# Maxwell Matters

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## Abstract

Charges are everywhere because most atoms are charged. Chemical bonds are formed by electrons with their charge. Charges move and interact according to Maxwell's equations in space and in atoms where the equations of electrodynamics are embedded in Schrödinger's equation as the potential. Maxwell's equations are universal, valid inside atoms and between stars from times much shorter than those of atomic motion (0.1 femtoseconds) to years (32 mega-seconds). Maxwell's equations enforce the conservation of current. Analysis shows that the electric field can take on whatever value is needed to ensure conservation of current. The properties of matter rearrange themselves to satisfy Maxwell's equations and conservation of current. Conservation of current is as universal as Maxwell's equations themselves. Yet equations of electrodynamics find little place in the literature of material physics, chemistry, or biochemistry. Kinetic models of chemistry and Markov treatments of atomic motion are ordinary differential equations in time and do not satisfy conservation of current unless modified significantly. Systems at equilibrium, without macroscopic flow, have thermal fluctuating currents that are conserved according to the Maxwell equations although their macroscopic averages are zero. The macroscopic consequences of atomic scale fluctuating thermal currents are not known but are likely to be substantial because of the nonlinear interactions in systems like these, in which 'everything interacts with everything else'.

Conclusion: ***current needs to be conserved in models of material systems, even in simplified versions.***

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# Maxwell Matters

*The reader who prefers equations to words can turn to p.6.*

**Introduction.** Atoms have electric charge, so electricity matters. All of life occurs in solutions with ions. Water without ions is toxic. The ions have charge. Ions are dissolved by water molecules that are strongly charged in some places, although the total charge of one water molecule is zero. The macromolecules that make the structures of life are charged. The proteins, nucleic acids (DNA and RNA), and organic molecules that are the biochemical machinery of life have electric charge, often at surprisingly high density (Jimenez-Morales, Liang, and Eisenberg 2012). Charges are likely to be highly concentrated where they are important, in technology and in life.

Charge creates forces (and moves) according to the Maxwell equations celebrated in every textbook of electrodynamics. Those equations accurately describe an enormous range of phenomena. Our electrical technology is possible because it is designed by equations, much more than by trial and error. Equations can be used, without trial and error, because they are accurate and transferable from one set of conditions to another. The equations of electrical and electronic technology require little tuning of parameters as conditions change. The contrast with biochemistry is striking. The equations of biochemistry need substantial tuning as conditions change (Eisenberg 2014). The important success of semiconductor technology–that has remade our world in less than fifty years–would hardly be possible if the trial and error methods of experimental biochemistry and biophysics were used to design semiconductor devices and the integrated circuits and computers built from them.

Biochemistry (along with most of chemistry) is about making new molecules by changing their electrons and their orbitals. The energy of these electrons is described by the combination of quantum mechanics and Maxwell's equations written as the Schrödinger equation. The potential term of the Schrödinger equation is a solution of the Maxwell equations.

Electrons of course are an ultimate source of charge with diameter less than $10^{-17}$ meters (Gabrielse and Hanneke 2006) and no detectable substructure. They have the remarkable property that their charge is the same, no matter how fast they move, unlike their mass or their spatial dimensions, all of which change as velocities approach the speed of light, according to the Lorentz transformations of special relativity. This special relativistically invariant property of electrons is confirmed experimentally in the many bright photon sources used in structural biology: those sources are synchrotrons that depend on the relativistic properties of electrons moving at speeds very close to the speed of light. (The 7 GeV beam in the Advanced Photon Source at Argonne moves electrons at >99.999999% of the speed of light.)

But the equations of electricity do not play a prominent role in textbooks or teaching of chemistry. Maxwell equations are not found there and electricity itself is hardly mentioned in biochemistry and its textbooks, elementary or advanced.

**Maxwell Matters.** Equations (1-4) are meant to show that *Maxwell Matters* in a concise, convincing, but somewhat abstract way.

