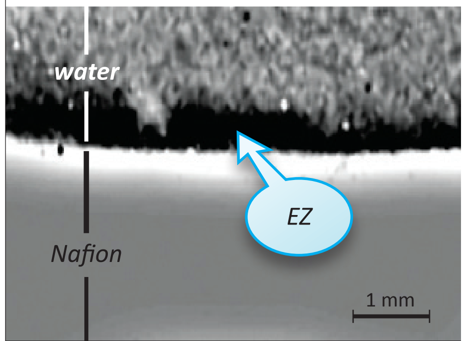


Fig. 3.15 *Infrared emission image of Nafion next to water. Sample was equilibrated at room temperature. Black band running horizontally across the middle of the image corresponds to the expected location of the exclusion zone.*

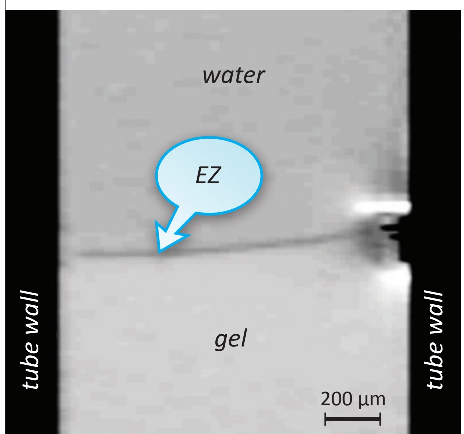


Fig. 3.16 *MRI map of relaxation times. The lower half of a capillary tube was filled with polyvinyl alcohol gel, while the upper half was filled with water. The dark band, corresponding to the gel's EZ, indicates more molecular restriction.*

This conclusion is not unique. An earlier study reported similar a restriction extending over even longer distances from material surfaces;[11] and a subsequent report from our laboratory[12] found that water near a surface exhibited a "chemical shift," which is jargon for implicating a different chemical species. Magnetic resonance techniques reveal substantial differences between EZ water and bulk water.

(v) Viscosity. We also measured viscosity, which reflects the degree of liquidity. Honey, for example, is more viscous than water. To test whether the viscosity of the EZ differs from that of bulk water, we used a technique called falling-ball viscometry. We lined the bottom of a small chamber with a sheet of Nafion and filled the chamber with water. Spheres of polymeric material were then dropped into the water. The spheres descended at a roughly constant velocity but progressively slowed as they entered the region of the exclusion zone **(Fig. 3.17)**. Speed reduction implies higher viscosity. This demonstrated that EZ water has a higher viscosity than bulk water.

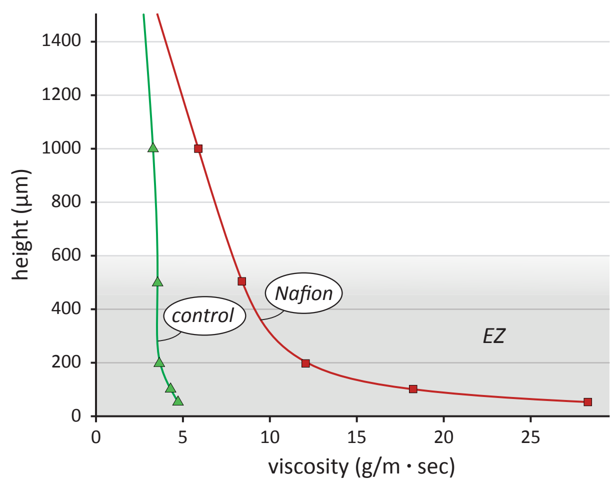


Fig. 3.17 *Viscous character of the EZ (shaded). We measured viscosity in water at various heights above a Nafion surface (red curve). Control (green curve) was obtained with a surface exhibiting little or no exclusion zone.*

(vi) Optical features. Two Russian groups independently measured the exclusion zone's refractive (light-bending) properties.[13,14] Both found that the EZ had a refractive index about 10 percent higher than that of bulk water. A higher refractive index ordinarily implies higher density; this suggests that EZ water is denser than bulk water.

