The Arrow of Time and Its Irreversibility

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Quantum thermodynamics strives to extend classical thermodynamics and nonequilibrium statistical physics to ensembles of sizes below the thermodynamic limit with the full inclusion of quantum effects. This paper uses the nonrelativistic quantum mechanics of a lone system in a thermal bath to relate its wave function's local phase to Lorentz-Faraday forces acting thereon. In the intake of heat from its surroundings, such a system's entropy increases with the gain connected to the gradient field of its local phase whose subharmonicity within the boundary of its volume is a necessary and sufficient condition for it to comply with the second law of thermodynamics (SLT). The thermodynamic arrow of time necessitates irreversible over reversible processes as determined by the gradient field of the phase. Conservative Lorentz-Faraday forces identified herein impress on the system to engender irreversible (reversible) change and entropy gain (stasis) in its exchange of heat with its environment under the discernment of the thermodynamic arrow of time and regardless of the time-reversal symmetry of such venerable frameworks as electrodynamics and quantum mechanics. Entropy production is greatest when the local phase is subharmonic within the system's nominal volume. A means of time-averaging entropy and free energy changes under nonstandard-state conditions with the accommodation of phenomenological relaxation is provided. Both the SLT and Faraday's law of induction are of similar vintage and status. Surprisingly, they share a hitherto unrecognized connection at the microscopic level. Faraday's law of induction is shown to hold for a lone system provided the gradient of its local phase is finite, a necessary and sufficient condition for it not to present with its alleged paradoxes and contradictions despite its technological successes rivalling those of the SLT. There is no evidence to deny the successes of both the SLT and Faraday's law for science and technology. In compliance with Earnshaw's theorem, the potential of the Lorentz-Faraday force is shown to stabilize a lone system just like the Coulomb (or Newtonian) potential while continuing to fulfill the virial theorem. A consequence of the time asymmetry of entropy is the impossibility of travel to the past as to cause entropy changes to decrease contrary to the SLT. Further consequences of entropy's time asymmetry include at least the nonexistence of magnetic monopoles, the observed matter-antimatter asymmetry in leptonic and baryonic matter, and the role of axion-like particles in accounting for the absence of charge-parity violations in strong interactions without necessarily answering for dark matter. Within the range of validity of gravito(electro)magnetism, dark energy is identified as the work done by the Heaviside analog of the Lorentz-Faraday force in causing the accelerated expansion of the Universe without reference to either a finite cosmological constant or an unstable vacuum state transition. In the practice of reductionism, macroscopic physics supervenes upon the microscopic, the SLT being the most conspicuous exception to that superfluous tenet. The supersedence of classical thermodynamics over quantum mechanics and electrodynamics across spatio-temporal scales ranging from an individual quantized system to its known Universe has been shown herein. Additionally, in showing that reversible (irreversible) processes are affiliated with the particle (wave) behavior of matter, attention has been drawn to a heretofore overlooked connection between the different roles of classical thermodynamics and quantum mechanics and electrodynamics in respect to arrow-of-time asymmetry and wave-particle duality.

1 Introduction

1.1 Background and purpose

Charge conjugation (C), parity (P), and time (T) are the three most important discrete symmetries and hold for all physical phenomena in Nature: C symmetry conjugates all charges, P symmetry flips spatial orientations, and T-symmetry reverses the direction of time. The CPT theorem [1] asserts that any local field theory that is invariant under Lorentz transformations must also be invariant under the combined operation of the three discrete transformations for all fundamental interactions with causality and energy positivity as obligatory, if stealth, constraints [2,3, for e.g.]. The CPT triad is an exact symmetry

with any combination short of the three being a violation of the remainder so that, for example, a violation of CP symmetry is equivalent to a violation of T-symmetry [4]. Essentially, the CPT theorem links the charges C (matter and antimatter) of states with their spacetime PT symmetries. These symmetries are broken in the known Universe as first acknowledged in the early 1950's with the revelation of P asymmetry in weak interactions by Lee and Yang [5] and quickly confirmed by Chien-Shiung Wu and her team [6].

T-asymmetry is what gives rise to our experience of the passage of time. Its basis is the second law of thermodynamics (SLT), the only T-asymmetric law in physics, one which stipulates that the entropy of a system can never decrease. Time symmetry ensures that physical laws follow their time-reversed paths when we imagine reversing time. The SLT says differently. Max Planck, thermodynamicist and one of the founders of quantum physics, remarks [7, loc. cit., pp. 103–104] in respect to the SLT that:

> The limitations to the law, if any, must lie in the same province as its essential idea, in the observed Nature, and not in the Observer. That man's experience is called upon in the deduction of the law is of no consequence; for that is, in fact, our only way of arriving at a knowledge of natural law. But the law once discovered must receive recognition of its independence at least in so far as Natural Law can be said to exist independent of Mind. Should any one deny this, he would have to deny the possibility of natural science.

Planck foresaw that a myriad versions of the SLT would be proposed [8–10, for e.g.], not by Nature but by Mind.

T-symmetry is the symmetry of most physical laws under a time-reversal transformation. Physical processes – whether classical or quantum mechanical – are time-symmetric and following Newton's lead, Maxwell, Einstein, and Schrödinger expressed their respective theories in terms of deterministic equations necessitating initial and occasionally boundary conditions on the collegial assumption that there was a beginning and an ambient space from where such evolutions would occur.

It has been known [11] for some time that electroweak interactions in neutral K mesons exhibit a small violation of CP symmetry. Direct CP violation was observed in the KTeV Collaboration [12] so that, by the CPT theorem, T violation must occur. Independently of the CPT theorem (i.e. no assumptions about CP or CPT violation or invariance were made), direct detection of T reversal violation was achieved by the BaBar Collaboration [13] proving that the laws of physics are not identical whether time runs forwards or backwards. So far, CP violations have not been observed [14, 15, et passim] in strong interactions and since there is no known reason for this absence it is referred to as the strong CP problem. An extensive body of work exists on attempts to measure permanent electric dipole moments (EDMs) of subatomic particles which, with their spin angular momenta, would directly violate both CP and T symmetries [16, et passim]. Current searches for T reversal violations through precision laboratory measurements of the EDMs of atoms and molecules [17–23] are now sufficiently sensitive to detect signatures of some particles with masses of more than 10 TeV. There are many experiments [24, for e.g.] attesting to the inviolability of CPT in Nature. Among the phenomena that the Standard Model of Particle Physics (SM) – and extensions beyond the SM – do not explain include the absence of magnetic monopoles, matter-antimatter asymmetry, neutrino masses, supersymmetry, and gravity. While the possibility of CP violations in the baryon sector was anticipated in 1958 by Okubo [25], it is only lately that such effects beyond the SM have been observed [26, 27].

Nor does the SM provide the connection between microscopic T violations and irreversibility in thermodynamics. Discrete symmetries have just recently been investigated with entangled neutral kaons [28] and in ortho-positronium decays [29]: neither investigation drew any connection between their null results with the T-asymmetry of the SLT as established herein. That T-symmetry is counterintuitive is generally excused by the claim that the SM handles only local properties, not global ones like entropy. One outcome of this paper is to provide that connection in which the two rub shoulders to the advantage of entropy and its governing SLT.

The Standard Model of Cosmology (SMC) is based on the SM and the General Theory of Relativity (GTR) [30, for e.g]. It also depends on several additional assumptions: that the Universe was created in the Big Bang from pure energy; that the known mass-energy content of the Universe is given by luminous matter whose gravitational interaction is described by the GTR; and the cosmological principle by which the idea that the Universe is homogeneous and isotropic on cosmic scales was popularized. The Λ Cold Dark Matter (ΛCDM) variant of the SMC, with six free parameters and several ansatzes, posits that only $\sim$ 5% of the content of the Universe is in the form of baryonic matter with the balance comprised of cold, slow-moving dark matter – invisible matter that interacts with baryons via gravity alone and thought to make up $\sim$ 25% of the total mass content in addition to dark energy – a repulsive force inferred from observational data of type Ia supernovae and thought to promote the accelerating expansion [31, 32] of the Universe against gravity and accounting for $\sim$ 70% of its matter-energy inventory. Cold dark matter is thought to have clumped into large masses which gravitationally attracted baryonic matter, forming the large-scale structures of the Universe. Remnants of dark matter clumps are observed as halos surrounding galaxies. Currently the primary candidates for dark matter are primordial black holes [33], axions [34], sterile neutrinos [35], weakly interacting massive particles (WIMP) [36, et passim], and the lat-

est, erebons [37]. Despite a wealth of evidence favoring their existence [38, 39, for e.g.], neither dark matter [40] nor dark energy [41] have been conclusively detected to date.

With improvements in the accuracy of cosmological observations, so too do challenges [42] to ΛCDM appear. Alternatives [43, 44, et passim] to ΛCDM that dispense with dark matter, dark energy, or both do so [45] by altering the known long-range nature of gravity, an approach not without its own perils and pitfalls [46, 47]. As with the SM and its shortcomings, the ΛCDM, for all its successes, cannot explain such key concepts in our understanding of the known Universe as dark matter, cosmic inflation [48], dark energy, and with the advent of the JWST data, the surprising appearance of massive candidate galaxies [49–51] within ∼ 600 Myr of the Big Bang.

First introduced by Sadi Carnot [52] and Rudolf Clausius [53], the concept of entropy in classical thermodynamics related to systems away from equilibrium. What is meant here by entropy is that which the early adopter of Bayesian probability [54], the physical chemist Linhart [55–57] considered in deriving an expression for the heat capacity as a function of temperature from classical thermodynamic principles that he then successfully applied to the experimental standard entropy data of many substances over a broad range in temperature. As Bekenstein remarked (*Scientific American*, April 1, 2007), "This law is central to physical chemistry and engineering; it is arguably the physical law with the greatest impact outside physics." Without regard to the microscopic details of a system, thermodynamics is tasked with identifying which operations are technically feasible and which resources can be exploited to effect economically sustainable state transformations. Generally, macroscopic phenomena are not time-reversal invariant, prompting Eddington [58] to term this dichotomy in the nature of time as the thermodynamic "arrow of time".

Statistical mechanics was developed later and applied to many-bodied systems at or near equilibrium by such luminaries as Gibbs, Boltzmann, Planck [7] et *inter alia*. Discounting any perceived disrespect, that framework and its principles, in the absence of evidence to the contrary, does not regulate a single molecule or its known Universe. Just so, a horde of molecules in their Universe(s) are subject to the SLT without exception. This is the primary premise of this paper.

Many papers and books [59–70, for e.g.] intended to provide an explanation of the arrow of time focus on the initial (and to a lesser extent, boundary conditions) of the Universe whose initial conditions unknown [71, 72, et passim]. Feynman [73, loc. cit., p. 116]'s "past hypothesis" posits that the early Universe had low entropy in compliance with the SLT. Subsequently, Roger Penrose argued [74, 75, et passim] that the curvature of the Weyl tensor vanishes at any initial singularity (including the Big Bang) so that the evolution of the Universe be close to a Friedman-Robertson-Walker model of matter in near perfect thermal equilibrium at $\sim 10^{15}$ K $\simeq$ 1 GeV whose gravitational degrees of freedom remain unexcited until triggered at the ∼ 375,000 yr cosmic microwave background (CMB) milestone in the aftermath of a low-entropy constraint as had been hypothesized by Feynman.

Penrose [76] proposed a conformal cyclic cosmology (CCC). This is an eternal recurrence process, whereby universes are spawned, grow, and die in a sequence of aeons, with post-evaporating black holes and the arguable loss of information [77] at their singularity leaving traces of Hawking points (large temperature gradients between ring-like anomalies) of their primordial existences in the CMB of progeny universes based on evidence [78, for e.g.] that has so far failed to hold up to scrutiny [79–81]. By hypothesis, aeons have neither a beginning nor an end and contain only massless particles, photons and gravitons. Penrose's theory includes the existence of erebons, hypothetical heavy particles with masses of about the Planck mass that are candidate particles for dark matter but which are ultimately unstable since at the end of an aeon there must be an absence of mass to get to the conformal invariance pivotal to CCC.

It is a popular claim that because entropy is an extensive property, the reason violations of the SLT are not seen is due to molar statistics: as systems reduce in size, fluctuations (sic uncertainties) increase so that violations ought to become more probable. Challenges to the SLT and proposals for its replacement abound [8–10, 82–84, for e.g]. However, without their independent verification including computer simulations that openly demonstrate the positivity* of dynamics [85, 86], the SLT is indomitable regardless of premature reports of its putative demise.

Pioneering work by Hill [87] in the early 1960s showed how thermodynamics could be applied to many small systems – aerosols, colloids, dust, and nanosystems. The thermodynamics of small systems has taken on a new importance due to the development of nanoscience, with thermodynamics as applied to nanoscale particles being now known as nanothermodynamics [88, 89]. The nanothermodynamics community has for some time broadened its enquiries into the single-molecule domain beyond the thermodynamic limit [90–93] without invoking quantum phenomena. Quantum thermodynamics [94, 95] tries to go even further by striving to extend classical thermodynamics and nonequilibrium statistical physics to ensembles of sizes below the thermodynamic limit with the full inclusion of quantum effects, even for nanoscale objects [96] and single trapped quantum systems [97]. It differs from statistical mechanics in its attention to dynamical processes out of equilibrium [98]. Kosloff [99] has provided a perspective on a dynamical view of quantum thermodynamics in which the laws of thermodynamics are true in any quantum circumstance [100, et passim].

Extending thermodynamics beyond its bulk matter limits

*Adjusting what should be a positive solution to zero on first detecting it going negative is an all too-common programming practice.

is increasingly prevalent in the push towards the fabrication of miniaturized systems offering technological advantages. The main benefit of single-molecule investigation is the deconstruction of ensemble averages to provide information about complex systems since in natural systems the average outcome of the group is rarely the same as the outcome of the individual which may be all that is important. Ensemble averages depend on probability distribution functions and a medley of principles and assumptions that are not applicable to a lone system. Even though the time average of an observable of a system is directly related to experiment, empiricism has lost favor lately to computer simulation that replaces averages over time by instantaneous averages over an ensemble. Quantum mechanics governs the dynamics of individual subatomic, atomic, and molecular systems with well-predicted outcomes. Whether a system is small (a molecule) or not (the known Universe) is relative to its context and how that affects it and our attention to it.

Interest in single molecule behavior received a significant boost following Neher and Sakmann's 1991 award of the Nobel Prize in Physiology or Medicine for discoveries revealing the function of single ion channels via their development of the patch clamp technique (*Scientific American*, March 1992) through which biological scientists could inexpensively isolate ion channels of cell membranes that engage in cellular signaling processes. This resulted in a momentous revolution in cell biology – unseen in physics notwithstanding Schrödinger's *What is Life* manifesto proclaiming physics' dominance over biology – leading to greater understanding of disease mechanisms and the discovery of new therapeutic drugs. As recently as the early 1980s, the notion of cell membranes and their information networks of single ion channels were being challenged by the now debunked [101] and obdurate belief [102] that the cell and even life itself is explicable in terms of the "nano-protoplasm" whose function and properties are inextricably tethered to the framework of statistical mechanics. The rapid progress in quantitative single-molecule measurements are well documented [103, 104, et passim] and contrast with the obsolete "new view" [105, et passim] energy landscape ensemble approach to the protein folding problem which relies almost exclusively on computer simulation of the chemical physics modeling [106, 107] of such.

X-ray crystallography and cryo-electron microscopy have traditionally allowed the imaging of biomolecules at the atomic level using samples that have been crystalized at ultracold temperatures. Atomic force microscopy (AFM) of molecules allows them to be probed under more physiologically appropriate conditions. A localization image reconstruction algorithm [108] can process data from multiple scans of single molecules and can even be used retroactively to reveal new details hidden in old AFM data. Instead of observations on hundreds of molecules, the same molecule is observed hundreds of times in calculating a high-resolution map. Such a map, from the same molecule as it transits from one conformation to the next and not from thousands of molecules in one or the other conformation, mitigates the potentially misleading results that can occur when averaging data from many molecules when only one matters. Advances in single-molecule microscopy have evolved to permit the study of systems ranging from small molecules to living cells with the prospect of revolutionizing the modern biosciences [109–111, for e.g.].