This paper is a successor to a long paper arXiv:1502.0725 (Eisenberg 2016) that is more concrete than abstract, showing how *Maxwell Matters* as electricity and charge move in many situations and giving many references to the extensive literature. The discussion of Fig. 2 (Eisenberg 2016) in particular describes how charge moves in wires, salt solutions, resistors, commercial capacitors, vacuum capacitors, vacuum tube diodes, and semiconductor diodes and devices. The current through all these devices is exactly equal at all times and locations and

conditions because of conservation of current (Kirchoff's law) in the series circuit, ***even though the physics of current flow is very different in each device.*** The displacement current $\varepsilon_0 \partial \mathbf{E}/\partial t$ takes on whatever value it needs—at every time and location—to guarantee conservation of current, see eq.(4).

Maxwell introduced the idea of 'displacement current' $\varepsilon_0 \partial \mathbf{E}/\partial t$ so the pre-existing laws of electrostatics (Coulomb's law and Poisson's equation), and magnetism (Ampere's law), could describe the unlimited propagation of waves, including the propagation of light. Displacement current exists (and thus flows) in a vacuum in a way Maxwell found hard to visualize or explain, as have many others including me.

But there is no doubt that $\varepsilon_0 \partial \mathbf{E}/\partial t$ exists. Light exists because of the $\varepsilon_0 \partial \mathbf{E}/\partial t$ term, so displacement current exists in a vacuum, whether or not I can visualize its causes. Light exists because $\varepsilon_0 \partial \mathbf{E}/\partial t$ helps create magnetic fields according to Maxwell's version of Ampere's law—our eq. (1)—that in turn creates electric fields. Electric and magnetic fields are coupled together to form radiation like light, that propagates through a vacuum forever.

Here I show again what has been known for a very long time: the fundamental equation of electromagnetism—Maxwell's generalization of Ampere's law eq. (1)—implies that 'current' is conserved.[1] I use a derivation and representation that emphasizes the generality of conservation of current.

Our formulation eq. (1-4) does not involve the problematic (and bewilderingly complex) properties of polarization charge and displacement current in matter. This formulation avoids the misleadingly named 'dielectric constant' $\varepsilon_r$. ***The textbook name for $\varepsilon_r$ as dielectric 'constant' seems bizarre to me*** because experiments show that $\varepsilon_r$ is almost never constant. It varies as conditions change and it always depends on time. For example, $\varepsilon_r$ varies by a factor of around 40× in sea water in experiments or in simulations starting at $10^{-15}$ sec reaching to phenomena at $10^{-6}$ sec. The polarization charge conventionally described by a supposedly constant $\varepsilon_r$ actually varies in so many different ways that no one knows how to describe it in a reasonably general way. Formulas that involve $\varepsilon_r$ cannot be universal unless formulas for $\varepsilon_r$ are universal.

**Conservation of current is universal.** Maxwell equations are true everywhere, at all times and locations, from inside atoms to between stars, we are told by physicists who spend lifetimes comparing theory and experiment.

If the Maxwell equations are universal, eq. (1-3) show that conservation of current is also universal. Conservation of current is then true everywhere, at all times and locations. ***The electric field takes on whatever value it needs—***at every time and location—***to guarantee conservation of current,*** see eq.(4). New mechanisms of current flow appear if needed to satisfy Maxwell's equations and conservation of current.

The formulation of conservation of current in eq. (1-4) is important because it displays conservation in terms of universal variables without confusion from the nonuniversal properties of matter and $\varepsilon_r$.

The universality of conservation of current is important. Many simplified models in the literature of biochemistry and biophysics do not satisfy conservation of current (Eisenberg 2014)

[1] The definition of current as whatever creates **curl B** is discussed in Section 2, along with alternative definitions.

until they are significantly modified. Most chemical kinetic models (using the law of mass action) and Markov models using only ordinary differential equations in time suffer from this defect.

**Physical mechanisms accommodate conservation of current.** Current is conserved no matter what the detailed mechanism of that current flow.

Maxwell's equations change the value of $\varepsilon_0 \partial \mathbf{E}/\partial t$ (and thus the value of $\mathbf{E}$ specified by eq. 4) to force physical mechanisms to obey the conservation of current (eq. 2 & 3) exactly, no matter what the physical mechanism, or what new physical mechanism needs to appear.

The physics of charge movement is illustrated at length in the discussion of many different types of current flow, in the series circuit shown in Fig. 2 of (Eisenberg 2016). Atomic scale mechanisms accommodate the Maxwell equations as illustrated in the wires, salt solutions, resistors, commercial capacitors, vacuum capacitors, vacuum tube diodes, and semiconductor diodes and devices of that circuit.