All six sets of experiments — additional details of which are given elsewhere[4] — show that the water in *the exclusion zone differs in character* *from the water beyond the exclusion zone*. The differences are appreciable. EZ water is more viscous and more stable than bulk water; its molecular motions are more restricted; its light-absorption spectra differ in the UV-visible light range, as well as in the infrared range; and it has a higher refractive index. These multiple differences imply that EZ water fundamentally differs from bulk water. The EZ hardly resembles liquid water at all.

Order in the Exclusion Zone

To account for the nature of the EZ, our favored hypothesis was ordered water. The experimental results just considered seemed consistent with water ordering, but those experiments did not address the structural issue directly. For that, we needed other kinds of evidence.

We had good experimental reason to suspect order. Mae-wan Ho's wonderful book, *The Rainbow and the Worm*,[15] already adduced evidence for long-range order. Ho **(Fig. 3.18)** used a sensitive polarizing microscope. Polarizing microscopy is a standard method for detecting order, particularly in minerals. The principle is simple: if molecular structures line up, then the optical properties in the lined up direction will differ from those in orthogonal directions, giving rise to so-called birefringence. Ho shows structural lineups that extend over vast regions of a worm's body, concluding that the observed ordering comes largely from the ordering of water. **Figure 3.19** shows an image from her book.

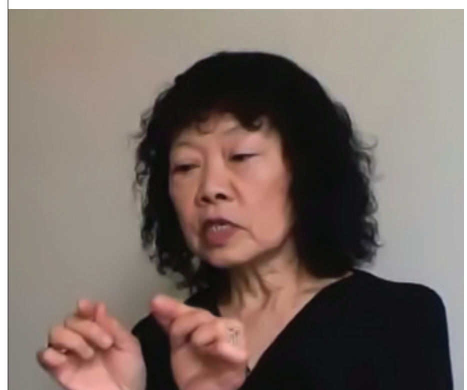


Fig. 3.18 *Maewan Ho.*

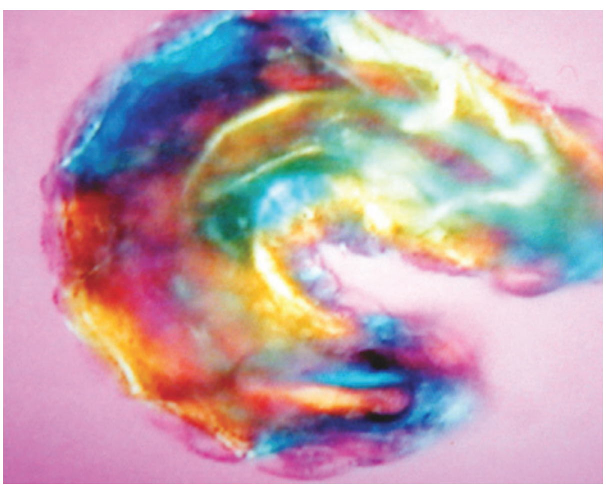


Fig. 3.19 *Freshly hatched Drosophila larva under the polarizing light microscope set up to optimize detection of liquid crystalline phases based on interference colors. The colors indicate that essentially all the molecules, including the water, are aligned; the particular colors depend on the orientation of the molecular alignment and their degree of birefringence. For more details, see Ho[15] pp. 219–221.*

Motivated by Ho to investigate this phenomenon, we set up our own polarizing microscopy system, which we used to explore water ordering in the vicinity of Nafion. Some experiments showed no clear birefringence, possibly because of insufficient sensitivity; other experiments gave positive results, which confirmed Ho's observations. **Figure 3.20** shows the water far from the Nafion interface as blue, indicating no preferred molecular orientation. Closer to the interface, the green color indicates a preferred molecular orientation. The ordered region corresponds to the zone of exclusion immediately adjacent to the Nafion. In other words, water in the exclusion zone is more ordered than the bulk water farther away.