In principle, reliable structural information in conjunction with the use of computational methods should guide structure-based screening to drug discovery and design. Long after Dirac [112, loc. cit., p. 714] advised that it "... becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation," such pursuit led to the realization [113, loc. cit., p. 109] of the "central embarrassment of molecular mechanics, namely that energy minimization or molecular dynamics generally leads to a model that is less like the experimental structure," whether through such excuses as deficiencies in force fields (potentials), limitations in computational power allegedly to be solved with supercomputers of the past but now demanding quantum computers of tomorrow, artifacts in structures [114] that result from collecting crystallographic data under cryogenic conditions to minimize radiation damage, etc.

With its roots in phenomenology, Clausius' inequality defines the change in entropy for a cyclic process (including full-body immersion in its surroundings) and its role as a measure of the dispersal of energy or heat at a specified temperature. If the amount of energy added by heating and the temperature can be measured during the process, Clausius' inequality can be used to determine whether the process is reversible or irreversible by carrying out the integration in the inequality. The following provides an alternative way of distinguishing between the two extremes for systems whose notion of work is no different than that in all of physics even if their dynamics is governed by time-reversible quantum mechanics without resort to any particular entropy functional.

Introduction of the concept of entropy and its permissible changes through Clausius' expression of the SLT predates both Gibbs' notion of the statistical ensemble and Boltzmann's specific entropy functional connecting the macroscopic system with the probabilistic populations of microscopic states amenable to that ensemble. Unlike thermodynamics, Boltzmann-Gibbs statistical mechanics, whatever its successes, has limited domains of applicability as known to its practitioners, including so-called anomalous systems that have strong long-range effects, nonlocal correlations between different subsystems of a system, nonMarkovian behavior, violations of reductionism for such thermodynamic properties as entropy and internal energy, etc. Having found no systematic way to uniquely determine how to describe the en-

tropy of dynamical systems who survey their configuration spaces in ways more complex than prescribed by ergodicity, Tsallis [115] proposed a nonextensive (nonadditive) measure [116] which generalizes Boltzmann-Gibbs extensive (additive) metric to deal with such anomalous systems. The Boltzmann-Gibbs and Tsallis entropies are each time invariant and applicable at best to systems at or near thermal equilibrium. Neither of these entropies are *a priori* applicable to nonequilibrium systems which is why here, in consideration of a single molecule, no appeal to either extensive or nonextensive statistical mechanics is made but rather to classical thermodynamics, electrodynamics, and quantum mechanics as appropriate descriptors in their respective macroscopic and microscopic milieus. Time-dependent entropy changes are given by Clausius' inequality as follows from his formulation of the SLT on the basis of a cyclical thermodynamic process to distinguish an irreversible from a reversible change of a lone system in a thermal field.

Thermodynamic systems under sentient observation are embedded in the known Universe and are never "isolated" [117] or "notional": they are either closed or open, closed if they exchange only heat with their environment and open if they exchange mass with or without the exchange of heat with their surroundings. For all their intrigue, such quasi "isolated" systems as Bose-Einstein [118, 119] and Fermi-Dirac [120] condensates do neither and are of no interest here. According to the SLT, systems of interest generate entropy in a time-asymmetric way in accord with the macroscopic concept of entropy and common experience. That classical and quantum dynamics and electrodynamics suggest otherwise has led to a deluge of researches in recent years that offer explanations for this so-called time-reversal symmetry breaking or claims that the SLT is subject to regular violations. Here, the primary intent is to show that, at the microscopic level, entropy is T-asymmetric and requires neither the intercession of time-reversal symmetry breaking mechanisms nor assent to the belief that the SLT can be controllably broken.

The purpose of this paper is to provide the physical basis for the SLT's T-asymmetry from T-symmetric quantum mechanics and electrodynamics without obliging either of them to relinquish their mutual time-reversal invariance. The route to this is simple if somewhat circuitous relative to that of Stenger [121, loc. cit., 3972]'s, say:

> It is hard to see how the breakdown of T-symmetry at the microscale implies time irreversibility at the macroscale, although I am not prepared to rule it out,

an opinion easily brought up to speed as will be shown by beginning in the first instance at the molecular scale before moving on to reveal that the same considerations apply in larger-scale self-gravitating systems.

Materials and structures are the products of the evolution of the Universe. How they appeared and their subsequent transformations are pivotal to our understanding of the Universe and our place within it. All dissipative structures in the Universe including all forms of life, owe their existence to the fact that the Universe started in a low entropy state and has not yet reached equilibrium [122, et passim]. Deep considerations of such phenomena are beyond the scope of this paper and its specific purpose: to explain why the arrow of time is asymmetric regardless of the time-reversal invariance of quantum mechanics and electrodynamics.

The paper uses the nonrelativistic quantum mechanics of a single molecule to relate its wave function's local phase to forces acting on its nuclei and electrons in the presence of a thermal environment. In the intake of sensible heat from its surroundings, such a molecule's entropy increases with the gain in entropy determined by its molecular structure as connected to the gradient field of its wave function's local phase whose subharmonicity is shown to be a necessary and sufficient condition for it to comply with the SLT. The thermodynamic arrow of time necessitates irreversible over reversible processes as determined by the gradient field of the local phase. Conservative Lorentz-Faraday forces impressing on the nuclei and electrons of the molecule engender irreversible (reversible) change and entropy gain (stasis) in its exchange of heat with its environment under the discernment of the thermodynamic arrow of time and regardless of the time-reversal symmetry [123], [124, cf. Ch. 26] of quantum mechanics or electrodynamics. The implications of the gradient of the local phase on entropy production and Faraday's law of induction are also explored. Additionally, it is shown that in a heat bath a molecule in molar amounts is stable provided its internal electrodynamic potential is subharmonic within its nominal volume V, a fact first anticipated long ago by Earnshaw [125]. This leads into the question of molecular stability as gauged by the virial theorem and by extension to the stability of self-gravitating objects.

A molecule – with its myriad of allowed relative motions determined by its stabilizing potential in analogy with the vibrations of an oscillating string – serves here as a spoiler to its Universe and its equally important if less familiar subsystems. The paper draws a comparison between a single molecule described quantum mechanically in the nonrelativistic limit and its Universe treated in the weak field limit of general relativity, each interrogated under similar thermal circumstances, prior to their respective destinies in anticipation that across such disparate spacetime scales what one learns might surprise in their similarity and simplicity.

1.2 Notation

Rationalized Planck units are used throughout unless otherwise indicated (wayward 4π's excepted). The gradient ∇ formally operates on vector and scalar fields drawn from a Euclidean space whose fiber bundle is a trivial Cartesian product mapping $R^n = \boldsymbol{R}^M \times \boldsymbol{r}^N$ of the molecular structure of an elec-

trically neutral molecule of M nuclei (base, $\boldsymbol{R}$ with gradient $\partial/\partial\boldsymbol{R} = \nabla_{\boldsymbol{R}}$) of known elemental composition (atomic number Z_i, $i = 1, M$) and the coordinate space (fiber, $\boldsymbol{r}$ with gradient $\partial/\partial\boldsymbol{r} = \nabla_{\boldsymbol{r}}$) of its N electrons so that each of the $n = M+N$ elements of $\mathbf{x}$ lies in R^3. If $m_{k_j} > 0$, $j = 1, 2, 3; k = 1, \ldots, n$ are the masses of the particles and [] denotes the integer part, $k_j = 1 + [(j-1)/3]$ in order that all three coordinates of a particle relative to a body-fixed origin in the observer's frame at the center of mass are scaled by the same mass. The kinetic energy, its virial, and related quantities of any system of interest (be it an atom, molecule, ion, the known Universe, etc.) free from the clutter of the masses of nuclei and electrons are expressed here as Lebesgue integrals whose operative measures (for volumes V, positions $\mathbf{x}$, etc.) use mass-weighted coordinates. The only limit on n is that imposed by Nature [126, et passim] so that neutral (i.e. $\sum_{i=1}^{M} Z_i = N$) polyatomic molecules (governed by the Coulomb potential) or the known Universe (governed by the Newtonian potential), while their sizes cannot estimate *a priori*, both are $n \geq 4$-body systems whose dynamics are unknown and perhaps even unknowable. The inner product $\langle \mathbf{x},\mathbf{y} \rangle$ of $\mathbf{x}, \mathbf{y} \in R^n$ is a scalar as is the Euclidean norm $\|\mathbf{x}\| = \sqrt{\langle \mathbf{x},\mathbf{x} \rangle}$. An orientable surface ∂V has a unit normal $\hat{\mathbf{n}} = \nabla V/|\nabla V|$ at a regular point where* $\nabla = \nabla_{\boldsymbol{R}} \times \nabla_{\boldsymbol{r}}$ and is undefined at a critical point where ∇V vanishes. The normal $\hat{\mathbf{n}}$ to V twists and turns from regular point to regular point as the boundary ∂V bends in different directions, behavior captured by the local self-adjoint shape operator $\mathbf{S} = -\nabla \cdot \hat{\mathbf{n}}$ [130, cf. Ch. 5], [131, cf. Ch. 6, Ex. 11, pp. 141–142]. The directional derivative of V at a regular point is $D_{\hat{\mathbf{n}}} V = \nabla V \cdot \hat{\mathbf{n}} = \partial V/\partial \hat{\mathbf{n}}$ which is a maximum of $|\nabla V|$ (minimum of $-|\nabla V|$) when $\hat{\mathbf{n}}$ is in the same (opposite) direction as (to) $\hat{\mathbf{n}}$, respectively. The eigenvectors and eigenvalues of $\mathbf{S}$ provide the principal directions and principal curvatures of V, respectively. The principal directions specify the directions a curve embedded in V must travel to have maximum and minimum curvature, these being given by the principal curvatures. Quantum expectation values are denoted by angular parentheses $\langle \blacksquare \rangle$ and their time averages by an over bar $\overline{\langle \blacksquare \rangle}$. Without loss of generality, generic functions are smooth with compact support $C^\infty(R^n)$.

1.3 Outline

The article is organized as follows: In the next section, the thermodynamics of a single molecule in contact with a heat bath is considered. This is followed by consideration of the Faradaic induction of a single molecule. In the succeeding section the relation of the two featured topics are discussed in detail. The central finding of the T-asymmetry of entropy is shown to rest on the hypothesis that the thermodynamic arrow of time is set by the local phase of the wave function of the system of interest whose falsifiability is illustrated through a number of demonstrations for self-gravitating systems. The requirement that the phase be subharmonic in a volume under curvature flow is emphasized whatever the size and shape of the system.

It is not the intent here to calculate the entropy in any system, be it a single molecule or any other particle or structure in its known Universe, but rather to point out that, whatever their fate in a thermal field, the T-asymmetry of entropy changes will feature in their evolution until it hardly matters. Both experimental demonstration and computer simulation are outside the scope of this paper. Equally, deliberations of generalized thermodynamics specific to black holes are not part of this paper.

2 Thermodynamics in a thermal field

Recall that quantum theory distinguishes between two types of system states, viz. pure and mixed [132]. A system in a pure state possesses both a well-defined probability amplitude and phase. In contrast, the mixed state describes a system whose phase information is incomplete. Since the density matrix ϱ for a system to be in a statistical ensemble of different pure states is a positive semi-definite, self–adjoint operator, it has a spectral decomposition $\varrho = \sum_i \lambda_i |\varphi_i\rangle\langle\varphi_i|$ where $|\varphi_i\rangle$ are orthonormal state vectors with $\lambda_i > 0$ and $\sum_i \lambda_i = 1$. ϱ evolves via the von Neumann equation $\dot{\varrho} = [H, \varrho]$ where H is the Hamiltonian operator of the system. The von Neumann entropy of the ensemble of pure states is [133] $S(\varrho) = -\sum_i \lambda_i \ln \lambda_i = -\mathrm{Tr}(\varrho \ln \varrho)$, with the number of states needed to describe the system being the number of eigenvalues λ_i of ϱ, each of which provides the weight of its respective state. Thus, $S(\varrho) > 0$ for a mixed state and $S(\varrho) = 0$ for a pure state (with $\lambda_1 = 1$). As $\varrho = |\psi\rangle\langle\psi|$ casually goes from a pure ($\mathrm{Tr}(\varrho^2) = 1$; $S(\varrho) = 0$) to a mixed ($\mathrm{Tr}(\varrho^2) < 1$; $S(\varrho) > 0$) state, the entropy gain ΔS increases. For mixed states the entropy measures how far the state is from being pure. Apart from a factor of $k_{\mathrm{B}} \ln(2)$ involving the Boltzmann constant, Gibbs thermodynamic entropy is identical to the von Neuman entropy and is most relevant for systems with a large number of degrees of freedom.

Consider a single molecule in a pure state $\psi(\mathbf{x}, t)$ of charge density $\rho(\mathbf{x}, t) = |\psi(\mathbf{x}, t)|^2$ that is $(-1)^{2s}$-symmetrized for boson (s, integer spin) and fermion (s, half-integer spin) coordinates [134, et passim]. The molecule is free of spatial confinement other than that provided by the Coulomb potential. Nuclei with integer spins are bosons and those with half-integer spins are fermions as are electrons which are spin 1/2 elementary particles. Both $\psi(\mathbf{x}, t)$ and the operator $O(\mathbf{x}, t)$ are time dependent in the interaction picture of quantum dynamics. A state is pure if the density matrix $\varrho = |\psi\rangle\langle\psi|$ for some unit state vector ψ so that $\varrho^2 = \varrho$ and the expectation value

*Finite binary cross products $\times$ exist only in R^3 and R^7 [127]. Their extension to R^n is through the Hodge dual of the exterior product $\wedge$ of $n-1$ vectors in R^n and their Gramian determinant [128, cf. Ch. 7], [129, cf. Ch. 8]. The use here of vector calculus instead of the exterior calculus of differential forms is that it more clearly serves as the universal lingua franca of general physics for the disparate topics under discussion.

of a self-adjoint operator O is $\langle O\rangle = \mathrm{Tr}(\varrho \mathrm{O}) = \langle \psi, \mathrm{O}\psi\rangle$. Pure states are relevant if they come from the ground state in which the first excited state has a large energy gap that exceeds $\sim k_\mathrm{B}T$ at the absolute temperature T. If O has a complete set of eigenvectors ϕ_j with real eigenvalues o_j, then $\langle \psi, O\psi\rangle = \sum_j o_j |\langle\psi|\phi_j\rangle|^2$ where the o_j's are the possible outcomes of the measurement of O and $|\langle\psi|\phi_j\rangle|^2$ is the transition probability that this outcome occurs. This choice of state is consistent with Bridgman [135]'s operationalism with the inclusion of quantum mechanical considerations by Giles [136, 137] in a rigorous formulation [138] of thermodynamics. By and large the paper adopts the Ithaca [139] interpretation of quantum mechanics.

It is always the case that $\psi(\mathbf{x}, t)$ complies with the Pauli exclusion principle (PEP). Any pair of point particles whose exchange is constrained by the PEP are distinguishable if their separation is large compared to their de Broglie wavelength ($\lambda_\mathrm{th} \sim 1/k_\mathrm{B}T$ for massless particles [140] such as the photon or the graviton). Thus, while symmetrization is of undoubted importance, it is increasingly less crucial the further away from equilibrium a system is driven to where the very identification of $\psi(\mathbf{x}, t)$ is in doubt. Entropy quantifies the extent to which the exact state of a system of interest is in doubt and reflects deficits in whatever information is at hand to correctly make that specification. For arbitrary t, $\psi(\mathbf{x}, t)$ is given. When the system is perturbed, the state evolves with increasing loss of information or gain in entropy about its current condition. The system of minimum entropy evolves via the time-dependent Schrödinger equation and its probabilistic underpinnings. Subsequent entropy production will be related in what follows to the spontaneous work done on such a system in a heat bath by electrodynamic forces internal to the system and not to a statistical prescription of entropy more appropriate to an ensemble of such systems at or near thermal equilibrium.