Continuity of current does not arise as a consequence of atomic properties or of conservation of matter. It arises because of the universal properties of electrodynamics.

Conservation of current is exact because of the $\varepsilon_0 \partial \mathbf{E}/\partial t$ term. The $\varepsilon_0 \partial \mathbf{E}/\partial t$ does not involve material properties. The $\varepsilon_0 \partial \mathbf{E}/\partial t$ term can vary so that Maxwell's equations and current conservation are exact, at every time and location. The time rate of change of the electric field $\partial \mathbf{E}/\partial t$ can take on whatever value it needs (at any time and any location) to guarantee that current is conserved exactly everywhere and at every time.

Amazingly, the abstract conservation law (eq. 2) changes the atomic properties of systems and sometimes introduces new physics and mechanisms into a system. In every day experience, $\partial \mathbf{E}/\partial t$ and electric fields can become large enough to change the physics of charge flow, introducing phenomena not in the original intuitive description of circuits.

Pulling the power plug from the electrical socket in a wall can create electric fields large enough to create a spark. The fields ionize air, creating a plasma that sparks in the dark. The electric fields become large enough to destroy the normally insulating properties of air. ***The equations of the normally insulating air must be changed if we wish to describe the spark we observe***. ***The constitutive equations need to be generalized to deal with the effects of the enormous electric field needed to preserve continuity of current.***

**Maxwell Matters in the models and theories of science** in a way not widely recognized. ***Current is conserved everywhere, so it must be conserved in the theories and models of science.*** Many of the models and theories of science are simplified so they depend only on time, using ordinary differential equations in time. These models do not satisfy conservation of current unless additional constraints are added.

Sadly, the equations of chemical and enzyme kinetics, and of Markov models in general, are in this class. A simple computation of the charge that moves in the kinetic or Markov scheme $\mathbf{A} \rightleftarrows \mathbf{B} \rightleftarrows \mathbf{C}$ (Eisenberg 2014) shows that the current from **A** to **B** does not equal the current flowing from **B** to **C** unless additional constraints are imposed. The additional constraints are likely to change the ***qualitative*** nature of the kinetic or Markov scheme because it needs to include the displacement current $\varepsilon_0 \partial \mathbf{E}/\partial t$ .

**History.** Kinetic schemes of chemical reactions, and of Markov models use ordinary differential equations that depend only on time. They ignore differential terms in space. The simplification to deal with just time is more than understandable historically. Ordinary equations could be

understood and computed long ago, before computers and numerical methods were available to deal with partial differential equations in space and time. But the laws of physics do not change because of our technological and intellectual limitations. ***Conservation of current involves space. Models and theories that use only time derivatives need to conserve current.***

**Equilibrium systems.** Maxwell matters even in equilibrium thermodynamic systems that seem at first not to involve current flow, because all systems, including thermodynamic systems at equilibrium without macroscopic flow, are made of atoms in thermal motion. These thermal motions produce local currents even in systems without global current flow. The thermal motion of the charged atoms that make up matter produce local variations in the density of charge and thus in the local electric field. These local variations are different in different places. (After all, that is what the word 'local' means.) Spatial variations in the electric field imply current flow. Molecular dynamics simulations visualize these current flows and confirm their size and importance.

Thermal fluctuating movements of charge average to zero, but the fluctuations produce $\varepsilon_0 \partial \mathbf{E}/\partial t$ and thereby fluctuating currents that are not zero. The ***fluctuating thermal currents are conserved*** just as all current is conserved. Even though the thermal fluctuations average to zero, they need to satisfy equations (1)-(2) ***in every time interval and region of space, no matter how brief or small.***

Thermal fluctuations are described by coupled nonlinear field equations in which 'everything interacts with everything else.' The thermal fluctuations in current are likely to have effects on many time and length scales as the nonlinearity converts atomic fluctuations into macroscopic phenomena.