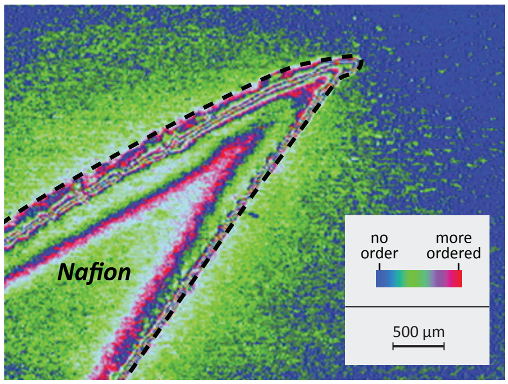


Fig. 3.20 *Arrowhead-shaped piece of Nafion sheet (delineated by broken line) in water, examined using polarizing microscopy. Blue color indicates a random orientation of molecules; red (see scale at right) indicates the highest degree of molecular ordering.*

The ordered zone in **Figure 3.20** is huge relative to water's molecular dimensions. Think of the water molecule's diminutive size: on the order of 0.25 to 0.3 nanometers (less than a millionth of a millimeter). The ordered zone in the figure corresponds to a lineup of approximately a million of those water molecules — like the lineup of marbles over dozens of football fields.

Two papers address the theoretical plausibility of such long-range ordering. One paper comes from the late Rustum Roy, a pioneer in the materials science field. Roy and his colleagues[16] stressed the precedent for certain surfaces to have a template-like effect, ordering molten materials into extensive crystalline arrays. Routinely used with semiconductor materials such as silicon, this process has made possible modern integrated circuits. It is also employed with molten aluminum. A similar process occurs during the formation of ordinary ice. Such precedents led Roy and his colleagues to suggest a similar template-based ordering of water molecules. They suggested that it was inevitable.

Arguing from a physicochemical point of view and from the results of numerous experiments, Ling[17] came to a similar conclusion: extensive ordering of water molecules nucleated from surfaces. Under ideal conditions, that ordering can extend to huge distances. That is, the proclivity to order can easily outweigh the natural tendency to disorder.

These two papers provide theoretical underpinnings for the molecular ordering we observed. They also offer a counterbalance against the commonly presumed impossibility of long-range ordering. On the other hand, unanswered questions remain. Neither the experimental evidence nor these theoretical considerations answers the questions: How exactly do the water molecules order themselves? Do water molecules merely stack? Or is some more elaborate type of reorganization at play? Answers to those questions will be coming next.

Reflections

I recognize that people nurtured on textbooks of modern chemistry may find little here that strikes a resonant chord. Textbooks imply something quite different from what we have found. Their emphasis on double-layer theory leads to the presumption that no more than a few layers of water molecules could possibly organize next to charged surfaces. Beyond those few layers, not much of note should be happening.

On the other hand, scientists have begun to recognize that water has properties not quite so mundane. Many water-based phenomena — a number of them considered in this book's opening chapter — have resisted explanation. Because of those difficulties, unsuspected features of water are now being considered more openly; i.e., the field has begun opening up to fresh and unexpected findings, one of which includes the long-range ordering of water.

Building on the evidence for long-range ordering, the next group of chapters uncovers an EZ structure surprisingly like ice. However, it is not ice. The ice-like ordering turns out to be the proverbial tip of the iceberg: something deeply consequential drives the buildup of ordered water in the EZ. That driving agent turns out to be a kind of energy common in everyday life and simple enough for anyone to understand.

Section V

Summing Up: Unlocking Earthly Mysteries


CONCLUSIONS

18 The Secret Rules of Nature

While chatting with students in the laboratory several years ago, suddenly the lights went out — I almost fainted. My health had been perfectly robust — so much so that my family doctor hardly knew my name or even recognized my face. Suspecting a tumor, he now recommended a brain scan. I wound up inserted into that long scary tunnel, waiting to learn whether my life was soon to be snuffed out.

The MRI (magnetic resonance imaging) technicians showed no hint of alarm. In fact, their nonchalance left me half expecting to hear some quip about the quality of my brain. No such quip came. I did nevertheless find myself musing over what we'd recently heard about someone else's brain — a prominent US politician of rather dubious intellect: following the MRI scan of his brain, his physician allegedly reported: "Sorry sir, but it seems there's nothing right on the left side, and nothing left on the right side."

Well, some healthy grey matter apparently remained in my own brain, after all. Everything seemed normal (as far as they could tell from the MRI).

The subject of MRIs is pertinent to all you've read. The MRI machine provides a detailed image of the brain's nooks and crannies based on the relaxation properties of protons. Since the overwhelming majority of the body's protons come from water, this means the MRI measures the properties of the body's water. If water were unaffected by local structures, then the machine would produce no image; everything would look the same. The MRI can successfully visualize your brain — for better or worse — because the brain's local environment profoundly affects nearby water.