In electromagnetic theory charge density is idealized as a smooth scalar function of position to be regarded as a continuous distribution, somewhat like a fluid or field. If the wave vector in its coordinate $\mathbf{x}$ representation is accompanied by an arbitrary local phase factor, nonrelativistic quantum mechanics is invariant under a local gauge transformation whether in an external [141, cf. Sec. 22 and 27] or internal [142, 143] electromagnetic field. In the latter case the evolution of the probability density $\rho = |\psi|^2$ fulfills the continuity equation, a quasilinear first-order conservation law partial differential equation (PDE),

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0\,, \tag{1a}$$

within a deformable volume element dV centered at $\mathbf{x}$ in terms of the divergence of the probability current

$$\mathbf{j}(\mathbf{x}, t) = -\frac{i}{2}\left(\psi^*(\mathbf{x}, t)\nabla\psi(\mathbf{x}, t) - \psi(\mathbf{x}, t)\nabla\psi^*(\mathbf{x}, t)\right) \tag{1b}$$

to ensure unitarity at all $(\mathbf{x}, t)$ in analogy with the maintenance of mass, charge, and heat balance in continuum mechanics, electrodynamics, and thermodynamics, respectively. When $\nabla \cdot \mathbf{j} > 0$ so that the number density is decreasing in dV then $\partial\rho/\partial t < 0$ and conversely. If V is large enough to be essentially unbounded, ψ is square integrable and vanishes at infinity where Sommerfeld [144, cf. §28]'s radiation condition ensures that infinity is an absorber (sink) but not an emitter (source) and that once probability current exits the scene it does not reenter (a rigorous requirement for the existence and uniqueness of ψ). For future reference, notice that the current density $\mathbf{j}(\mathbf{x}, t)$ is an even function of time [145], i.e. $\mathbf{j}(\mathbf{x}, t) = \mathbf{j}(\mathbf{x}, -t)$, under Wigner [123], [124, cf. Ch. 26]'s prescription for time reversal in quantum mechanics. Recall [145] also that the probability density ρ is even in t.

For ψ expressed in polar form as $\psi(\mathbf{x}, t) = e^{i\theta(\mathbf{x},t)}\sqrt{\rho(\mathbf{x}, t)}$, the continuity equation reduces to

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\nabla\theta) = 0 \tag{2}$$

in terms of the probability density ρ and a finite local phase factor θ which has units of action, i.e. [energy][time] or [momentum][length]. With ψ being single valued so too is ρ. Wherever ψ vanishes so too do ρ and $\mathbf{j} = \rho\nabla\theta$.

If $\nabla\theta$ vanishes so does $\mathbf{j}$ and the system is in a stationary state with normalizable ρ. Here the focus is on the situation where $\nabla\theta$ is finite almost everywhere, a circumstance governed by the Morse-Sard theorem [146, 147] to the effect that critical points at which $\nabla\theta = 0$ are few to none compared to regular points where $\nabla\theta \neq 0$. That said, there are several reasons to support the view that θ is subharmonic ($\nabla^2\theta > 0$) in V [148, 149], viz.

1. At nodes in ψ, $\theta = \tan^{-1}(\mathrm{Im}\,\psi/\mathrm{Re}\,\psi)$ is indeterminate. If the potential energy part of H has no explicit time dependence, Hamilton's principal function $\theta(\mathbf{x}, t)$ (classically, W) is additively separable in $\mathbf{x}$ and t, i.e. $\theta(\mathbf{x}, t) = \phi(\mathbf{x}) - Et$, where $E = \langle\psi|H|\psi\rangle$ is the energy expectation value for normalized ψ, $\phi(\mathbf{x})$ (classically, S) is Hamilton's characteristic function, and $\nabla\theta(\mathbf{x}, t) = \nabla\phi(\mathbf{x})$ is the time-invariant gradient or relative phase*. In the hydrodynamic interpretation [152], [153, et passim] of quantum mechanics, where substituting $\psi = e^{i\theta}|\psi|$ into the Schrödinger equation gives a system of two coupled PDEs, viz. a continuity equation for ρ treated as a classical fluid and a surreal quantum potential modification of the classical Hamilton-Jacobi equation for θ which is of $O(\hbar^2)$ in the rationalized Planck constant $\hbar$, $\nabla\theta = \nabla\phi$ is taken to represent the momenta of all particles (nuclei and electrons), an interpretation adopted by Schrödinger in formulating wave mechanics following both Hamilton's analogy between geometric optics

* Schrödinger [150] explained how he had come upon the wave equation and identified ϕ as what he termed the "phase angle of the wave function" [150, loc. cit., p. 499; p. 505] it regulates, as inspired by de Broglie [151].

and classical mechanics and de Broglie's wave-particle hypothesis [151, 154], [155, cf. Ch. VIII], [156], [157, cf. Ch. 2.2.4] in which a wave train is associated with the motion of a material particle, the frequency and wavelength being related to the energy and momentum by the Planck-Einstein relation for radiation quanta.

The optico-mechanical analogy invoked by Schrödinger [158] in arriving at his eponymous wave equation for $\psi(\mathbf{x}, t)$ is well documented [159–162] and does not need to be rehashed here. Suffices to say that in his interpretation and adaption of de Broglie's "phase wave" ideas, Schrödinger denied any real meaning to ϕ since to do so would imply that one could speak meaningfully of electric charge being in a particular place or following a single path (sic trajectory) in an atom and capitalized *inter alia* on two interrelated observations [163], viz. (i) recognition that the gradients $\nabla\theta(\mathbf{x}, t) = \nabla\phi(\mathbf{x})$ are normal to the wave fronts or level sets of $\theta(\mathbf{x}, t)$, the surfaces of constant action; and, (ii) that since the light rays of optics are normal to those wave fronts, so too are particles whose uncertain loci follow the undulations in $\nabla\phi(\mathbf{x})$ so that the direction of $\mathbf{j} = \rho\nabla\phi$ is locally normal to the level sets of de Broglie waves* of local phase ϕ. Note that $\nabla\phi$ is distinct from the group velocity of its localized wave packet†.

In retracing this optico-mechanical analogy one sees that to $O(\hbar^0)$ the Hamilton-Jacobi equation for the relative phase $\nabla\phi$ is

$$\frac{1}{2}(\nabla\phi)^2 = E - \mathcal{V}\,, \tag{3a}$$

where $\mathcal{V}$ is the potential energy. Schrödinger recognized that (3a) has the solution $e^{i\nabla\psi}$ whereupon

$$\frac{1}{2}(\nabla\psi)^2 - (E - \mathcal{V})\,\psi^2 = 0\,, \tag{3b}$$

and a variational problem [168] on ψ leads to the time-independent wave equation which he applied to the H atom and post haste produced its time-dependent equivalent wherewith wave mechanics was born [163, et passim]. At this point ϕ and $\nabla\phi$ appear to have fallen through the cracks to be replaced by all things ψ until de Broglie [151, 154]'s and Madelung [152]'s earlier work was resuscitated by David Bohm in the early 1950s, through his retention of the connection $\nabla\phi = \mathbf{j}/\rho$ as a guidance law governing particle motions pursuant to their deterministic trajectories in what is an active alternative [169–171, et passim] to the Copenhagen interpretation of quantum mechanics with its focus on probabilistic energy and angular momentum eigenvalues, and dubbed de Broglie-Bohm mechanics, pilot-wave theory, causal interpretation, etc. by its practitioners [172, for e.g.]. Hereon while $\mathbf{j} = \rho\nabla\phi$ in terms of the wave-particle velocity $\nabla\phi$ and the charge density $\rho = |\psi|^2$ is acknowledged, Bohmism is otherwise ignored in proceeding.

Invoking de Broglie [151,154]'s interpretation of Sommerfeld [173]'s (and Wilson [174]'s) quantization rule, a condition which ensures that matter waves make standing waves only at discrete energies, suggests that

$$\oint_{\partial V} da\,\hat{\mathbf{n}}\cdot\nabla\phi = \int_V d\mathbf{x}\,\nabla^2\phi = 2\pi k\,, \tag{4}$$

where $\hat{\mathbf{n}}$ is a unit normal to ∂V on a patch of area da, ϕ is both multivalued and subharmonic in V, and $k \in \mathbb{Z}^+$. At nodes in ρ, $\mathbf{j}$ vanishes but not necessarily $\nabla\phi$ which may jump in discrete amounts and, since by Stoke's theorem $\int_V d\mathbf{x}\cdot\nabla\times\nabla\phi$ vanishes, there are no accompanying vortices should any such jumps occur. A measurement on a system subject to (4) would result in a jump in its state, a collapse of its wave function ψ following which its phase ϕ and its gradient $\nabla\phi$ would vanish whereupon it would find itself in a reversible state.

2. The flux of the probability current $\mathbf{j}$ has two contributions, viz.

$$\nabla\cdot\mathbf{j} = \rho\,\nabla^2\phi + \nabla\rho\cdot\nabla\phi\,, \tag{5}$$

the first of which is positive if ϕ is subharmonic while the second governs whether the amount of charge within a differential volume dV is decreasing (increasing) according as it is of positive (negative) sign.

This allows (1a) to be rewritten as

$$\frac{D\rho}{Dt} + \rho\,\nabla^2\phi = 0 \tag{6}$$

in terms of the substantial derivative $D/Dt = \partial/\partial t + \nabla\phi\cdot\nabla$. In an Eulerian specification of the flow field of ρ, the total derivative consists of two terms, the first $\partial/\partial t$ of which provides the changes at a fixed position due to unsteadiness in the flow while the second $\nabla\phi\cdot\nabla$

*In showing the equivalence of his formulation of wave mechanics to the matrix mechanics approach of Heisenberg et al [164–166], Schrödinger acknowledged [167, loc. cit., p. 735, fn. 2] his indebtedness to de Broglie's extension of wave-particle duality for photons to matter and Einstein's advocacy of that extension to him.

†The amplitude $\sqrt{\rho}$ has no unique position or velocity but is smeared over space as a wave packet of phase ϕ. In a double-slit interferometer it is particles that are detected, not delocalized waves as $\sqrt{\rho}$ implies: photons and particles travel as waves but hit the detector as particles. This raises the problem of how $\sqrt{\rho}$ from its source changes from wave to particle. Bohr and Heisenberg (in their Copenhagen interpretation of quantum mechanics) claimed that it was the observer who decides the outcome. ρ is a wave of probability (via Born's conjecture, according to which one must expect to find the particle where ρ is high) provided $\sqrt{\rho}$ collapses at the screen regardless that it arrived there as a wave travelling through all slits without prejudice while interfering as a wave enroute to the detector. Just how $\sqrt{\rho}$ collapses is an open question whose resolution endures as the so-called "measurement problem" whose most popular if arguable rationalization is the many worlds interpretation of quantum mechanics.

gives the rate at which ρ is convected to that location. Neither contribution vanishes in an unsteady flow. The substantive flow of ρ will be accelerating if ϕ is subharmonic ($\nabla^2\phi > 0$). Physically, pursuit of ρ whether it relates to a single molecule or any other particle or structure in its known Universe from a Lagrangian or an Eulerian perspective is a matter of convenience. For the present purposes the latter is chosen.

3. If $\mathbf{j}$ is decomposed via the Helmholtz-Hodge theorem [175–178] to the sum of longitudinal and transverse parts whereby $\mathbf{j} = \mathbf{j}_\parallel + \mathbf{j}_\perp$ with $\mathbf{j}_\parallel$ and $\mathbf{j}_\perp$ being parallel and orthogonal to $\nabla\phi$ and $\nabla\times\mathbf{j}_\parallel = 0$ and $\nabla\cdot\mathbf{j}_\perp = 0$, respectively, then $\rho\nabla^2\phi = \nabla\cdot\mathbf{j}_\perp = 0$ and $\nabla\rho\cdot\nabla\phi = \nabla\cdot\mathbf{j}_\parallel$, where for $\mathbf{x}, \mathbf{x}' \in V \subseteq R^n$

$$\mathbf{j}_\parallel(\mathbf{x},t) = -\int_V d\mathbf{x}'\,\frac{\nabla'\cdot\mathbf{j}(\mathbf{x}',t)}{4\pi|\mathbf{x}-\mathbf{x}'|} + \oint_{\partial V} da'\,\frac{\hat{\mathbf{n}}'\cdot\mathbf{j}(\mathbf{x}',t)}{4\pi|\mathbf{x}-\mathbf{x}'|} \tag{7a}$$

and

$$\mathbf{j}_\perp(\mathbf{x},t) = \int_V d\mathbf{x}'\,\frac{\nabla'\times\mathbf{j}(\mathbf{x}',t)}{4\pi|\mathbf{x}-\mathbf{x}'|} - \oint_{\partial V} da'\,\frac{\hat{\mathbf{n}}'\times\mathbf{j}(\mathbf{x}',t)}{4\pi|\mathbf{x}-\mathbf{x}'|}\,, \tag{7b}$$

so that $\nabla\cdot\mathbf{j} = \nabla\cdot\mathbf{j}_\parallel$. If V recedes to infinity and $\mathbf{j}$ is regular there, the above surface integrals vanish. This decomposition of $\mathbf{j}$ results in ϕ being harmonic which is not pursued for the aforesaid reasons in addition to the following.

4. By the maximum principle [149, 179], if ϕ is subharmonic in V it attains its maximum on ∂V and not in the interior of V.
5. In the finale of this paper, an arguably propitious ending to a moribund and timeless Universe [180, 181, for e.g.] is suggested.

A molecule is a sufficiently stable, electrically neutral group of at least two atoms in all manner of configurations and shapes held together by covalent bonds in the long-range Coulomb field acting between its constituent electrons and nuclei. It may consist of atoms of a single or different elements or of isotopes of the same element. Molecules are of many types and shapes but for each the problem in describing their nuclear motions differ. The arrangement of their atoms allows them to rotate coupling to the vibrations of their nuclei as well as to the orbital and spin angular momenta of their electrons. Condensed phases exhibiting metallic bonding, noncovalent bonds (ionic and hydrogen bonds), glasses (solids in a vitreous state), and materials of several classes (dielectrics, conductors, semiconductors, insulators, etc.) do not strictly present as single molecules, that object whose response to minimal interrogation is consistent with reductionist inquiry. As a single molecule contacts a heat bath of low-to-moderate temperature on ∂V it becomes excited: its nuclei move with the absorption of photons (vibrational energy) or rotons (angular momentum energy) and under the aegis of its Hamiltonian operator the configuration of its electrons and nuclei changes while endeavoring to maintain stability as it restores equilibrium through the redistribution of energy among its low-frequency degrees of freedom. If equilibrium is unattainable or the heat reservoir is at a high enough temperature the molecule will rip apart, dissociating into other smaller molecules or sundry reactive fragments (free radicals, atoms, ions, bare nuclei, free electrons, etc.) which eventually relax to stable entities through collisional deactivation with each other or the spontaneous emission of light. In macromolecules the transduction of the energy available falls within physiologically sustainable thermal limits of biological processes when mediated by specific enzymes with the involvement of ancillary molecular devices (membranes, filaments, channels, templates, etc.) [182].

Thermodynamics [183, for e.g.] is independent of quantum mechanics and its concepts which equate the internal energy U to the sum of the kinetic and potential energies of all elementary particles that comprise the system. Molecular stability does not rest solely with the Hamiltonian operator of the "isolated" molecule. Neither the system's state ψ nor its expected energy $\langle H\rangle$ is a stationary state or an energy level of the molecule, respectively, whose environment contains both matter and radiation [184], the molecule being amenable to the receipt of sensible heat only from its environment. In addition to the conservative Coulomb interactions included in the potential part of the Hamiltonian operator are Lorentz-Faraday interactions between the electrons and nuclei of the molecule that are affected by the surroundings in which a molecule resides. The internal force $\boldsymbol{F}_{\text{int}}(\mathbf{x},t)$ acting within a molecule viewed as a closed conservative system (*vide infra*) is

$$\boldsymbol{F}_{\text{int}} = \frac{\partial\mathbf{j}}{\partial t}\,u(T)\,, \tag{8a}$$

where $u(T)$ is the Heaviside step function, it being 1 if $T > 0$ and 0 otherwise (when the system is "isolated"). Hereon $u(T)$ is dropped in $\boldsymbol{F}_{\text{int}}$, its requisite presence being understood. At finite T, $\boldsymbol{F}_{\text{int}}$ is a conservative Lorentz-Faraday force acting on the nuclei and electrons of the molecule and gives rise to an energy contribution $\nabla\cdot\boldsymbol{F}_{\text{int}}(\mathbf{x},t)$ to their kinematic motions; otherwise $\boldsymbol{F}_{\text{int}}$ is zero and inoperative. Like $\mathbf{j}(\mathbf{x},t)$, $\boldsymbol{F}_{\text{int}}(\mathbf{x},t)$ is a self-adjoint operator.