The significance of these thermal fluctuating currents in thermodynamic equilibrium systems—in systems without macroscopic flow—is not clear to me. In some cases the fluctuating thermal currents will average out and not have macroscopic effects (although atomic scale effects will be observable by experiments with atomic resolution). But the question remains what are those cases? What are the situations in which the fluctuating thermal currents do not average out? The implications of conservation of current in thermodynamics remains to be investigated.

## Conclusion: Maxwell Matters

**Maxwell's equations need to be included in all our models** and theories, in my view. Approximate and reduced models need to respect the conservation of current with little error because of the enormous strength of the electric field so vividly described in the third paragraph of Feynman's textbook on electricity and magnetism (Feynman, Leighton, and Sands 1963).

The rest of this paper is written tersely to emphasize the generality of its results. Extensive verbal discussion can be found in (Eisenberg 2016) including estimations of the size of various effects.

# Section 1: Conservation of Current[2]

Maxwell's generalization of Ampere's law is needed to ensure the existence of (a wave equation for) light.

$$\mathbf{curl}\left(\mathbf{B}/\mu_0\right) = \underbrace{\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}}_{\text{'Current'}} \qquad \textit{Note the subscript zero on } \varepsilon_0 \textit{. It is crucial.} \qquad (1)$$

In math language,

$$\mathbf{div}\underbrace{\left(\mathbf{J} + \varepsilon_0\, \partial\mathbf{E}/\partial t\right)}_{\text{'Current'}} = 0 \qquad \textit{because } \textbf{\textit{div curl}} \textit{ = 0 is an identity.} \qquad (2)$$

In physical language,

$$\underbrace{\mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}}_{\text{'Current'}} \text{ is conserved exactly, always, everywhere.} \qquad (3)$$

**Remark:** The special term $\varepsilon_0\, \partial\mathbf{E}/\partial t$ also describes what happens in empty space, where $\mathbf{J} = 0$. $\varepsilon_0\, \partial\mathbf{E}/\partial t$ is sometimes called the vacuum displacement current. In a vacuum, no matter interferes with the perfect time-independent linear relation between 'current' and the magnetic and electromagnetic field. The 'current' is a linear function of $\mathbf{E}$ that is instantaneous (without delay) with a proportionality constant that is truly constant, independent of anything.

***The special term*** $\varepsilon_0\, \partial\mathbf{E}/\partial t$ ***also exists inside matter:*** atoms are almost all empty space (with their mass concentrated into a tiny nucleus). Maxwell equations are 'universal' in vacuum and in matter, from inside atoms to between stars, from time scales of $\gamma$-rays (even cosmic rays) to steady state, with an accuracy of at least 1 part in $10^{18}$.

**In words,** the continuity equation (2) says

'Current' defined as $\mathbf{J} + \varepsilon_0\, \partial\mathbf{E}/\partial t$ is conserved exactly, always, everywhere

$\mathbf{E}$ can be whatever it needs to be to ensure that $\mathbf{div}\left(\mathbf{J} + \varepsilon_0\, \partial\mathbf{E}/\partial t\right) = 0$.

$\mathbf{E}$ can be whatever it needs to be because of the vacuum term $\varepsilon_0\, \partial\mathbf{E}/\partial t$.

The vacuum term $\varepsilon_0\, \partial\mathbf{E}/\partial t$ is ***independent of matter.***

so $\partial\mathbf{E}/\partial t$ can assume ***any value it must*** to ensure $\mathbf{div}\left(\mathbf{J} + \varepsilon_0\, \partial\mathbf{E}/\partial t\right) = 0$,

no matter what are the properties of matter and $\mathbf{J}$.

[2] The definition of current is discussed in Section 2, along with alternative definitions.

# Section 2: J in Maxwell's Generalization of Ampere's Law

The definition of current requires discussion. A different way to write eq. (2) is to use the variable $\mathbf{J}_{\text{transport}}$ instead of $\mathbf{J}$.

$$\mathbf{curl}\left(\mathbf{B}/\mu_0\right) = \mathbf{J}_{\text{transport}} + \underbrace{(\varepsilon_r - 1)\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}}_{\text{Material Displacement}} + \underbrace{\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}}_{\text{Vacuum Displacement}} \qquad (2^*)$$

$\varepsilon_r$ is the dielectric coefficient that involves many parameters of the material system. It is not clear how these dependencies can be written in general because this is a system in which everything interacts with everything else. The dielectric coefficient $\varepsilon_r$ has the dimensionless value of 79 for water at room temperature at long times and the value ~2 at the short times involved in atomic motion ($10^{-15}$ sec). The polarization charge described by the dielectric coefficient responds with delay to changes in the electric field: the dielectric coefficient must be specified by a constitutive equation that involves convolutions with time even in the simplest cases. For that reason, I avoid statements of the continuity equation (2) that display the problematic term $(\varepsilon_r - 1)\varepsilon_0$ as if it were a constant.