Which brings us back to the central message of this book: water participates in virtually everything. Its behavior depends on location and microenvironment, and the efficacy of MRI technology testifies to that dependence, since it relies on water's capacity to organize itself differently next to different surfaces.

After wading through 17 watery chapters, you are surely entitled to a summary of the foregoing material and an indication where it might lead. Let me begin by describing how our approach fits into the general framework of science and then proceed to substantive matters — the messages you may wish to take home from this book.

The Culture of Science

Until the modern era, scientists focused on seeking foundational mechanisms. They tried to understand how the world works. If their efforts uncovered paradigms that could explain diverse phenomena in simpler ways, then they knew they were onto something meaningful. Thus, Mendeleev's periodic table could predictably account for the multitude of known chemical reactions, and Galileo's sun-centered solar system obviated the need to invoke complex epicycles to describe planetary orbits.

The pursuit of simplicity seems to have largely evaporated from the scientific scene. In four decades of doing science, I have seen this noble culture yield to one less audacious and more pragmatic. The chutzpah has vanished. Scientists content themselves with short-term gains in narrowly focused areas rather than seeking fundamental truths that may explain broad areas of nature. A quest for detail seems to have supplanted the quest for simple unifying truths (**Fig. 18.1**).

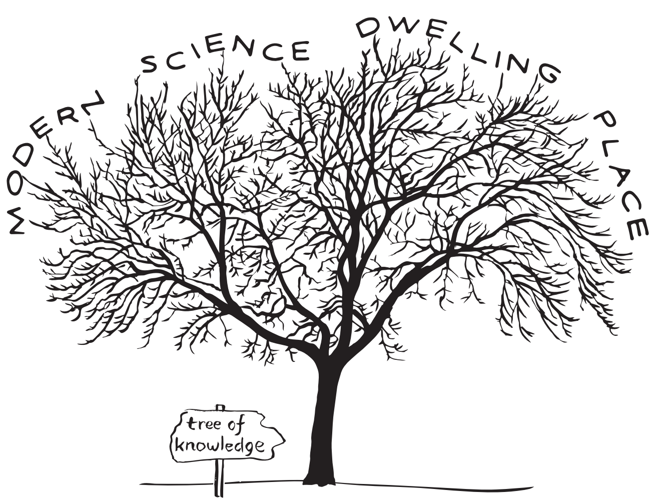


Fig. 18.1 *Science today focuses mainly on the twigs of the tree of knowledge, attempting to add incremental detail. It assumes that supporting limbs are robust.*

This minutae-oriented approach seems to me to bespeak a culture gone awry. You can judge this for yourself by considering the results — the scant number of conceptual revolutions that have emerged in the past three decades. I don't mean technical advances, like computers or the Internet, and I don't mean hype or *promised* revolutions, like cancer cures or endless free energy. I mean *realized conceptual revolutions* that have already *succeeded* in changing the world. How many can you identify?

Once bold, the scientific culture has become increasingly timid. It seeks incremental advances. Rarely does it question the foundational concepts on which those incremental advances are based, especially those foundational concepts that show signs of having outlived their usefulness. The culture has become obedient. It bows to the regality of prevailing dogma. In so doing, it has produced mounds of data but precious little that fundamentally advances our understanding.

I have tried to reverse this trend in these chapters by returning to the traditional way of doing science. By observing common, everyday phenomena and applying some simple logic, I have sought to answer the "how" and "why" questions that can lead to fundamental truths, while avoiding the "how much" and "what kind" questions that characterize the incremental approaches. I know it is not the fashion, but I think it offers a better path for achieving scientific progress.

The specifics of this book emerged out of a sense that something was dreadfully wrong with current thinking about water. I felt that nature should be simple at its core, yet everything I read seemed complicated. I could spout off textbook basics to anyone interested, but scratching beneath that veneer of understanding consistently exposed a substrate of questions that I found difficult to answer. That troubled me.