Since $\mathbf{j}(\mathbf{x},t) = \rho(\mathbf{x},t)\,\nabla\phi(\mathbf{x})$ and with the use of (1a), (8a) may be rewritten as

$$\frac{\partial\mathbf{j}}{\partial t} + \nabla\phi\,\nabla\cdot\mathbf{j} = 0\,, \tag{8b}$$

a quasilinear first-order PDE for $\mathbf{j}(\mathbf{x},t)$. In contrast to (1a), (8b) is not a continuity but rather an advection equation. Un-

der time reversal (8b) is

$$\frac{\partial \mathbf{j}}{\partial t} - \nabla\phi\,\nabla\cdot\mathbf{j} = 0. \tag{8c}$$

If the initial/boundary-value problem PDE in (8b) has the solution $\mathbf{j}(\mathbf{x},t) = \rho(\mathbf{x},t)\,\nabla\phi(\mathbf{x})$, the backward initial/boundary-value problem PDE in (8c) is physically equivalent to the forward time (8b) with the sign of $\nabla\cdot\mathbf{j}$ flipped. If ϕ is subharmonic, $\nabla^2\phi > 0$ independently of the sign of t.

A thermodynamic process changes the state of a system under the action of a driving force, external or internal. The larger the force, the more the process proceeds, perhaps, subject to kinetic constraints. A reversible process is an idealization that can be reversed at any time by an infinitesimal change in the driving force that reverses its sign; it must occur infinitely slowly so that the system and its surroundings have time to relax through staged equilibria ultimately leading each to reach stasis. There are no truly reversible processes in Nature, only calculations for them that are applied to real processes which are irreversible and whose original state cannot be restored without concomitant changes to the surroundings.

Thermodynamics is concerned only with the effects of heat and work in the interaction between a system and its environment. Its laws not only exert their influence in every field of the natural sciences, but also play a part in all industrial processes in which energy is transferred. It does not inquire into the mechanism of phenomena and so it is unconcerned with what happens on an atomic or subatomic scale even though that perspective can help to give deeper meaning to its laws and concepts. The branch of science concerned with this is statistical mechanics, the mechanics of such a large number of atoms or molecules that specifying the state of each is impossible and one is forced to use statistical methods. Entropy is calculated via Boltzmann-Gibbs statistics applicable to ensemble representations of the system under study which, however, are unavailable here. Single molecule techniques [185,186] reveal behavior masked in ensemble averages of complex systems.

There are many physical statements of the SLT any one of which can be used to show its equivalence to another and to prove the mathematical statement of the SLT: there exists a state function (entropy, S) whose change ΔS for any spontaneous process satisfies the Clausius inequality [53, 187]

$$\Delta S(t) \geq \oint_{\partial V} \frac{đQ}{T} \geq 0 \tag{9}$$

which encapsulates the increase in entropy principle. The distinction between the system and its surroundings must be unambiguous through the presence of a *bona fide* boundary across which the flux of matter, charge, heat, etc. can freely pass. A constant-temperature (T) heat bath with which the system is in contact through its boundary ∂V serves as the surroundings. The integral is over the surface ∂V that constitutes the boundary between the molecule of volume V and its environment. The Clausius integral $\oint_{\partial V} đQ/T$ is positive for irreversible processes, is zero for reversible processes, and can never be negative. The inequality implies that the entropy given to the environment is greater than the entropy transferred as heat from the hot reservoir. The operative Carnot cycle here is a fiduciary audit of the net exodus of efflux over the coverage of ∂V contacting the heat bath. It is this audit that undermines all supposed objections to the SLT, just as Planck [7, loc. cit., pp. 103–104] anticipated. If $\oint_{\partial V} đQ/T$ vanishes, $1/T$ is an integrating factor [188, 189] for $đQ$, an inexact differential.

The two best-known statements of the SLT are: (1) If a system undergoes a Carnot cyclic process it cannot turn heat entering the system into work done on the surroundings with unit fractional efficiency (Kelvin-Planck statement); (2) Heat cannot flow spontaneously from a cooler to a hotter object (Clausius' statement). Historically, the mathematical formulation of the SLT was reached through the empirical study of the limitations of steam-driven heat engines designed to convert one form of energy (sensible heat) into mechanical energy (work) at the start of the industrial revolution. Nowadays engines or motors run the gamut from electrical, pneumatic, hydraulic, molecular, etc. using sundry working media. The exchange of work and the working element between a system and its surroundings is always an irreversible process. An alternative mathematical approach to the foundations of thermodynamics emerged from the study of nonlinear deformations of continuous media [190, for e.g.].

The Clausius inequality provides a means of delimiting the entropy change of any process that begins at equilibrium to which state it returns as if nothing happened with no overall change in the entropy of the system and its surroundings, or begins in an arbitrary state to end with a net production of entropy; it means that no process can decrease the entropy of the Universe and, together with the zeroth law of thermodynamics, implies that a temperature of absolute zero is unreachable. Equipped with a false antecedent, the claim that the concept of entropy is inapplicable to single systems (a molecule and its Universe, for e.g.) but only to ensembles of them is as counterfactual [191] as it is casuistic [192]. The Clausius inequality is based on his statement of the SLT and provides a means of distinguishing reversible from irreversible processes based on the earlier findings of Carnot (without his view that heat is a fluid) and independently of volume number density (sic thermodynamic limit).

The first law of thermodynamics relates the internal energy or enthalpy U to heat Q and work W as

$$dU = đQ + đW\,, \tag{10a}$$

or

$$-đW \leq -dF\,, \tag{10b}$$

an expression of the fact that the same change dU in U can be produced either by the sole addition of sensible heat $đQ$ or work $đW$ or by contributions from both. The signs used correspond to the IUPAC* and not the Clausius convention whereby all net energy transfers from the surroundings (system) to the system (surroundings) are positive (negative), respectively. Here, $đQ = TdS$ and relates U to T, S, and the Helmholtz free energy $F = U - TS$, this being the amount of energy free to do work in response to entropy losses. Gradients in F are the driving forces of all biochemical processes and their reliable calculation [193, et passim] is intensively pursued. The internal energy U is the sum of the sensible heat Q accumulated by the system and the work W done by it although physically each differs from the other. Like $đQ$, $đW$ is an inexact differential and is called the configuration work; it is the amount of work done changing the configuration of a system from one to another and depends on how the work is done, i.e. on the path taken between the initial and final configurations. Energy (kinetic, potential) is an attribute that matter and radiation have or can acquire or lose. Unlike entropy, energy is a conserved quantity but this is difficult to audit especially when it dissipates or thermalizes. Both kinetic and potential energies are interconvertible and their scales are arbitrary. Heat (thermal, radiation) is a process in which a system acquires or loses energy as a consequence of it having a different temperature than its surroundings. Work is a transfer of energy to or from a system by any means other than heat; it can be fully converted into heat as in friction but heat can only be partially converted to work. There is no entropy associated with energy transfer as work. Although the first law places no restriction on the direction of a process, it does not guarantee that the process will occur, that being decided by the SLT in conjunction with physical and chemical kinetics considerations.

The SLT asserts that [133, 194, for e.g.] natural processes are irreversible, i.e. the entropy $S(t)$ always increases as the system strays from equilibrium at an absolute temperature $T(\mathbf{x}, t)$ via an exchange of heat (and its transformation to mechanical work) $đQ = d\mathbf{x} \cdot \boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ with its surroundings. The zeroth law of thermodynamics leads to a definition of temperature via the relation $1/T = (\partial S/\partial U)_V$ that forms the empirical basis for the calorific measurement of entropy, with $TdS = đQ$ describing how entropy changes in the amount dS when an inexact differential amount of energy $đQ$ is introduced as heat into the system at a finite temperature $T > 0$ delineated by the zeroth law of thermodynamics.

The Clausius inequality in (9) stipulates that ΔS equals or exceeds the quantity $\oint_{\partial V} đQ/T$. Here $đQ$ is heat or energy or work. There is nothing in science or beyond to prevent the integrand in $\oint_{\partial V} đQ/T$ from being taken to be and applied to an arbitrary system without reference to Boltzmann-Gibbs or Tsallis statistical mechanics. This is precisely what is done here in accepting $đQ$ for what it is, i.e. the heat (energy) or work (mechanical energy) conversion that occurs between the system of interest and a heat bath (its minimal environment) which it ineluctably contacts.

Regardless of the notion of temperature fluctuations [195–197, et passim] or indeterminacy providing justification for the complementarity relation $\Delta U \Delta(1/T) \geq k_{\text{B}}$ [198–200] in analogy with Heisenberg's uncertainty principle for position and momentum in quantum mechanics, here T is taken to be a parameter that is characteristic of the heat reservoir and is known *a priori* with thermal noise viewed as [201, loc. cit., p. 191] "the least disturbing for the physicist" unconcerned with emerging technologies. If T is the known temperature of the heat bath, $T(\mathbf{x}, t)$ is the temperature at $\mathbf{x} \in \partial V$. To de Broglie [202, loc. cit., p. 29] in discussing no less than the Boltzmann-Gibbs canonical distribution "... the notion of temperature is meaningful for just one molecule when that molecule is found to be in energetic contact with a thermostat of temperature T that *imposes* its temperature upon the molecule." For present purposes the thermostat is not hidden as is de Broglie [202]'s based on Bohm and Vigier [203]'s subquantum hypothesis, but rather $T = T(\mathbf{x}, t) \,\forall\, \mathbf{x} \in \partial V$ at any time t [188] as tacitly assumed by Clausius. Consequently

$$\begin{aligned} \Delta S(t) \geq \oint_{\partial V} \frac{đQ}{T} &= \oint_{\partial V} \frac{da}{T}\, \hat{\mathbf{n}} \cdot \boldsymbol{F}_{\text{int}} \\ &= \oint_{\partial V} \frac{da}{T}\, \hat{\mathbf{n}} \cdot \frac{\partial \mathbf{j}}{\partial t}\,. \end{aligned} \tag{11a}$$

Quantum mechanically $\hat{\mathrm{T}}\mathbf{j}(\mathbf{x}, t)\hat{\mathrm{T}}^{-1} = \mathbf{j}(\mathbf{x}, -t)$ so that $\mathbf{j}$ is even in t since the Wigner time reversal operator $\hat{\mathrm{T}}$ is antiunitary and $\hat{\mathrm{T}} i \hat{\mathrm{T}}^{-1} = -i$ as was noted earlier. Consequently, $\boldsymbol{F}_{\text{int}}(\mathbf{x}, t) = \partial \mathbf{j}(\mathbf{x}, t)/\partial t$ is odd in t. Since $\boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ is odd because $\mathbf{j}(\mathbf{x}, t)$ is even under time reversal, it follows with reference to (8b) and (8c) that the gain in entropy $\Delta S(t)$ as given in (11a) is asymmetric in time†, i.e. $\Delta S(t) = \Delta S(-t)$. Traveling backwards in time as is permitted by both quantum mechanics and electrodynamics would cause $\Delta S(t)$ to decrease contrary to the SLT and is consequently forbidden. Whether the process is reversible or irreversible, ΔS treats time $t \geq 0$ as a positive semi-definite parameter. Using (1a), (5), and (11a) it is clear that

$$\langle \Delta S(t) \rangle \geq \oint_{\partial V} \frac{da}{T}\, \rho \left(\rho \nabla^2 \phi + \nabla \rho \cdot \nabla \phi\right) \hat{\mathbf{n}} \cdot \nabla \phi \tag{11b}$$

which is the quantum Clausius inequality for the expectation value of the asymmetric $\langle \Delta S(t) \rangle = \langle \Delta S(-t) \rangle$ entropy change of a molecule in contact with a thermostat at time t. $\langle \Delta S(t) \rangle$ is monotone increasing [122, cf. Fig. 9] provided ϕ is subharmonic.

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†A real function $f(x)$ of a real variable x is odd (asymmetric via a π reflection through the origin) iff $f(x) = -f(-x)$ or even (symmetric about the $f(x)$ axis) iff $f(x) = f(-x)$ in the domain of f.

If the single molecule under investigation here were one of an ensemble of noninteracting replicas, each similarly prepared in the same state ψ and to which considerations of Bose-Einstein, Fermi-Dirac, or Maxwell-Boltzmann statistics are not required [204, cf. §2.01], one has the same problem treated by von Neumann [205, cf. §5.2] in his appeal to Szilard [206]'s one-molecule heat engine, a scenario criticized by some [207, for e.g.], validated by many [208, cf. Ch. VI], [97, 209–213], and the first to point out the connection between entropy and information. In the absence of demons and pistons*, the thermodynamic limit [214–217], [218, cf. Ch. 14] issue is irrelevant since it does not apply to a lone molecule in a thermal bath whose sole task is to supply heat to maintain that molecule's fluctuating charge density $\rho(\mathbf{x}, t)$, current density $\mathbf{j}(\mathbf{x}, t)$, and deformable volume V. Nor does a thermodynamic limit apply to the known Universe. Previously, using only the elementary notion of work, $đQ = d\mathbf{x} \cdot \boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ was identified as the action over a differential displacement $d\mathbf{x}$ in V of the quantum mechanical Lorentz-Faraday force $\boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ given in (8a) in terms of the thermally-driven current density $\mathbf{j}$ of a single molecule.

The integrand of the integral in (11b) is also the integrand in the Claussius inequality given in (9). If it is to be estimated, it is best done using statistical methods where the integrand's dependencies $(\rho, \phi, T, \mathbf{x})$ at time t are treated as independent and identically distributed random fluctuating variables drawn repeatedly from appropriate probability distributions under the auspices of the law of large numbers. That part of the integrand in parenthesis is the outward flux of $\mathbf{j}$ across ∂V. The two inner products $\nabla\rho \cdot \nabla\phi$ and $\hat{\mathbf{n}} \cdot \nabla\phi$ in the integrand each involve outbound gradients and are positive [219–224] since these gradients make more probable glancing and head-on egress across ∂V than the biased presumption that they be tangent to the boundary ∂V, exclusively or otherwise. The only term that can cause the integral to change from positive to negative in violation of Clausius' inequality is that involving $\nabla^2\phi$ thus making it necessary and sufficient that ϕ be subharmonic [148, 149] in V so that no such transgression occurs. Whether the Hamiltonian operator of the system of interest is autonomous or not has no bearing† on the T-asymmetry of $\langle \Delta S(t) \rangle$ and likewise does not negate the T-symmetry of either quantum mechanics or electrodynamics.

Besides distinguishing between two possible types of processes on the basis of changes in entropy as determined by finite $\nabla\phi$, there are several other features of Clausius' inequality worth recalling: (a) it is a consequence of the SLT; (b) it is not an evolutionary relationship; (c) it does not rely on knowledge of a system's microstates, just the current state; (d) entropy is the outcome of a process; (e) it is T-asymmetric without obliging the same of any allied dynamical framework including quantum mechanics‡.