Everyone knows $(\varepsilon_r - 1)\varepsilon_0$ is not constant. Statements of conservation of current that include $(\varepsilon_r - 1)\varepsilon_0$ should be avoided (in my opinion) because they are misleading unless they describe $(\varepsilon_r - 1)\varepsilon_0$ realistically over the whole range of time and conditions relevant to the problem at hand. Statements of conservation of current that involve $(\varepsilon_r - 1)\varepsilon_0$ cannot be universal because $(\varepsilon_r - 1)\varepsilon_0$ is not universal.

**Conservation of current need not involve properties of materials.** The statement of conservation of current (eq. 1-3) does not involve the properties of matter. Eq. (1-3) depend on the properties of the vacuum $\varepsilon_0$ not on the material dielectric coefficient $\varepsilon_r$. Eq. (2-3) seem as universal as they are because they do not include the material variables $\varepsilon_r$ and $\mathbf{J}_{\text{transport}}$.

**Transport flux is more complex than it seems.** $\mathbf{J}_{\text{transport}}$ includes flux (i.e., transport) of charged particles, as specified by (for example) *PNP* (Poisson-Nernst-Planck) equations for electrodiffusion. But $\mathbf{J}_{\text{transport}}$ also includes subtle and complex coupled types of transport.

Dielectrophoresis is an example of complexities that occur in real ionic systems. Consider dielectrophoresis of 'uncharged' particles in an ionic solution. In dielectrophoresis, particles with zero permanent charge can be transported by the electric field because the particles have induced polarization charge. That is to say, in formal terms, $\partial^2\mathbf{E}/\partial x^2 \neq 0 \implies \mathbf{J}_{\text{transport = dielectrophoresis}} \neq 0$. Phenomena like dielectrophoresis produce ***both*** transport $\mathbf{J}_{\text{transport}}$ and material displacement as defined in eq.(2*).

I prefer the formulation eq. (2) to that of eq. (2*) because eq. (2) does not separate one physical phenomenon (like dielectrophoresis) into misleadingly distinct terms described by two apparently independent constitutive equations, one for $\mathbf{J}_{\text{transport = dielectrophoresis}}$; the other for $\varepsilon_r - 1$.

The first and second terms on the right hand side of eq. (2*) are rarely independent. In most cases, the terms are coupled to many other charges through the electric field that they all share. In dielectrophoresis, the terms are actually produced by the same underlying mechanism.

**Variational methods.** In my opinion, coupled phenomena like dielectrophoresis need to be described by energy variational methods that derive field equations from an Euler Lagrange

process. The Euler Lagrange process ensures that all cross terms in constitutive equations are consistent.[3]

Attempts to separate transport and material terms before deriving the Euler Lagrange field equations are tricky and likely to lead to error. Cross terms are easy to overlook, inadvertently. The definition of 'transport' and 'material displacement' is unlikely to be unique before Euler Lagrange equations are actually derived from a variational principle. Different workers are likely to classify components of transport and displacement in different ways until the Euler Lagrange is used to display explicitly all the components needed in a self-consistent analysis.

***After*** the variational analysis is completed and Euler Lagrange equations have been actually derived, coupled phenomena like dielectrophoresis are described by a unique set of field equations and boundary conditions, including cross terms. Coupled phenomena can ***then*** be separated into transport and material displacement terms and workers can agree on the names and classification of cross terms.