My search for understanding necessitated venturing into fields entirely new to me. At times, I found this unnerving, for vast bodies of knowledge seemed to lie beyond my scope of vision. On the other hand, I had the advantage of significant intellectual liberty: I wandered freely through those fields unencumbered by the constraints of the fields' orthodoxies. Few areas seemed sacred enough to remain unchallengeable.

My one goal has been to develop simple foundational principles that can lead to broad understanding. I did not pull those principles from a hat. Extracting them from the mass of relevant observations involved a long, hard journey. In the end, I believe those foundational concepts can be distilled into four central principles that govern our understanding of water.

Four Foundational Principles

Principle 1: Water Has Four Phases

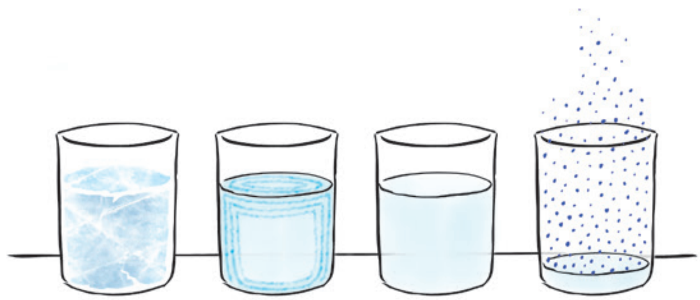


Fig. 18.2 *Water's four phases.*

From childhood, we have learned that water has three phases: solid, liquid, and vapor. Here, we have identified what might qualify as a fourth phase: the exclusion zone (**Fig. 18.2**). Neither liquid nor solid, the EZ is perhaps best described as a liquid crystal with physical properties analogous to those of raw egg white.

The term "exclusion zone" may be an unfortunate one. My friend John Watterson coined the term early on, when the most obvious feature of that zone was its exclusionary character. That definition stuck. We had fun quipping that "EZ" sounded like "easy," the opposite of hard. Hard water is full of minerals, which EZ water excludes. So the name seemed apt. In retrospect, the "liquid crystalline" phase, or the "semi-liquid" phase might have made better sense, as those descriptors fit more naturally within the phase-oriented taxonomy.

Be that as it may, the sequence of phases usually spouted off reflexively differs from what we have learned here. If the foregoing chapters offer a valid explanation of water's character, then a more appropriate phase sequence would be solid, liquid-crystalline, liquid, and vapor — *four phases, not three*.

With this fresh understanding, who knows? Undergraduates could one day find freshman chemistry far less daunting.

Principle 2: Water Stores Energy

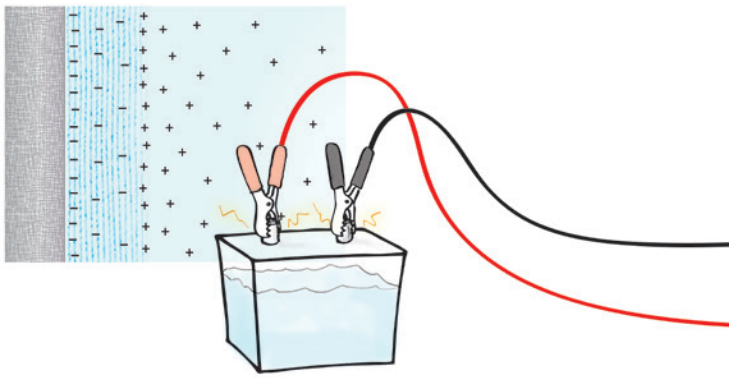


Fig. 18.3 *The water battery.*

Water's fourth phase stores energy in two modes: order and charge separation. Order constitutes configurational potential energy, deliverable as the order gives way to disorder. For the working cell, this order-to-disorder transition constitutes a central energy delivery mechanism.[1] Charge separation, the second mode, entails electrons carrying the EZ's usual negative charge, while hydronium ions bear the corresponding positive charge. Those separated charges resemble a battery — a local repository of potential energy (**Fig. 18.3**).

Nature rarely discards repositories of available energy. It wisely parses out that energy for its diverse needs. Examples have been described throughout this book, and many more exist.