The lone molecule ensconced in a heat bath is free to visit the entirety of its configuration space demarcated by V. Since it has been shown that $\langle \Delta S(t) \rangle = \langle \Delta S(-t) \rangle$ and as an alternative to ensemble averaging, its Laplace long-time average $\overline{\langle \Delta S_\tau \rangle}$ may be taken [235, cf. p. 68] as

$$\begin{aligned} \overline{\langle \Delta S_\tau \rangle} &= \frac{1}{\tau} \int_0^\infty dt\, e^{-t/\tau} \langle \Delta S(t) \rangle \\ &= \int_0^1 dt\, e^{-t} \langle \Delta S(\tau t) \rangle \,, \end{aligned} \tag{11c}$$

where $\tau > 0$ is a phenomenological relaxation time for ubiquitous exponential decay [236] that has both system and environment dependencies. Independently of τ, $\langle \Delta S(t) \rangle$ fluctuates en route to $\overline{\langle \Delta S_\tau \rangle}$ with a variance $\sigma_\tau^2 = \overline{\langle \Delta S_\tau^2 \rangle} - \overline{\langle \Delta S_\tau \rangle}^2$. Since (11c) provides a means of time averaging under nonstandard state conditions and with the accommodation of relaxation, it obviates subjective biases related to the unmeasured properties of an ensemble of replica systems. Unlike electromechanical systems where molar statistics is apropos, Avogadro quantities of macromolecules are not always available in biological and nanoscale systems where finite-time measurements come to the fore, ergodic behavior is arguably applicable, and ensembles are moot. The same applies to the known Universe. The provision of $\Delta S(t)$ data is through calorimetry or via Monte Carlo-Markov chain techniques [237, 238]. This Laplace time-averaging is equally applicable to Helmholtz $\overline{\Delta F(t)}$ and Gibbs $\overline{\Delta G(t)}$ free energies whose time averages $\overline{\langle \Delta F_\tau \rangle}$ and $\overline{\langle \Delta G_\tau \rangle}$ are roughly equal for entropy-driven pro-

*Zurek [210, loc. cit., p. 152]'s rebuttal of Jauch and Báron [211]'s primary argument reads "One may argue that the one-molecule engine cannot be analyzed by means of thermodynamics (sic statistical mechanics), because it is nowhere near the thermodynamic limit. This objection is overruled by noting that arbitrarily many "Szilard's engines" can be linked together to get a "many-cylinder" version of the original design. This will cut down fluctuations and allow one to apply thermodynamic (sic statistical mechanics) concepts without difficulty". Indeed, the entropy increase in time of an ensemble of entities is determined by their current states as affected by internal conservative potentials (Coulomb, Newtonian, thermal Lorentz-Faraday, etc.), prevailing pair-wise force fields (Lennard-Jones and more-exotic empirical variants), and external nonconservative potentials (catalysts, lasers, particle beams, etc.) that aspire to control them.

†This is consistent with Landau and Lifshift [225, loc. cit., p. 51]'s observation that "The form of the Hamiltonian for a system of particles which interact with one another cannot be derived from the general principles of quantum mechanics alone."

‡Bohm, Gadella and coworkers [226, et passim] postulate a time asymmetric quantum theory (TAQT) by associating states and observables to two different Hardy subspaces dense in the same Hilbert space that does not distinguish between the in-states and out-states of scattering theory but which in TAQT would cause the dynamical equations (in the Schrödinger and Heisenberg pictures) to integrate to a semigroup evolution. TAQT is not without its critics [227–230]. Within a cellular automaton interpretation of quantum theory, 't Hooft [231] makes similar claims. Oliver Penrose (esteemed thermodynamicist and older brother of Roger)'s critical review [232] of Mackey [233]'s book are equally apropos to any proposal that requires quantum mechanics to waive its time reversal invariance, an imposition obviated by the SLT as will be revealed in this paper. Kuzemsky [234, et passim] has surveyed foundational issues of the problem of time and its asymmetry, a consideration outside the scope of this paper.

cesses and identical for an uncompressed single molecule [183].

Entropy generation S_{gen} (what Clausius [239, cf. Eq. 71] called production rate) is the entropy produced during a process as given by

$$S_{\text{gen}}(t) = \Delta S(t) - \oint_{\partial V} \frac{đQ}{T}\,. \tag{11d}$$

It is zero or positive for a reversible or irreversible process [240, 241], respectively. Irreversibilities degrade the performance of systems and S_{gen} is a measure of their magnitude during a process. It is impossible for $S_{\text{gen}} < 0$ so that it cannot influence the thermodynamic arrow of time any more than can F_{int}. However, whereas F_{int} is inherent to the system and its dynamics, S_{gen} is part of the process. The entropy generation S_{gen} would vanish if the requirement that ϕ be subharmonic were relaxed to it being simply harmonic in V which was previously dismissed: (11b) and (11d) imply that

$$S_{\text{gen}}^{\nabla^2\phi>0}(t) \geq S_{\text{gen}}^{\nabla^2\phi=0}(t) \geq 0\,, \tag{11e}$$

so that subharmonic ϕ favors entropy generation more than harmonic ϕ.

In thermodynamics, work performed by a system is energy it transfers to its surroundings and the surroundings transfers energy to the system and both transfers incur a price. Even though $\oint_{\partial V} đQ/T$ is finite for natural processes, reflecting the fact that entropy is not conserved, use of the divergence theorem on $\oint_{\partial V} đQ$ gives

$$\oint_{\partial V} đQ = \oint_{\partial V} da\,\hat{\mathbf{n}}\cdot\boldsymbol{F}_{\text{int}} = \int_V d\mathbf{x}\,\nabla\cdot\boldsymbol{F}_{\text{int}} \tag{12a}$$

as the work done by $\boldsymbol{F}_{\text{int}}$. The orientable manifold V of configuration space encloses the flux $\nabla\cdot\boldsymbol{F}_{\text{int}}$ of $\boldsymbol{F}_{\text{int}}$ and the generalized Stokes theorem [242, 243, for e.g.] further provides

$$\oint_{\partial V} đQ = \int_V d\mathbf{x}\,\nabla\cdot\boldsymbol{F}_{\text{int}} = \int_V d\mathbf{x}\cdot\nabla\times\boldsymbol{F}_{\text{int}}\,. \tag{12b}$$

The divergence and curl of $\boldsymbol{F}_{\text{int}}$ are

$$\nabla\cdot\boldsymbol{F}_{\text{int}}(\mathbf{x},t) = \psi^*(\mathbf{x},t)\nabla^2\psi(\mathbf{x},t) - \psi(\mathbf{x},t)\nabla^2\psi^*(\mathbf{x},t)\,, \tag{12c}$$

and

$$\nabla\times\boldsymbol{F}_{\text{int}}(\mathbf{x},t) = \nabla\psi^*(\mathbf{x},t)\times\nabla\psi(\mathbf{x},t) - \nabla\psi(\mathbf{x},t)\times\nabla\psi^*(\mathbf{x},t) \tag{12d}$$

respectively. The curl of $\boldsymbol{F}_{\text{int}}$ vanishes for all $\mathbf{x}\in R^n$. However, the divergence of $\boldsymbol{F}_{\text{int}}$ vanishes locally only when ψ or $\nabla\psi$ does so. Since there is no creation or destruction of charge within V and the Laplacian operator is self-adjoint, $\oint_{\partial V} đQ$ vanishes so that $\boldsymbol{F}_{\text{int}}$ does no work, i.e.

$$\begin{aligned} Q = \int_{\partial V} d\mathbf{x}\,đQ &= \int_V d\mathbf{x}\,\nabla\cdot\boldsymbol{F}_{\text{int}} \\ &= -\int_V d\mathbf{x}\nabla^2\mathcal{V}_{\text{int}} = 0\,, \end{aligned} \tag{12e}$$

where $\boldsymbol{F}_{\text{int}}(\mathbf{x},t) = -\nabla\mathcal{V}_{\text{int}}(\mathbf{x},t)$ with $\mathcal{V}_{\text{int}}(\mathbf{x},t)$ being the potential energy function of $\boldsymbol{F}_{\text{int}}(\mathbf{x},t)$. Thus, despite its spatial and time dependence, $\boldsymbol{F}_{\text{int}}(\mathbf{x},t)$ is a conservative and not a dissipative force like friction or viscous drag that does negative work in the direction opposite to the displacement of its target which consequently loses energy as heat in the amount removed by such a force. The subharmonicity of ϕ is what makes $\boldsymbol{F}_{\text{int}}$ a conservative force, one that conserves mechanical energy.

3 Faradaic induction in a thermal field

Gauge theories [244] enable a reduction in the number of variables necessary to define a physical state quantum mechanically (configuration space, $\mathbf{x}$) over that required classically (phase space, $\mathbf{x}$ and $\mathbf{p}$). Electrodynamics was the first field theory to exploit gauge symmetry by recognizing that any function that can be written as a gradient could be added to the vector potential without affecting the magnetic field. Acting on a suggestion by London [245], Weyl [246, pp. 100-101] replaced the gauge scale factor with a complex quantity and turned the scale transformation into a change of phase. The gauge field of electrodynamics associates an element of the group $U(1)$ of unit complex numbers under multiplication to each path: the phase that a charged particle gets when going through a loop is the magnetic flux through the loop. The physical states of quantized systems are described [141, for e.g.] by vectors ψ of unit norm belonging to a complex Hilbert space $\mathcal{H}$. Physical observables are associated with self-adjoint operators O acting on $\mathcal{H}$ whose expectation values are scalar inner products $\langle\psi|\,O\psi\rangle$ in $\mathcal{H}$ that are unaffected by unitary transformations which act on both state vectors $\psi \mapsto U\psi$ and operators $O \mapsto OUO^\dagger$, where U is unitary. Thus, the multiplication of state vectors by a phase (a $U(1)$ global group transformation) $\psi \mapsto e^{i\phi}\psi$ leaves operators and physical predictions unchanged provided O does not differentiate ψ either spatially or temporally. Neither $\mathbf{j}(\mathbf{x},t)$ nor $\partial\mathbf{j}(\mathbf{x},t)/\partial t$ are such-like operators so that their inclusion of $U(1) = e^{i\phi}$ cannot be disregarded since the $U(1)$ phase $\phi(\mathbf{x})$ is local. This is reminiscent of earlier speculations by Schrödinger [247] based on Weyl [246]'s spacetime theory in connection with the Wilson-Sommerfeld [173, 174] quantization condition for Bohr's old quantum theory of the H atom. For this reason, ϕ is referred herein as the unadorned "phase", rather than Schrödinger [150]'s "phase angle", de Broglie's "phase wave", or Weyl's "gauge transformation", all three being essentially one and the same. Failure to notice that the Schrödinger equation is not gauge invariant under a local gauge transformation is due in large to two commonly-held notions, viz. that it takes an external electromagnetic field to do so when in fact it does not [142, 143], and that, in confounding local with global, the phase of the wave function is arbitrary when in fact it is not [248] unless it is global.

The thermal field induces an internal electromagnetic con-

servative force field $\boldsymbol{F}_{\rm int}(\mathbf{x},t)$ of scalar potential Φ and vector potential $\mathbf{A}$ in the system whose Helmholtz-Hodge decomposition [176–178] reads as

$$\boldsymbol{F}_{\rm int} = -\nabla\Phi + \nabla\times\mathbf{A} \tag{13a}$$

into the scalar longitudinal (irrotational, curl-free) potential $\Phi(\mathbf{x},t)$ and the vector transverse (solenoidal, div-free) potential $\mathbf{A}(\mathbf{x},t)$ which provide, via Maxwell's equations, for the *internal* microscopic electric

$$\boldsymbol{E}_{\rm int} = -\nabla\Phi - \partial\mathbf{A}/\partial t \tag{13b}$$

and the *internal* microscopic magnetic induction

$$\boldsymbol{B}_{\rm int} = \nabla\times\mathbf{A} \tag{13c}$$

fields which at every point in space and time obey the microscopic Maxwell equations. There is only one kind of charge and the amount of it anywhere can be positive, negative, or zero subject solely to its conservation regardless of whether it is believed to be associated with a nucleus or an electron. The prominence of electromagnetic potentials in quantum theory is due in large to the work of Aharonov and Bohm [249,250].

Rhetorically, $\mathbf{A}(\mathbf{x},t)$ generates $\boldsymbol{B}_{\rm int}(\mathbf{x},t)$ through its circulation and $\boldsymbol{E}_{\rm int}(\mathbf{x},t)$ through its time dependence with $\rho(\mathbf{x},t)$ and $\mathbf{j}(\mathbf{x},t)$ playing supporting roles encapsulated in the Lorentz microscopic force density

$$F_{\rm int} = \rho\boldsymbol{E}_{\rm int} + \mathbf{j}\times\boldsymbol{B}_{\rm int}\,, \tag{13d}$$

where

$$\begin{aligned} F_{\rm tot}(t) &= \int_V d\mathbf{x}\cdot F_{\rm int}(\mathbf{x},t) \\ &= \oint_{\partial V} da\,\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}_{\rm int}(\mathbf{x},t) - \frac{d}{dt}\int_V d\mathbf{x}\cdot\boldsymbol{S}_{\rm int}(\mathbf{x},t)\,, \end{aligned} \tag{13e}$$

is the total electromagnetic field on the charges in V, $\boldsymbol{\sigma}_{\rm int}$ is the Maxwell stress tensor, and the Poynting vector $\boldsymbol{S}_{\rm int}$ is given by

$$\boldsymbol{S}_{\rm int} = \boldsymbol{E}_{\rm int}\times\boldsymbol{B}_{\rm int}\,, \tag{13f}$$

and

$$\boldsymbol{F}_{\rm int} = \nabla\cdot\boldsymbol{\sigma}_{\rm int} - \dot{\boldsymbol{S}}_{\rm int} \tag{13g}$$

pursuant to the conservation of linear momentum. In (13g) the last term on the right is the time derivative of the field's photon momentum density while the first is the divergence of the stress tensor bearing on the charges in V.

Both $\Phi(\mathbf{x},t)$ and $\mathbf{A}(\mathbf{x},t)$ retain their spatial and nonretarded time dependencies without the $\boldsymbol{E}_{\rm int}$ and $\boldsymbol{B}_{\rm int}$ fields descending to electrostatics since the Lorenz condition [251–255] has not been invoked. Mathematically, the potentials $\Phi(\mathbf{x},t)$ and $\mathbf{A}(\mathbf{x},t)$ are volume integrals of the divergence and curl of $\boldsymbol{F}_{\rm int}(\mathbf{x},t)$ scaled by the Green's function for the Laplacian analogously to (7a) and (7b), respectively. It is clear from (1a), (5), and (13a) that the irrotational part of $F_{\rm int}$ is

$$\nabla\Phi = \rho\nabla^2\phi\nabla\phi \tag{14a}$$

while the solenoidal part is

$$\nabla\times\mathbf{A} = -\nabla\phi\cdot\nabla\rho\nabla\phi\,, \tag{14b}$$

with both parts being in the same direction as $\nabla\phi$. Neither potential is directly measurable and may be replaced by gauge-equivalent potentials θ and $\mathbf{A}+\nabla\phi$, respectively, to yield the same $\boldsymbol{E}_{\rm int}(\mathbf{x},t)$ and $\boldsymbol{B}_{\rm int}(\mathbf{x},t)$.

Maxwell's equations are linear dynamical PDEs that have a unique solution for given initial and boundary conditions. From these equations it is straightforward to show that the scaler $\Phi(\mathbf{x},t)$ and vector $\mathbf{A}(\mathbf{x},t)$ potentials satisfy

$$\Box\,\Phi = -\frac{\partial}{\partial t}\left(\nabla\cdot\mathbf{A} + \frac{\partial\Phi}{\partial t}\right) - \rho \tag{15a}$$

and

$$\Box\,\mathbf{A} = \nabla\left(\nabla\cdot\mathbf{A} + \frac{\partial\Phi}{\partial t}\right) - \mathbf{j}\,, \tag{15b}$$

respectively, where $\Box = \nabla^2 - \partial^2/\partial t^2$ is the d'Alembertian operator. These promote use of the Lorentz condition in which the term in parenthesis common to both is set to zero, a gauge strategy of historic [244] importance to physics.