## Section 3: Formulae for E

We now write a formula for the electric field that guarantees that Maxwell eq. (1) and continuity of current (2) are satisfied. We start with equation (2)

$$\mathbf{div}\left(\mathbf{J}+\varepsilon_0\,\partial\mathbf{E}/\partial t\right)=0 \tag{2}$$

Eq. 2 is satisfied if

$$\mathbf{E}=-\int\left(\mathbf{J}/\varepsilon_0\right)dt+f(t),\ \text{where}\ f(t)\ \text{is independent of location.} \tag{4}$$

In words, the electric field is the time integral of the (scaled) flow, plus any flow $f(t)$ independent of location. In the simplest electric circuits with all components in series, $f(t)$ can be determined at any location since current is everywhere equal in a series system. In the branched circuits, discussed below, $f(t)$ could be specified by the 'battery' or signal generator (or power supplies) driving the system. Other currents are determined then from Kirchoff's current law.

**Branched circuits with capacitors** allow consistent treatments in one dimension. A strictly series circuit like that shown in Fig. 2 of Eisenberg 2016 can be extended to include branches. The branched one dimensional circuit can represent important spatial properties of real three dimensional systems. Capacitors can be introduced at each node allowing the current $i_c$ to flow from node to node or node to ground with $i_c = C\,\partial V/\partial t$ where $V$ is the electrical potential and $C$ is a true constant perhaps different for each capacitor. These capacitors introduce a variable potential $V$ that allows the branched one dimensional system to be consistent with $V$ computed from Maxwell's equations, including conservation of current and charge. The details of such representations need to be worked out to see if they introduce significant realism into rate constant models (of chemical or Markov theories) worth the increase in complexity. The revised representations will be rather involved because they need to compute flows over energy landscapes of any shape (Eisenberg 2011) that vary with conditions, as determined by Poisson's equation and boundary conditions .

[3] 'Consistent' means that all independent variables satisfy all field equations and boundary conditions in all circumstances.

## **Conclusion** of Section 3

**Electric field in a vacuum**,
including the vacuum within atoms,
**can always assume the value given by eq. (4)**

$$\mathbf{E} = -\int \frac{\mathbf{J}}{\varepsilon_0} dt + f(t),$$

so that continuity of current defined in eq. (2) is exact,
**no matter what the constitutive equation for $\mathbf{J}$**.

# Section 4: Kirchoff's Current Law

Kirchoff's current law is a restatement of eq. (2) appropriate for electrical circuits. Electrical circuits are one dimensional systems that are usually branched, but hardly ever extend significantly into three dimensions. They do not have the spatial singularities characteristic of Maxwell's equations in two or three dimensions even when they include transmission lines described by the telegrapher's equation.

In one dimensional systems of components in series, $f(t)$ is the location independent 'current' of Kirchoff's current law. In the series circuit of Fig. 2 (Eisenberg 2016) the current is the same at every time and every location in the wires, salt solutions, resistors, commercial capacitors, vacuum capacitors, vacuum tube diodes, and semiconductor diodes and devices although the physics of each of these devices is very different. The electric field changes the specific physics of each device so the current is exactly equal. Indeed, the electric field will recruit new physical phenomena if that is the only way to satisfy Maxwell's equation, as it does when a power plug is pulled out of the electrical socket in the wall, when the $\mathbf{E}$ field becomes strong enough to strip electrons from the atoms of air, making it a plasma.

# Section 5: Equilibrium Systems

Systems without current flow, for example.

The discussion of the previous pages seems to apply only when current flows. It might seem not to apply to classical equilibrium systems of thermodynamics or to systems in which the flow of current is zero.

I argue here, however, that conservation of $\mathbf{J} + \varepsilon_0 \partial \mathbf{E}/\partial t$ is important in systems without net flow, even in classical equilibrium systems of thermodynamics because ***all systems have atomic scale flows of current arising from thermal motion.*** These flows need to satisfy the Maxwell equations because those are universal. These facts are obscured by the many classical treatments of Brownian motion in which electric fields are assumed to be independent of time, location, or charge density.