Albert Szent-Györgyi, the father of modern biochemistry, famously opined that the work of biology could be understood as the exploitation of electron energy. The EZ offers a ready source of electrons that could drive any of numerous biological reactions. The complementary hydronium ions may play an equally vital role. Positive ion concentrations build pressure, which can drive flows. Flows exist practically everywhere: in primitive and developed cells; in our circulatory systems; and in the vessels of short plants and tall trees. Hydronium ions could drive many of those flows.

The EZ's potential energy can also drive practical devices. One such device is a water purifier. Because the EZ excludes solutes, including contaminants, harvesting the EZ amounts to collecting untainted water. A simple and remarkably effective prototype has already been demonstrated.[2] It amounts to a filterless filter that achieves purification courtesy of incident electromagnetic energy.

So the potential energy associated with water's fourth phase can be exploited in different ways. Energy and water are practically synonymous. That's the reason for proposing (Chapter 7) the equation $E = H_2O$. That equation may suffer a mismatch of units, but it does capture the essence of the second principle: *water stores energy*.

Principle 3: Water Gets Energy from Light

Fig. 18.4 *The main source of electromagnetic energy on earth.*

Everyone understands that the sun illumines the earth and drives many earthly processes. What's new here is that the sun (along with, perhaps, other cosmic and earthly sources) may drive processes beyond the obvious — especially those involving water (**Fig. 18.4**).

The sun's electromagnetic energy builds potential energy in water. Photons recharge the EZ by building order and separating charge. They do this by splitting water molecules, ordering the EZ, and thereby setting up one charge polarity in the ordered zone and the opposite polarity in the bulk water zone beyond.

We don't ordinarily think of water as receiving energy. A glass of water is considered more or less in equilibrium with its environment. However, the evidence outlined in these chapters shows distinctly otherwise: a glass of water is generally far out of equilibrium. This concept may sound outlandish, but the foregoing chapters have amply demonstrated that water continually absorbs energy from the environment and transduces that energy into work.

The transduction concept may seem less exotic once you realize that plants do the same. Plants absorb radiant energy from the environment and use it for doing work. Plants, of course, comprise mostly water; therefore, it should hardly surprise that the glass of water sitting beside your potted plant may transduce incident photonic energy much like the plant does.

It may be worthwhile to take a fresh look at any scenario in which radiant energy falls incident on water. Our focus has been mainly on chemistry, but physics — and especially biology — should be considered as well. For example, when the sun breaks through the clouds, we may feel a surge of energy. That sensation surely involves our psyches; however, we may feel energized also because the incident solar energy builds real chemical energy in our cells. Some wavelengths penetrate deeply into our bodies — just place a flashlight behind the palm of your hand and watch the light penetrate all the way through to the other side.

To suggest that incident solar energy may build energy in our bodies may seem a stretch, but cells do grow faster with warmth, i.e., when exposed to infrared energy (light). Since light builds energy in water, and we are mostly water, it seems plausible that we might harvest energy from the environment. Multiple light-harvesting mechanisms can be envisioned throughout biology.

Similar principles may apply in physics and engineering. For example, harvesting light energy absorbed in water may enable the production of useful electrical energy. EZ charge separation closely resembles the initial step of photosynthesis, which entails the splitting of water next to some hydrophilic surface. This resemblance may be auspicious: if that first step works as effectively as it does in photosynthesis, then some kind of water-based harvesting of light energy may have a promising future. Designs built around water might one day replace current photovoltaic designs.

At any rate, *electromagnetic energy builds potential energy in water*, which then becomes an energy repository. That energy can radiate back toward the source from which it came, and/or it can be harvested for doing work. The energy is a gift from the environment; it is genuinely *free* energy, which we can perhaps exploit for resolving today's energy crisis.

Principle 4: Like-Charged Entities Can Attract One Another

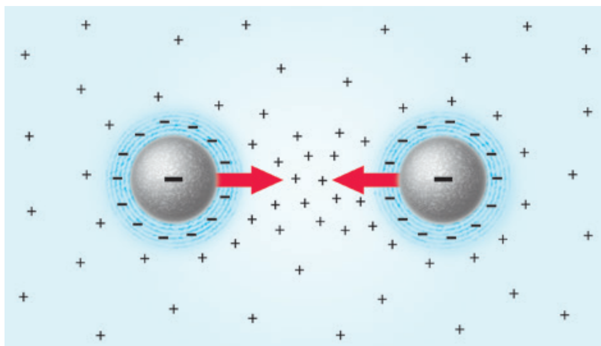


Fig. 18.5 *Mediated attraction of likes by unlikes.*

Perhaps the least obvious principle is the like-likes-like attraction (**Fig. 18.5**). The idea that like charges can attract one another seems counterintuitive until you recognize that it requires no violation of physical principles. The like charges themselves don't attract; the attraction is mediated by the unlike charges that gather in between. Those unlikes draw the like charges toward one another, until like-like repulsion balances the attraction.