Alternatively, use of the curl of the curl identity, Gauss's law of electricity in the curl of Faraday's law, and Gauss's law of magnetism in the curl of Maxwell-Ampère's law, allows one to arrive at the coupled inhomogeneous wave equations [256] for the $\boldsymbol{E}_{\rm int}(\mathbf{x},t)$ and $\boldsymbol{B}_{\rm int}(\mathbf{x},t)$ fields as

$$\Box\,\boldsymbol{E}_{\rm int} = 4\pi\left(\nabla\rho + \frac{\partial\mathbf{j}}{\partial t}\right) \tag{16a}$$

and

$$\Box\,\boldsymbol{B}_{\rm int} = -4\pi\nabla\times\mathbf{j}\,, \tag{16b}$$

respectively. In (16a) and (16b), $\Box$ acting on $\boldsymbol{E}_{\rm int}(\mathbf{x},t)$ and $\boldsymbol{B}_{\rm int}(\mathbf{x},t)$ generates inextricably coupled electromagnetic waves given sources in gradients of ρ, time-varying changes in $\mathbf{j}$, and circulations of $\mathbf{j}$. The Lorentz-Faraday force $\boldsymbol{F}_{\rm int}(\mathbf{x},t)$ first introduced here in (8a) is none other than one of two source terms for the wave equation of $\boldsymbol{E}_{\rm int}(\mathbf{x},t)$ and leads to the possibility of the oscillation or acceleration of charge which radiates more or less transverse to the direction of propagation. At idealized $T = 0$ where $F_{\rm int}(\mathbf{x},t)$ is absent, the charges in an "isolated" (sic stationary state) molecule oscillate in place without accelerating and their Coulomb radiation field decays as $1/|R'|^2$ where R' is the line of sight distance to a charge [256]. More realistically, $T > 0$ causes charges in the molecule to oscillate and accelerate. This produces self-sustaining electric and magnetic fields propagating as electromagnetic waves at the speed of light which transport energy

and momentum to charged particles at large distances from the source at the expense of the accelerated charge. The electric and magnetic fields are orthogonal to each other. When $T > 0$ such that $F_{\rm int}(\mathbf{x}, t)$ is operative, the charges oscillate and accelerate and their radiation field decays as $1/|R'|$ to surpass their shorter-ranged Coulomb radiation field [256]. Since $\nabla\rho$ ultimately vanishes* and $\nabla\times\mathbf{j} = \nabla\rho\times\nabla\phi$, the internal $\boldsymbol{E}_{\rm int}(\mathbf{x}, t)$ and $\boldsymbol{B}_{\rm int}(\mathbf{x}, t)$ fields are pervasive and are the source of photons to be absorbed and emitted within V in the manner first treated by Einstein [257, 258] and later by Dirac [259, 260] in analogy with gravitoelectromagnetic phenomena [261, 262], e.g. Lense-Thirring frame-dragging effects [263, 264], whose internal $\boldsymbol{E}_{\rm int,g}$ and $\boldsymbol{B}_{\rm int,g}$ fields (or equivalently, $\Phi_{\rm int,g}$ and $\mathbf{A}_{\rm int,g}$) are caused by the gravitational interaction of massive celestial objects with neighboring ones.

The $U(1)$ gauge symmetry of electromagnetism represents the group of rotations around a fixed axis. Since the end of the quark era, $U(1)$ has broken the $SU(2)$ x $U(1)$ gauge symmetry of the electroweak force whose three massive bosons $W^{\pm}$ and Z^0 are accompanied by a fourth massless one, the photon. Helmholtz-Hodge photons induce electrically neutral currents in a molecule, in analogy with the decay of Z^0 to neutrinos which scatter off electrons in electroweak interactions [265], and mediate scattering between nuclei and electrons that entail the transfer of momentum, spin, and energy via photon exchange but to the exclusion of charge. $U(1)$ symmetry comes from the fact that the absolute phase ϕ of ρ cannot be measured unlike its finite relative change $\nabla\phi$ as first pointed out by Weyl [248] and adopted by Dirac [266]. The importance of $U(1)$ symmetry comes from Emmy Noether's theorem which states that such gauge symmetries lead to the conservation of a related quantity. Two types of $U(1)$ gauge symmetry are salient, viz. global gauge symmetry where the phase change $\nabla\phi$ vanishes at critical points in space and leads to the conservation of charge; and local gauge symmetry where the phase is not the same at all locations and requires the introduction of an additional gauge field to keep it invariant under such finite relative changes. One may view the local gauge field as signaling phase changes from one point to another by radiatively communicating such changes and in doing so leading a molecule to engage in its own intramolecular entanglement frontier†. Molecules have many degrees of freedom but only two types of material constituents whose positions are not only correlated with each other – a type of correlation known as entanglement [267, cf. Ch. 16], [268, cf. Ch. 5], [269, cf. Ch. 17] and a key property of quantized systems exploited to effect quantum computation [270] in concert with the superposition principle – but also with its internal Helmholtz-Hodge photons whose "wave functions" [271] are inherently part of ψ.

At their prevailing low energies, Helmholtz-Hodge photons serve as the carriers of the nonconservative electromotive force (emf) [272, Sec. 6.1], [273, cf. Ch. 7]

$$\mathcal{E}(t) = \oint_{\partial V} da\,\hat{\mathbf{n}}\cdot(\boldsymbol{E}_{\rm int} + \nabla\phi\times\boldsymbol{B}_{\rm int}) = -\frac{d}{dt}\Phi_{\boldsymbol{B}_{\rm int}}(t) \quad (17a)$$

of molecules through their in situ photon absorption and emission regardless of Faradaic fixtures (wires, circuits, electrodes, batteries, etc.). Emf produces a charge imbalance that causes the lighter electrons to move from nucleophilic to electrophilic regions, this movement being what is recognized as electric current. Electrons can gain or lose energy due to their interaction with $\boldsymbol{B}_{\rm int}$ and $\boldsymbol{E}_{\rm int}$ whereby $\boldsymbol{B}_{\rm int}$ guides their motion, $\boldsymbol{E}_{\rm int}$ accelerates them, and Lenz's law prescribes their direction. Of course, being internal fields rooted in the molecule's structure, $\boldsymbol{B}_{\rm int}$ and $\boldsymbol{E}_{\rm int}$ are not amenable to manipulation or so-called control. The deformation of V due to the magnetic Lorentz force acting on charges is the motional emf while the remaining part of $\mathcal{E}$ is the transformer emf generated by an electric field induced by a changing magnetic field. Eddy currents induced in the cores of transformers and generators dissipate energy as heat loss giving rise to temperature increases.

The quantity on the far right in (17a) is formally

$$\frac{d}{dt}\Phi_{\boldsymbol{B}_{\rm int}}(t) = \oint_{\partial V} da\,\hat{\mathbf{n}}\cdot\left[\frac{\partial\boldsymbol{B}_{\rm int}}{\partial t} - \nabla\times(\nabla\phi\times\boldsymbol{B}_{\rm int})\right], \quad (17b)$$

where $\Phi_{\boldsymbol{B}_{\rm int}}(t)$ represents the internal magnetic flux of the molecule and the Maxwell relation $\nabla\cdot\boldsymbol{B}_{\rm int} = 0$ holds due to the absence of magnetic charges in Nature. The induced $\mathcal{E}(t)$ and the rate of change in $\Phi_{\boldsymbol{B}_{\rm int}}(t)$ have opposite signs so that the cause (induced field) opposes the effect (changing current) in analogy with Newton's third law.

Recall that the binding of electrons to nuclei is modified somewhat by parity-violating Z^0 exchanges that manifest as parity nonconservation in both atoms [274, 275] and molecules [276, 277].

4 Discussion

4.1 Going forward

Obviously

$$\nabla\phi(\mathbf{x}) = \frac{\partial\mathbf{j}(\mathbf{x}, t)}{\partial\rho(\mathbf{x}, t)} \quad (18)$$

thus exposing the elusiveness of the relative phase which clearly changes sign under P because $\mathbf{j}$ does and ρ does not. Neither C nor T changes $\nabla\phi$. The popular assertion that the phase of ψ is arbitrary and has no physical significance is true only if that phase is global. The phase is local, however, and provides an unequivocal link to the Lorentz-Faraday force

*$\nabla\rho$ is the source of charge that is accelerated by $F_{\rm int} = \partial\mathbf{j}/\partial t$. Its inclusion in Clausius' inequality is unnecessary since $\langle\overline{\nabla^2\rho}\rangle$ vanishes.

†With two entangled particles one knows something about their combined properties but their individual properties are indeterminate until one makes a measurement of the state of one particle at which point one has some, but not all, information about the other. Entanglement is a nonlocal correlation between nonseparable states.

$\boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ whose effects are manifest in the unremitting operation of the SLT in blockading quantum mechanics from providing a portal to the past and without curtailing even massive objects from ultimately reaching stasis in going forward. The Lorentz-Faraday force $\boldsymbol{F}_{\text{int}}(\mathbf{x}, t)$ is intrinsically T-asymmetric regardless of the initial and boundary conditions of this or other universes and without electrodynamics or quantum mechanics having to forfeit their innate time-reversal symmetries.

Weak measurement techniques [278–280] have now been extended beyond the massless photon. As long anticipated by Aharonov et al. [281], Bednorz et al. [282] have shown that weak measurements are time-reversal symmetric classically but not so quantum mechanically. More recently, Jayaseelan et al. [283], in weak measurements of the spin of ultra-cold atoms, provided evidence for absolute irreversibility and a strictly positive average arrow-of-time captured by a fluctuation theorem; they further demonstrated absolute irreversibility for measurements performed on a many-body entangled wave function. These demonstrations are consistent with Borel [284, loc. cit., pp. 2–3]'s quip that "Events with a sufficiently small probability never occur," following which he goes on to quantify "sufficiently small" for probabilities that are negligible on the human, terrestrial, and cosmic scale as descending in the order $10^{-6}, 10^{-15}$, and 10^{-80}, respectively. Recall that in particle physics, the gold standard for a discovery is $5\,\sigma$, in which there is a one in 3.5 million chance of the result being a fluke. The BaBar Collaboration found [13] a 1 in 10^{43} $(14\,\sigma)$ level of certainty for their T-asymmetry measurements and CP violation was also observed at the $16\,\sigma$ level, far more than needed to declare a discovery. These observations of T reversal violations in electroweak interactions are consistent with the SLT being T reversal forbidden, the primary revelation of this paper. It remains to be seen (*vide infra*) if T reversal violations are also observed in strong-force interactions.

Manifestly, $\Delta S(t)$ increases and the process is reversible or irreversible according as the gradient in ϕ vanishes or not on ∂V, respectively. The entropy gain ΔS will be proportional to the area of the boundary ∂V enclosing the nominal volume V of the system interfacing its surroundings, just as with black holes. Unlike black holes, however, molecules lack horizons and their gain of entropy is settled by the gradient field of their local phase ϕ in guaranteeing their participation in natural processes without losses from the universe of itself and its heat reservoir. Since the vorticity $\nabla \times \nabla\phi$ vanishes except [285] at nodes in ρ (and $\nabla\phi$ is singular), the entropy gain by the molecule in contacting a heat bath is sheltered from meteorological losses consistent with the absence of swirl in $\boldsymbol{F}_{\text{int}}$ when the heat is withdrawn.

Equations (17a) and (17b) reveal that Faraday's law of induction holds for a single molecule provided the gradient of its local phase is finite, a condition necessary and sufficient for it not to present with its well-known paradoxes [286–288]. Measurements of the emf $\mathcal{E}(t)$, the Helmholtz-Hodge fields $\boldsymbol{E}_{\text{int}}$ and $\boldsymbol{B}_{\text{int}}$, and their ancillary lines of force first envisioned by Faraday [289], for a single molecule using a test charge would be as difficult as it is in quantum electrodynamics [290] but perhaps for different reasons. The long-standing validity of Faraday's law $\mathcal{E}(t) \sim \pm d\Phi_{\boldsymbol{B}_{\text{int}}}(t)/dt$ in engineering applications now has a quantum basis. Of course Faraday's law induces potential, not current which is simply the induced voltage divided by the resistance of the loop. With multiple identical loops Faradays law is additive (sic extensive), i.e. $N\mathcal{E}(t)$ where $N \gg 1$ is the number of loops (windings).

4.2 The stability of a molecule

Clausius' classical virial theorem [291] relating the time averages of the kinetic energy ("vis viva") of a system of discrete particles and the virial ("ergal" or mechanical work) of the system, that being the work done by the gravitational forces (or equivalently, by $-\nabla\mathcal{V}_C$ for a molecule of Coulomb potential $\mathcal{V}_C$) has long served [292] cosmology in accounting for the stability of the most virialized objects in the Universe, clusters of stars and galaxies. The latter are filled with the intrastellar (cluster) medium (IS(C)M), an X-ray-emitting hot plasma with a typical temperature $\sim 10^7$ K. The interstellar medium (ISM), consisting of the matter (atomic, ionic, molecular, dust, cosmic rays) and radiation that occupies the space between the star systems in a galaxy, interacts magnetohydrodynamically with the ICM. Clusters are characterized by the virial radius within which the cluster's mass can be determined under the assumption of the ICM being in hydrostatic equilibrium. Clusters are thought to grow into larger systems through mass accretion flows which are merged into the ICM at a radius of several times the virial radius. Properties such as the temperature or density around the virial radius are not well known because of observational difficulties. The virial theorem holds even for systems that are not in thermal equilibrium. Dark matter's existence was first hypothesized by Zwicky [293] to account for the mass deficit found when the total sum of the masses of individual members in a galactic cluster falls far short of the virial mass whose use assumes that the cluster is stable, an assumption questioned by Ambastumian [294] who maintained that not only are the clusters unstable but they are also exploding, a controversial hypothesis whose history and impact on cosmology is reviewed by Bland-Hawthorn and Freeman [295, cf. 1.10]. A pivotal discovery in this history was Vera Rubin and Kent Ford's confirmation [296] that dark matter is required to account for the rotation of stars and spiral galaxies. Other indicators of the presence of dark matter comes from gravitational lensing [297] and from fluctuations in the power spectrum of the CMB [298].

As the Universe expanded and cooled following the Big Bang, energy was converted to subatomic particles which merged to form protons – the nuclei of H atoms, some of

those nuclei fused to form He so that the early Universe consisted almost entirely of hydrogen, helium, and in lesser amounts, lithium, beryllium, and boron. In time, these dense molecular clouds collapsed under gravity to form stars. Nuclear fusion reactions in these stars spawned more elements and stellar explosions forged even more in the process of nucleosynthesis. The most abundant (greater than 90%) element in the Universe is H followed by He all of whose isotopes are stable except for minuscule amounts of tritium (^{3}H). Molecules account for most of the observable matter in the Universe and are remarkably stable against change. That matter at equilibrium is stable is so self evident that were it otherwise its existential proof would be as redundant as it would be specious. Ordinary matter [299, for e.g.], as comprised of atoms and molecules, has both mass and volume with the former concentrated in its positively charged nuclei and the latter occupied mainly by negatively charged electrons that are of much smaller size than a typical nucleus and are ~ 2000 times lighter than a proton. The mass number A is the sum of the total number of protons (atomic number, Z) and neutrons with differing number of neutrons for the same Z giving different A's for the isotopes of that element. Bulk matter does not implode or eventually explode and is self-evidently stable across low-energy scales from fluids [300, for e.g], to solids [301, for e.g], to engineered structures designed and safety-certified without reference to atomistic considerations [302, for e.g.]. Whereas nuclei have the *Chart of the Nuclides* (~ 3000 in number) and atoms have the *Periodic Table of the Elements* (~ 120 in number), molecules (countless in number) have no such iconic organizational motif. The stability of matter resides in its nuclei, the majority of which are radioactive and undergo decay while the rest are located in the valley of stability between the proton and neutron drip lines as determined by their constitutive proton/neutron ratio and with an island of stability indicative of far longer-lived (but yet to be observed) isotopes of super-heavy elements than the known isotopes of these elements. The nucleons in the nucleus are fermions which obey the PEP and in the case of identical nucleons this results in the small but finite size of nuclei. Nuclides that do not undergo spontaneous decay are stable isotopes. There are about 252 stable isotopes among 80 elements with ^{56}Fe being the most abundant and ^{62}Ni the most stable. The nuclear (or residual strong) force binds nucleons into nuclei through the energy equivalence of their mass defects. This force is relatively short ranged compared to the Coulomb repulsion between protons, being attractive between spin-aligned nucleons until it falls off with distance and repulsive when their separations are small. Additionally, interactions between the spins and angular momenta of nucleons lead to the deformation of nuclei from purely spherical shapes. The nuclear force is known semi-empirically only but is more complicated than the Coulomb force operative between nuclei and electrons in atoms and molecules and its extension beyond the shell model is an active area of research [303, 304, for e.g].

Supersymmetry (SUSY) is the principle that there is an unknown symmetry between fermions and bosons. SUSY was developed to explain the hierarchial disparity between the strength of the electroweak force and gravity by proffering the existence of superpartners of known particles, each having the same properties as the originals except for spin, so as to curtail the magnitude of the Higgs mass from undermining the very stability of the SM construction. SUSY is the source of hypothetical WIMPs in galactic halos. There is currently no evidence for SUSY at high energies.