In my opinion, Brownian motion needs to be computed self-consistently, so the electric field varies with charge density, and thus with time and location, and electromagnetic phenomena are computed from the Maxwell equations (Eisenberg 2006). In this proper treatment of Brownian motion, thermal fluctuations in the density of charge must produce thermal fluctuations in the electric field. Fluctuations in the electric field imply that $\partial \mathbf{E}/\partial t \neq 0$. They must produce current according to eq.(1)-(3). Those fluctuating thermal currents $\mathbf{J} + \varepsilon_0 \partial \mathbf{E}/\partial t$ are conserved at every point in time and space by eq. (2-3), just as all currents are conserved. The stochastic thermal currents are local and fluctuate around a zero mean, since the space and time averages clearly have to be zero in thermodynamic systems, or systems with zero macroscopic $\mathbf{J} + \varepsilon_0 \partial \mathbf{E}/\partial t$. But the combination of thermal motion and Maxwell equations support very nonlinear phenomena and it is clear that produce phenomena on the macroscopic scale.

**Chemical reactions do not occur uniformly in ionic solutions.** It is important to see the consequences of thermal fluctuating currents in a thought experiment of a chemical reaction in an ionic solution.

Imagine a chemical reaction that depends steeply on concentration of reactants (as many do, but certainly not all). Many reactions occur on a time scale of $10^{-16}$ or faster because they involve movements of electrons in molecular orbitals that not delayed by inertia or friction. Clearly, these reactions will occur mostly in the regions of the solution that have large concentrations of reactants. Thermal fluctuations in concentration occur on time scales of say $10^{-9}$ seconds over regions involving large numbers of atoms. Regions of large concentration exist for times very much longer than the time of the chemical reaction itself. There is plenty of time for chemical reactions to occur in regions that thermally fluctuate to large concentrations. It is clear that ***the concentrations of the molecules actually reacting will not be the spatially average concentration.*** Chemical reactions in ionic solutions will occur mostly in regions that have concentrations far from the spatial average.

We expect that chemical reactions occur nonuniformly in ionic solution**.** The reactions are different in different locations. They occur mostly in special places where concentrations have fluctuated to large values.

Theories that only use average values of concentration will not describe what is happening in these situations. Theories are most useful when they are robust and from one situation to another without changing parameters. Theories of chemical reactions in solutions need to include spatial and temporal thermal variations, and concomitant thermal fluctuating flows of current (eq. 1-3). Everything is coupled to everything else in such systems and they are usually very nonlinear because of the coupling. Theories need to describe that coupling and the resulting nonlinearity. Only energy variational methods (that include dissipation) can do that, as far as I know.

**Kinetic Models of Biochemical Reactions** rarely fit experimental data if conditions are changed, even in quite simple ways (Eisenberg 2014). Models are said in chemical language to be not 'transferable' if different rate constants are observed in different situations.

Rate constants of chemical reactions observed experimentally usually change with (1) changes in 'background' salt concentration—by adding $Na^+Cl^-$ for example; (2) changes in the type of 'background' ion (from say $K^+Cl^-$ to $Na^+Cl^-$); (3) changes in divalent concentration (typically $Ca^{2+}$ or $Mg^{2+}$); even with (4) changes in concentrations of the reactant or enzyme.

Rate constants imply free energies. Changes in rate constants imply changes in free energies in the underlying chemical reaction. When changes in rate constants are needed to fit data in a new set of conditions, the chemical reaction and its kinetic model need an additional free

energy to fit experimental data in those new conditions. The last sentence is a polite way of saying the reaction scheme is incomplete, and in that sense incorrect.

Reaction schemes are not transferable because they leave out a component of free energy. Rate constants change as the reaction is transferred from one set of conditions to another because the reaction scheme and kinetic model leave out a component of free energy. The new model needs to adjust its rate constants to make up for the free energy it has left out.

Kinetic models can be revised so they are consistent with Maxwell equations. Perhaps the revised models will remove the unexplained free energy and allow reaction schemes to fit data with one set of rate constants, over a range of conditions, so they become transferable and more useful in dealing with physiological situations.

Transferable models of this type would be helpful in practical applications. Biochemical reactions are usually studied in idealized laboratory conditions quite different from the situations (e.g., salt concentrations) present in biological cells. Models are needed that calculate rates correctly in conditions different from those in the laboratory. Big data analysis will find it difficult to remove errors introduced by rate constants that are very different from those assumed.

Models of semiconductor devices do quite well over a range of conditions. They are designed to satisfy Maxwell equations. Perhaps chemical reaction schemes can do as well once they are modified to conserve current and be consistent with the Maxwell equations.

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