Many physicists presume that like-to-like attraction cannot exist in spite of acceptance by some well-known physicists, including

Richard Feynman. Feynman coined the phrase "like-likes-like through an intermediate of unlikes." He understood that such attraction might be fundamental to physics and chemistry. Nevertheless, the majority of scientists reflexively presume that like charges must always repel. Hardly a fleeting thought is accorded the prospect that those like charges might actually *attract* if unlike charges lie in between.

This resistance may originate from the semantics: who could imagine that "like charges attract"? Surely any such phenomenon must seem like the work of the devil or, at best, of some naive charlatan. The reflexive presumption that like charges must always repel has almost certainly led to unnecessarily complex interpretations or just plain wrong answers. What could be more fundamental than the force between two charges?

This book gives substance to the early understanding of like-likes-like. It goes on to identify a source of unlike charges. Abundant unlikes come from EZ buildup, providing the ample supply of protons needed to explain the attraction.

Beyond laboratory demonstrations, the like-to-like attraction may apply broadly throughout nature, from the microscopic to the macroscopic. One possible example is in life's origin. The origin of life likely involves the concentrating of dispersed substances into condensed entities; without such condensation, no cell or pre-cell could form. The like-like-likes attraction provides a natural mechanism for mediating this kind of self-assembly: just add light, wait a bit, and voila!

Another example can be found in atmospheric clouds. Clouds are built of charged aerosol droplets. By conventional thinking, such droplets should repel and disperse; however, the like-like-likes mechanism explains why those droplets can actually coalesce into the entities that we recognize as clouds. The sun provides the energy, and the opposite charges provide the force.

Whenever like-like repulsion is proffered to explain some phenomenon, ask yourself whether the opposite — a like-to-like *attraction* — offers a better explanation. In some instances, you might find yourself walking along a fruitful path, increasing the prospect of developing a simpler and more accurate understanding of nature.

• • •

The four principles just outlined can be viewed as rules of nature, formerly obscured in some remote corner and now unveiled in a clearer light (**Fig. 18.6**).

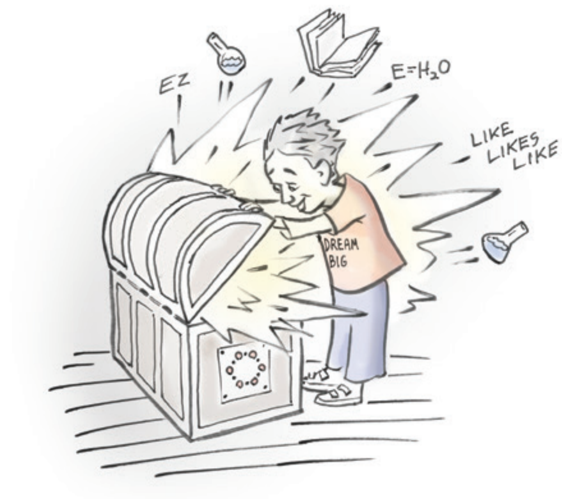


Fig. 18.6 *Bringing hidden principles to light.*

These principles seem rich with explanatory power. They help answer simple "why" and "how" questions: Why do gels hold water? How can champagne bubbles proliferate in streams seemingly without end? How can simple hydrated wedges split apart massive boulders? How does water rise to the tops of giant redwood trees? Why do you see clouds of vapor above your hot coffee? Why does ice make you slip and fall on your face? The principles can explain many other questions whose answers have remained elusive.

Because of their vast explanatory power, I believe these four principles may prove foundational for much of nature.

Why Have These Principles Remained Secret?

If these principles are as useful as claimed, then why have they remained secret for so long? How have they escaped inclusion in the repository of common understanding?