When Feynman remarked [305, loc. cit., pp. 3–4]:

> It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation ... This probably means that we do not have a complete understanding of the fundamental principle involved,

he was referring to the spin-statistics theorem (SST). Succinctly put, the SST [306] is more easily invoked than its basis and applicability are understood. The SST links the spin (half-integer or integer) property of a physical system comprised of fermions and bosons with the statistics (Fermi-Dirac or Bose-Einstein) it obeys and provides a foundation for the PEP which has long been part of even high school physics and chemistry curricula.

Proof of the SST lies outside the scope of nonrelativistic quantum mechanics: it requires the full arsenal of relativistic quantum field theory, specifically that the fields are invariant under the Poincare group, that there is a vacuum state that is invariant under this group, that all states can be built up from the vacuum by applying field operators, that the Hamiltonian is bounded below, and locality in that the fields either commute or anticommute at spacelike separations. The theorem then says that at spacelike separations boson fields of integer spin commute while fermion fields of half-integer spin anticommute whereupon the PEP emerges. As Feynman was later to recount [307], the CPT theorem illustrates why every subatomic particle must have an antiparticle partner and links to the SST with fermion wave functions changing by a sign under two CPT reflections while bosons do not. Some proofs use CPT invariance to prove the SST while other proofs do the opposite. Nonrelativistic quantum mechanics lacks analogs of both the CPT and SST. After almost a century of use, the PEP continues to lack a theoretical basis [308–311] even though experimental evidence indicates [312] that its violation has yet to be found although the search [313, 314] goes on. The PEP is a scientific principle whose philosophical status continues to be worthy of further scrutiny [315, 316, for e.g.] ever since Margenau [317] first identified it as such. Inspired as it was primarily by the work of Stoner [318] on atomic transitions and Pauli [319]'s own recognition of a binary ambiguity in the response of an electron to a Zeeman field with its intimation of a necessary "spin

quantum number" to be added to those already well known (principal, angular momentum) [154, 173, 174, 320, 321, for e.g.], few possess the deep insight into the PEP [322], particularly in respect to the conditions of its violation and their consequences for quantum gravity, say, regardless of its high-level rationale for the layout of the *Periodic Table* and its provision of degeneracy pressure accounting for the stability of white dwarfs and neutron stars.

The nuclei of many isotopes have a characteristic spin (I). Some nuclei have integral, some have fractional spins, and a few have no spin. Nuclear spin is related to the nucleon composition of a nucleus: odd A-nuclei (i.e. those having an odd number of nucleons) have fractional spins, e.g. $I = 1/2$ (^{1}H, ^{13}C, ^{19}F), $I = 3/2$ (^{11}B), and $I = 5/2$ (^{17}O); even A-nuclei composed of odd numbers of protons and neutrons have integral spins, e.g. $I = 1$ (^{2}H, ^{14}N); and even A-nuclei composed of even numbers of protons and neutrons have zero spin, e.g. $I = 0$ (^{12}C, ^{16}O, ^{32}S). Spin-1/2 nuclei have a spherical charge distribution, others have nonspherical (prolate or oblate) charge distributions and are often isomeric (long-lived excited states). Nuclei with finite spins have magnetic moments but the nonspherical nuclei also have an electric quadrupole moment. In an arbitrary molecule, some of its nuclei may be fermions (e.g. ^{1}H, ^{23}Na, ^{31}P, etc.). The PEP results in the "exclusion" of any state whose wave function does not change sign on exchanging a pair of indistinguishable fermions, whether they be spin 1/2 electrons or half-integer spin nuclei. Just so, with respect to pair interchanges, wave functions are asymmmetric on the exchange of identical fermions and are symmetric on the exchange of bosons. The bosons in a molecule are nuclei whose effective charges [323–325] are reduced or shielded by the innermost electrons thus lessening their Coulombic repulsion. For the wave function $\psi(\mathbf{x}, t) = e^{i\theta(\mathbf{x},t)}|\psi(\mathbf{x}, t)|$ the relative phase $\nabla\phi(\mathbf{x}) = \tan^{-1}\nabla(\mathrm{Im}\,\psi(\mathbf{x}, t)/\mathrm{Re}\,\psi(\mathbf{x}, t))$ is constrained by the PEP through its permutation symmetry action on $\psi(\mathbf{x}, t)$ by hypothesis. This is the essence of the PEP as it applies to an orbital-free single molecule.

Atoms and molecules have innumerable states the lowest of which is the ground state. This state persists indefinitely at the global minimum of the potential in joint compliance with the classical theorem of Earnshaw [125] and the nonrelativistic energy-time uncertainty relation [326] of Mandelshtam and Tamm for a quantum system in a nonstationary state ψ [327–331]. In the ground state, the system in dynamical equilibrium with its environment resists irreversible change in its structure unless driven beyond its thermodynamic stability, primarily through temperature and pressure changes. Excited states have finite lifetimes but not definite energies: each time they decay, the energy released is slightly different with the average energy of the emitted photon peaking at the nominal energy of the state but distributed with finite width, termed the natural linewidth. The faster they decay the broader their linewidths, and conversely [332, for e.g.]. In a thermal field, a molecule is not passively inert (sic dead) but is ready to go wherever the SLT takes it.

In engineering parlance, a molecule is a mechanical system whose input, if small, effects temporary changes through internal processes that disappear when the input is withdrawn and the system reverses to its original state with no apparent output, or whose input, if large, effects permanent changes to the system which is indelibly altered. This is like a rubber band or a balloon which when stretched or blown up too far breaks or bursts. If the stretching or blowing are not too great both objects revert reversibly back to their original states. If you repeat the stretching or blowing often enough elasticity diminishes until what a gentle tug or blow used to do no longer holds and ultimately an irreversible change occurs. The ability of a molecule to resist distortion by an outside agent and to return to its original size and shape in accord with Hooke's law when the perturbing force (optical tweezers, electromagnetic fields, interface surfaces, heat sources, etc.) is removed, qualifies it as elastic in that it undergoes reversible changes that make no distinction between the past and the future in agreement with both time-invariant classical and quantum mechanics. Most molecules are elastic only to small perturbations, beyond which permanent modification occurs with the disintegration of the molecule into sundry fragments. The limits of elasticity does not usually apply to electronic transitions, which, unlike distortions within an harmonic approximation where the energies and intensities of the disturbances are low, involve internal processes of higher excitation energies and larger oscillator strengths resulting in irreversible changes that distinguish the past from the future just as do time-asymmetric entropy increases. Stability, even in elastic systems, demands dynamical analysis [333–335, for e.g.] since static stability alone does not generally imply stability under more inelastic conditions so that just like engineered structures, molecular structures engender their own future depending on their imposed input. On opening, the Millennial Bridge across the Thames in London, forced its pedestrians to walk transversely in stride to keep their balance, unwittingly accentuating its sideways wobble until it could be cleared of people without injuries. The designers went back to the drawing board to correct what, for them, was an unanticipated synchronicity previously exhibited almost two centuries before at the Broughton Suspension Bridge near Manchester, UK, one of the earliest of such span bridge designs, where mechanical resonance induced by a platoon of troops marching in step across the bridge caused it to collapse, resulting in command to direct that in future, troops break stride on crossing bridges. The futuristic Millennial span opened some two years later to worldwide applause after remedial corrections and so far it has not duplicated Tacoma. The moral of this mechanical linear-nonlinear abyss is that caution and due diligence be exercised when dealing with bridges, aircraft, and even the macroscopic effects of molecules: Nature does not provide warranties, just

surprises. A modest Murano piece or an extravagant Koon bubble structure that shatters cannot be restored to its original state by the most skillful of artisans anymore than a denatured protein can regain its primary tertiary structure in the hands of a chemist, a biologist, or a physicist.

There is an important distinction to be made between the stability of bulk matter and the stability of a single molecule. Bulk matter stability requires [214, 215] that for a bounded potential* $E_0 > -\infty$ (stability of the first kind) or $E_0 > -a(M+N)$ (stability of the second kind), where $a > 0$ is constant and E_0 is the ground-state energy, in order that the grand canonical partition function exist in finite volume and that a thermodynamic limit exist. These prerequisites for the stability of bulk matter do not pertain to the stability of a single molecule.

The PEP was found by Dyson and Lenard [337] to be a sufficient requirement in their *pace* treatment of the stability of matter in its state of stationarity, an issue considered earlier by Onsager [338] and later by Fisher and Ruelle [339] among others where the notion of stability is not, as one would reasonably expect, related to the inclination to change because of electromechanical disturbances but rather to ensuring that the classical configuration energy or quantum mechanical ground state of a system be bounded extensively from below because energy is so and in warranting that the thermodynamic limit be shown to exist. A thermodynamic limit does not always exist and for single-molecule and some nanoscale systems in particular it does not, even though stable single molecules do exist [340, for e.g.] and their reaction dynamics are observable [341–345, for e.g.]. Dyson [346] further claimed that the PEP is necessary for the stability of a system whose electrons and nuclei are of equal or of greater mass and charge, neither of which is true in Nature any more than matter fails to implode before exploding because the PEP is operative as necessary to a bewildering explication via a cascade of inequalities [218, et passim].

Echoing Wigner [347], Astumian [348] ascribes the unreasonable effectiveness of equilibrium theory for interpreting single-molecule systems that are far from thermodynamic equilibrium to their closeness to mechanical equilibrium. The primary determinant of structures available to a molecule lies in its Coulomb potential, not in peripheral diversions such as the PEP, whether Pauli repulsions are in the mind of the beholder, etc. How the Coulomb potential responds to deformations is transparently gauged by Earnshaw [125]'s theorem which, as will be shown in the following, indicates that the Coulomb potential is robust against elastic distortions so that the molecule is consequently stable until it transitions to a mixed state under environmental influences whereupon to no great surprise it may destabilize.

Earnshaw's theorem [125], as recounted by Maxwell [349, cf. 116] and Jeans [350, cf. 192], basically states that harmonic matter is not stable since it has no interior minima in V the least of which could correspond to a configuration where the molecule has an equilibrium point, as first defined by Lagrange [351, cf. Part 1, §3, No. 16, p. 38] for mechanical systems, which computational scientists routinely detect in electronic structure calculations as positive definite second variations [352, for e.g.] of the energy functional $E = \langle\psi, H\psi\rangle/\langle\psi,\psi\rangle \geq E_0$, where E_0 is the true ground-state energy of the self-adjoint Coulomb Hamiltonian operator [336] from which molecular thermodynamic stabilities are assessed.

The Coulomb potential energy function $\mathcal{V}_{\mathrm{C}}(\mathbf{x})$ of a molecule is the sum of its attractive electron-nucleus, repulsive electron-electron, and repulsive nuclei-nuclei potentials of interaction, viz.

$$4\pi\mathcal{V}_{\mathrm{C}}(\mathbf{x}) = -\sum_{i=1}^{N}\sum_{j=1}^{M} Z_j/|\boldsymbol{r}_i - \boldsymbol{R}_j| + \sum_{1\leq i<j}^{N} 1/|\boldsymbol{r}_i - \boldsymbol{r}_j| + \sum_{1\leq i<j}^{M} Z_i Z_j/|\boldsymbol{R}_i - \boldsymbol{R}_j|\,, \tag{19a}$$

where $\mathbf{x} \in \mathbf{R}^M \times \mathbf{r}^N$. There are no self-repulsion terms (of nuclei or electrons) in $\mathcal{V}_{\mathrm{C}}$. Of course, the Coulomb force $\boldsymbol{F}_{\mathrm{C}}(\mathbf{x}) = -\nabla\mathcal{V}_{\mathrm{C}}(\mathbf{x})$ is conservative. Equally, $\nabla \times \boldsymbol{F}_{\mathrm{C}} = 0$ as is also required of a conservative force. Formally, the Laplacian of $\mathcal{V}_{\mathrm{C}}(\mathbf{x})$ is

$$4\pi\nabla^2\mathcal{V}_{\mathrm{C}}(\mathbf{x}) = -\sum_{i=1}^{M} Z_i\delta(\mathbf{x} - \boldsymbol{R}_i) + \sum_{i=1}^{N}\delta(\mathbf{x} - \boldsymbol{r}_i) + \sum_{i=1}^{M} Z_i^2\delta(\mathbf{x} - \boldsymbol{R}_i)\,, \tag{19b}$$

where the first two terms on the right are the net nuclear and electronic charge density, respectively. Thus

$$4\pi\int_V d\mathbf{x}\,\nabla^2\mathcal{V}_{\mathrm{C}}(\mathbf{x}) = \sum_{i=1}^{M} Z_i^2 - z\,, \tag{19c}$$

where

$$z = \sum_{i=1}^{M} Z_i - N \tag{19d}$$

is the net charge of a polyatomic ion. Earnshaw's theorem applies: $\mathcal{V}_{\mathrm{C}}(\mathbf{x})$ is subharmonic ($\nabla^2\mathcal{V}_{\mathrm{C}} > 0$) and sustains interior minima in V corresponding to stable mechanical configurations. Consequently, the Coulomb potential $\mathcal{V}_{\mathrm{C}}(\mathbf{x})$ is stabilizing. The stability of a polyatomic ion is due entirely to the bilateral repulsion between its nuclei. Any reduction in this repulsion through, say, nuclear screening [323] – a phenomenon unavailable to self-gravitating systems† – destabi-

*This is a condition deemed necessary [336] for the Coulomb Hamiltonian operator to be self-adjoint.

†Even though the gravitational and Coulomb forces are both inverse square relations, the former is always attractive because of the positive mass theorem [353, 354] while the latter may be attractive or repulsive according as the charges are different or alike.

lizes a neutral molecule or polyatomic ion. The PEP promotes stabilization by boosting nuclear screening through the dispersal of fermions and the assembly of bosons that characterizes its vague role.

The work done on an arbitrary particle (electron or nucleus) of charge q in V is

$$\int_V d\mathbf{x}\,\nabla\cdot\boldsymbol{F}_{\mathrm{C},q}(\mathbf{x}) = -q\sum_{i=1}^{n} q_i \int_V d\mathbf{x}\,\nabla^2_{\mathbf{x}_i}\left(\frac{1}{|\mathbf{x}-\mathbf{x}_i|}\right) = -4\pi q z\,, \tag{20a}$$

where

$$\boldsymbol{F}_{\mathrm{C},q}(\mathbf{x}) = -q\sum_{i=1}^{n} q_i \nabla_{\mathbf{x}_i}\left(\frac{1}{|\mathbf{x}-\mathbf{x}_i|}\right), \tag{20b}$$

with q_i and $\mathbf{x}_i \in \mathbf{R}^M \times \mathbf{r}^N$ as the charge and location, respectively, of any of the molecule's $n = M + N$ particles (including the one under consideration), which vanishes if $z = 0$, is exothermic if $z < 0$ as in anion formation, and endothermic if $z > 0$ as in cation formation and consistent with our previous finding that nuclear screening increases with stabilizing anion formation, and conversely. The propensity of an atomic or polyatomic species to form ions is a measure of its stability and consequent reactivity in context [355, 356, for e.g.]. The findings of Lieb and Loss [357] (whose assumptions on the separability or disentanglement of all nuclei – regardless if they in bulk supply have fractional integer spins as to follow Fermi-Dirac statistics – from the fermionic pool, we avoid) are in accord with our revelation of the preference for anion formation as observed empirically.

The Lorentz-Faraday conservative force $\boldsymbol{F}_{\mathrm{int}} = -\nabla\mathcal{V}_{\mathrm{int}}$ in (13a) is the sum of the negative gradient of the scalar potential Φ as given in (14a) and the curl of the vector potential $\mathbf{A}$ as given in (14b). Since the div curl vanishes, it is clear that $\nabla^2\mathcal{V}_{\mathrm{int}}(\mathbf{x},t) = \nabla^2\Phi(\mathbf{x},t)$ so that the Lorentz-Faraday force $\boldsymbol{F}_{\mathrm{int}}$ is stabilising just like the Coulomb force $\boldsymbol{F}_{\mathrm{C}}$ provided ϕ is subharmonic at $\mathbf{x} \in V$.