At least four reasons come to mind.

- First, *water science has had a checkered history*. The polywater debacle left scars; it kept curious scientists away from water for decades. Any researcher confident enough to enter the arena and fortunate enough to discover something unexpected was inevitably attacked with the recycled darts used to ridicule polywater. Surely their water must have been contaminated (even though natural water is anything but pure); therefore, their results can be safely dismissed with a wave of the hand. Then came water memory. Memory stored in water seemed so improbable that it became the butt of scientific jokes: Having trouble remembering names? Try drinking more water — it will restore lost information.

Thus, the field of water was twice stung. With critics and their scorn awaiting at every turn, what prudent scientist would venture into the field of water research? Water became treacherous to study. Immersing oneself in water science has become as perilous as immersing oneself in corrosive acid.

• A second reason for the slow emergence of understanding is water's ubiquity. Water is everywhere. Water occupies a place central to so many natural processes that *few people can conceive that the basics could remain open to question*. Surely someone must have worked out those basics, probably a century or two ago. This perception keeps scientists away. If anything, their reluctance has only intensified: today's science rewards those who focus narrowly on trendy areas, leaving little room for questioning widely taught foundational science. Especially for something as deeply rooted and common as water, the incentive to question fundamentals has all but vanished.

• A third reason for the slow emergence of such fundamental principles plagues all of science: intellectual timidity. *Relying on received wisdom feels safer than dealing with the uncertainties of revolutionary disruption.* You'd think that scientists would embrace dramatic advances in fundamental science, but most of them feel more comfortable restricting themselves to minor deviations from the *status quo*. Scientists can resist revolution in the same way as any other defender of orthodoxy.

• A fourth reason is *outright fear*. Challenging received wisdom means stepping on the toes of scientists who have built careers on that wisdom. Unpleasant responses can be anticipated. For example, I have here trampled on a lot of sacred ground. I anticipate due reprimand, particularly from those scientists whose recognition, grants, patents, and other attributes of power depend on defending their scientific standing. A child might be forgiven for such apostasy; senior scientists, alas, are rarely accorded the courtesy. Thus, many career-oriented researchers maintain conservative postures, keeping their distance from anything that even smells like revolutionary challenge. That posture helps keep bread on their scientific tables.

To summarize, at least four factors bear responsibility for the painfully slow emergence of new principles: (*i*) the blighted history of the water field has kept scientists away; (*ii*) water is so common that everyone presumes that the fundamentals have been resolved; (*iii*) deviating from mainstream views can be unsettling; and (*iv*) questioning the prevailing wisdom has always been a risky business, in science as elsewhere.

These obstacles have combined to produce a long-term stall. I am trying my best to crank up that stalled engine.

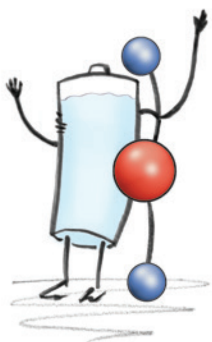
The Future

We began by asking a simple question: why do exclusion zones exclude? The more we looked, the more we found. Finally, there emerged four general principles, and various insights, which you have encountered scattered throughout the book.

Seeing how far those principles can take us is a temptation to which I have admittedly succumbed. I originally intended to include material on physics and biology in this book, but readers of preliminary drafts prevailed on me to stick to water's chemistry. However, the principles elaborated here extend naturally into other scientific domains; therefore, I plan to follow up with additional books. There is much to say, particularly about physics and biology.

The key to making progress in all of these arenas must include a fresh willingness to admit that the emperor has no clothes. Even the greatest of scientific heroes might have erred. Those scientists were human: they ate the same kinds of food we eat, enjoyed the same passions we enjoy, and suffered the same frailties to which we are prone. Their ideas are not necessarily infallible. It might seem irreverent, but if we hope to penetrate toward ground truth, we need the courage to question any and all foundational assumptions, especially those that seem vulnerable. Otherwise, we risk condemning ourselves to perpetual ignorance.

Where such explorations might lead, nobody can say. Within the domain of uncertainty lies the charm of the scientific pursuit: through unfettered experimentation, logical thinking, and the occasional good luck of stumbling upon the unexpected, we may begin to illumine the dark recesses of nature.



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