Earnshaw's theorem reveals the propensities of a fixed aggregation of nuclei and electrons acting collectively under the Coulomb potential to form mechanically stable species (molecules or polyatomic ions), isomers with identical chemical formulas but different arrangements of nuclei giving rise to structural isomerism in which chemical bonds between nuclei differ, or stereoisomerism in which the bonds are the same but the relative positions of the nuclei differ. Such isomers generally have different physical and chemical properties. Thus, the paradigmatic classical molecular structures [358–360] of chemistry are evidentially a consequence of the subharmonic nature of the Coulomb potential and not a self-styled conundrum [361] whose long-crusading resolution [362, et passim] would have it devolve to a foundational defect of quantum theory.

This proof of the mechanical stability of matter based on Earnshaw's theorem is within the grasp of anyone with high school "calculus and vectors" preparation. Additionally, the proof makes no distinction between the stability of a single molecule over that of molar amounts of them within the scope of the extensivity-intensivity [363, 364] divide. Mechanical stability of molecules as gauged by Earnshaw's criterion is of paramount importance regardless of quantum mechanics. Shell and orbital models are used to describe the arrangements of protons and neutrons in atomic nuclei and electrons in atoms and molecules, respectively. The shells or orbitals are filled with fermions in order of increasing energies except when the binding energy of the next addition is less than the last and in post hoc compliance with the PEP and Hund's rule of maximum multiplicity. The motion of the electrons in a molecule constrains the nuclei to a particular geometric configuration, one that minimizes their energy functional.

The widespread belief that the PEP is necessary and sufficient for the stability of molecules would appear to have entrenched itself in the lore of chemistry and physics when Niels Bohr proclaimed it to be so in his *Faraday Lecture* to the Chemical Society [198]. This should not come as a surprise given that the forces responsible for molecule formation in the most reductionist way from their constituent nuclei and electrons are entirely classical in origin. Since the Coulomb potential was shown to be subharmonic, Earnshaw's theorem lends credence to the fact that aggregates of nuclei and electrons can be mechanically stable independently of both the PEP and the overarching assumption that even the heaviest of nuclei cannot be fermions regardless of their spin. The Lorentz-Faraday potential is purely quantum mechanical in origin, it is operative under thermal conditions, and it is subharmonic and stabilizing.

As Chandrasekhar [365, 366] demonstrated in revealing the limiting mass above which electron degeneracy pressure in a star's core is insufficient to balance the star's own gravitational self-attraction, the PEP cannot be naively invoked independently of the Heisenberg uncertainty principle, although most chemists and high school science teachers routinely do so.

Slater [367] was first to point out the relevance of the quantum mechanical counterpart of Clausius' classical virial theorem for stationary state molecular systems [368, for e.g.]. The quantum mechanical virial theorem has been proved for polyatomics [369] and reads as

$$2\overline{\langle KE\rangle} + \overline{\langle\mathcal{V}_{\mathrm{C}}\rangle} = 0\,, \tag{21}$$

where $\overline{\langle KE\rangle}$ and $\overline{\langle\mathcal{V}_{\mathrm{C}}\rangle}$ are the time-averaged expectation values of the kinetic KE and potential $\mathcal{V}_{\mathrm{C}}$ energies, respectively, without drawing any distinction between the masses of nuclei relative to electrons, the sole difference being in relation to their spins. Since $E = \overline{\langle KE\rangle} + \overline{\langle\mathcal{V}_{\mathrm{C}}\rangle} = 1/2\overline{\langle\mathcal{V}_{\mathrm{C}}\rangle}$, clearly the virial theorem is closely related to the conservation of energy principle.

Clausius' derivation of the classical virial theorem used Jacobi [370]'s extension of Lagrange's treatment of the 3-

body problem to many-body systems which, in conjunction with the first law of thermodynamics, permitted him to investigate the stability of self-gravitating systems. Jacobi's approach applies equally to a molecule whether in a stationary state under Coulomb control or in a dynamic state under Lorentz-Faraday control. In this regard, the equivalence of the stability criteria of Jacobi and Earnshaw is clear: they both maintain that an harmonic molecule is unstable regardless of the PEP which of course was unknown to them. Whether molar quantities of harmonic molecules are stable or not depends on how they interact and in so doing could make each other anharmonic and potentially less stable or even unstable. Thus, water condenses to liquid and further solidifies under sundry conditions but with differences in their underlying stabilities determined by their hydrogen-bonding networks without necessarily invoking the PEP.

The virial theorem states that if any system whose conservative forces come from a potential energy function which is a power law of the distance between its constituents – such as a self-gravitating body ($\mathcal{V}_{\rm g}$) or a Coulomb molecule ($\mathcal{V}_{\rm C}$) – settles into equilibrium then its total energy will be balanced between the kinetic energy of those constituents and the potential energy stored due to their mutual interaction. As previously remarked, the virial theorem presupposes the applicability of the first law of thermodynamics for a stationary system. In a thermal field where the SLT reigns, the first law takes an hiatus and the steady-state virial theorem given in (21) is supervened upon by its dynamical counterpart as will now be explained. Before doing so, however, it is appropriate to note that Pollard [371] gave a derivation of the classical virial theorem which eliminates its unnecessary assumption that the system is bounded in the sense that distances between particles and the velocities of the particles remain bounded as was Ambartsumian [294]'s objection to Zwicky [293]'s use of the virial theorem, and replaced it by the condition that for the theorem to hold it is both necessary and sufficient that for $\mathbf{x}_{\rm i} \in \mathbf{x}$, $\max\limits_{i<j\leq n} |\mathbf{x}_{\rm i} - \mathbf{x}_{\rm j}| = o(t)$ as $t \to \infty$.

In an "isolated" molecule $\boldsymbol{F}_{\rm int}(\mathbf{x}, t)$ is dormant but the Coulomb molecule is stable and undergoes reversible ($\Delta S = 0$) processes without the involvement of the phase. The Coulomb potential is classical with a basis in field theory [3, for e.g.] that sees it as involving the exchange of "virtual" photons created only for the duration of the exchange process. Such an exchange force may be either attractive or repulsive and whose range is set by the energy-time uncertainty principle so that a particle of mass m and rest energy $E = mc^2$ has a range of no more than $1/2mc$ which is infinite for a massless photon whose finite momentum can exert a force known as radiation pressure. However, if it were to be driven out of equilibrium by the stabilizing $\boldsymbol{F}_{\rm int}(\mathbf{x}, t)$ at $T > 0$ the local phase would regulate irreversible ($\Delta S(t) > 0$) changes in the molecule. Unlike the Coulomb force, the Lorentz-Faraday force is quantum mechanical which, when operative at finite T, produces real Helmholtz-Hodge photons of unlimited range but of finite lifetime. Since photons are bosons of unit spin, transitions involving their absorption and emission must result in unit change in the angular momentum of the system for a net-zero change consistent with the absence of internal vortices in a heated molecule as was previously noted*.

The probability density $\rho(\mathbf{x}, t) = |\psi(\mathbf{x}, t)|^2$, written identically as

$$\rho(\mathbf{x}, t) = \int_V d\mathbf{x}'\, \psi^*(\mathbf{x}', t)\delta(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}', t)\,, \tag{22a}$$

where the configurational kernel is formally

$$\delta(\mathbf{x} - \mathbf{x}') = \sum_{i=1}^{M} \delta(\mathbf{x} - \boldsymbol{R}_i) + \sum_{j=1}^{N} \delta(\mathbf{x} - \boldsymbol{r}_j) \tag{22b}$$

with $\mathbf{x}, \mathbf{x}' \in V \subseteq R^n = \boldsymbol{R}^M \times \boldsymbol{r}^N$ and $n = M + N$ is a normalization constant so that

$$\int_V d\mathbf{x}\, \rho(\mathbf{x}, t) = n\,, \tag{22c}$$

to give the expectation value of the kinetic energy of motion of the molecule's constituents as

$$\begin{aligned} \langle KE(t)\rangle &= \frac{1}{2}\int_V d\mathbf{x}\, \rho(\mathbf{x}, t)|\nabla\phi(\mathbf{x})|^2 \\ &= \frac{1}{2}\int_V d\mathbf{x} \left(\sum_{i=1}^{M} |\nabla_{\boldsymbol{R}_i}\phi(\mathbf{x})|^2 + \sum_{j=1}^{N} |\nabla_{\boldsymbol{r}_j}\phi(\mathbf{x})|^2 \right). \end{aligned} \tag{22d}$$

The virial of $\boldsymbol{F}_{\rm int}(\mathbf{x}, t)$ being $\oint_{\partial V} da\, \hat{\mathbf{n}} \cdot \boldsymbol{F}_{\rm int}$, within V its expectation value is

$$\begin{aligned} \langle \nabla \cdot \boldsymbol{F}_{\rm int}(t)\rangle &= \int_V d\mathbf{x}\, \rho(\mathbf{x}, t) \nabla \cdot \boldsymbol{F}_{\rm int}(\mathbf{x}, t) \\ &= \int_V d\mathbf{x} \left(\sum_{i=1}^{M} \phi(\mathbf{x}) \nabla^2_{\boldsymbol{R}_i} \phi(\mathbf{x}) + \sum_{j=1}^{N} \phi(\mathbf{x}) \nabla^2_{\boldsymbol{r}_j} \phi(\mathbf{x}) \right) \end{aligned} \tag{22e}$$

which is the work done $Q(t)$ by $\boldsymbol{F}_{\rm int}$ that the change in entropy exceeds at $T > 0$ as given by the quantized Clausius inequality in (11a) or (11b).

The sum of $2\langle KE(t)\rangle$ and $\langle \nabla \cdot \boldsymbol{F}_{\rm int}(t)\rangle$ vanishes†

$$2\langle KE(t)\rangle + \langle \nabla \cdot \boldsymbol{F}_{\rm int}(t)\rangle = 0\,. \tag{22f}$$

*The Coulomb force acting between two charges is generally not parallel to the vector separating them and so exerts a torque on each which means that the angular momentum of any charge changes all the time with the two charges merely "exchanging angular momentum" whose total is conserved. A similar but more complex exchange process [372, for e.g.] undoubtedly takes place between the charged constituents of a molecule and its internal Helmholtz-Hodge electromagnetic field.

†Wigner has pointed out [373, loc. cit., p. viii] that "It is a well known fact ..." (pausing until resuming his unswerving accuracy) "It is well known to some people that every operator can be made self-adjoint." For $f \in L^2$, $\langle f, \nabla^2 f\rangle + \langle \nabla f, \nabla f\rangle = 0$, a fact acknowledged by Slater [367].

This extension of the virial theorem to nonstationary dynamics involving internal Lorentz-Faraday forces is consistent with Milne [374]'s demonstration that the virial theorem continues to hold true if the particles are acted on by external frictional forces proportional to their velocities and Collins' [375, loc. cit., p. 97] remark:

> To date the virial theorem has been applied to systems in or near equilibrium. It is worth remembering that perhaps the most important aspect of the theorem is that it is a global theorem. Thus systems in a state of rapid dynamic change are still subject to its time dependent form.

The relation of KE to Q often presents as an unwitting pitfall. Recall that heat and temperature are not the same: heat is the total kinetic energy while temperature is the average kinetic energy with the difference depending on the number of degrees of freedom of the system and the dispersal or spread of energy at that temperature as quantified by entropy [376, et passim]. Nor are work and heat synonymous. As remarked before, work is the transfer of energy by any means other than heat except if associated with a nonconservative force like friction, but heat can only be partly converted to work.

The Morse-Sard theorem [146, 147] precludes the sum $2KE + \nabla \cdot \boldsymbol{F}_{\text{int}}$ from vanishing locally except at the critical points of ϕ, a set of measure zero. This means that $2KE + \nabla \cdot \boldsymbol{F}_{\text{int}}$ does not vanish over subregions or fragments of the molecule (or a self-gravitating body) as to provide virialized building blocks transferable in noumena to other molecules (or self-gravitating bodies) in violation of the no-cloning theorem [377–379] of quantum mechanics.

Just as with entropy changes $\overline{\langle \Delta S_\tau \rangle}$ given by (11c) for arbitrary relaxation times (1/rates) under nonstandard state conditions, the Laplace long-time averages

$$\overline{\langle KE_\tau \rangle} = \int_0^1 ds\, e^{-s} \langle KE(\tau s) \rangle \tag{22g}$$

and

$$\overline{\langle \nabla \cdot \boldsymbol{F}_{\text{int}\,\tau} \rangle} = \int_0^1 ds\, e^{-s} \langle \nabla \cdot \boldsymbol{F}_{\text{int}}(\tau s) \rangle \tag{22h}$$

and their fluctuations are to be ascertained empirically. The time average of (22f) is $2\overline{\langle KE_\tau \rangle} + \overline{\langle \nabla \cdot \boldsymbol{F}_{\text{int}\,\tau} \rangle}$ and vanishes.

All objects at finite T emit thermal radiation as quantified by their emissivity [380], a dimensionless number $0 < \epsilon < 1$ covering the range from perfect reflector to perfect emitter and defined as the ratio of the energy radiated to that radiated by a blackbody at the same temperature and wavelength and under the same viewing conditions. An exception to this are black holes: classically, they are black body absorbers that do not emit anything but with the inclusion of quantum processes they can emit radiation and particles. Molecules emit energy that departs from a Planck distribution so the infrared light emitted by vibrating molecules can be used to identify their presence.

The energy density carried by an electromagnetic wave whose source lies in the internal fields of the molecule is given by their Poynting vector [381, 382, for e.g.] and the resultant radiation pressure is

$$\boldsymbol{p}_{\text{rad}}(\mathbf{x}, t) = \boldsymbol{E}_{\text{int}}(\mathbf{x}, t) \times \boldsymbol{B}_{\text{int}}(\mathbf{x}, t)\,. \tag{23a}$$

Ideally, the photons constitute a black-body photon gas of low but finite intensity due to their relativistic speed. Consequently,

$$W = \oint_{\partial V} đW = \oint_{\partial V} da\, \hat{\mathbf{n}} \cdot \boldsymbol{p}_{\text{rad}}(\mathbf{x}, t) = \epsilon\, \sigma_{\text{SB}}\, T^4 V\,, \tag{23b}$$

where $\sigma_{\text{SB}} = \pi^2/60$ is the Stefan-Boltzmann constant. This, together with (12e), ensures that U is in compliance with the first law of thermodynamics and with d'Alembert's principle from which the conservation of energy follows as a consequence [155, cf. Ch. IV]. In the absence of a thermal context, the molecule is a stationary system with the conservative internal force $\boldsymbol{F}_{\text{int}}$ inoperative and with the Coulomb force $\boldsymbol{F}_C$ providing for its stability. The wave function's local phase has no bearing on the first law and features only when the system is open to exchanges of heat with its surroundings at finite $T > 0$. Even in the absence of a cyclotron, a heated atomic-ionic-molecular system would be expected to exhibit cyclotron-like radiation emissions [383] contributing to W as its electrons and ions accelerate in the magnetic part of its internal Helmholtz-Hodge radiation field. If an atom at rest in the vicinity of a black hole can undergo spontaneous emission [384] there is nothing to prevent a molecule in a heat bath from doing likewise.

The Higgs potential determines whether the Universe is in a true (stable) or a false (metastable) vacuum state. The SM indicates [385] that the known Universe is in a metastable state that could spontaneously collapse through tunneling decay although not anytime soon since the lifetime of a metastable universe is predicted to be much longer than the current age (~ 13.8 Gyr) of the known Universe [386].

4.3 The absence of magnetic monopoles

Dirac [266] introduced magnetic monopoles to explain the quantization of electric charge [387] and to promote reciprocity between electricity and magnetism. He showed that the magnetic charge g_{D} and the electric charge e are related by $2g_{\text{D}}e = k$, where $k \in \mathbb{Z}$ thus uncovering the quantization of electric charge, so that when $k = 1$, say $g_{\text{D}} = e/2\alpha \simeq 68.5e$, where α ($\simeq 1/137$) is the Sommerfeld fine-structure constant. Assuming that the classical radius of an electron and the "radius" of a Dirac monopole are equal, one finds that their masses m_e and m_m are related by $m_m \simeq 4700 m_e$, making the magnetic (and gravitational forces) between two monopoles many times stronger than those between two electrons, on which basis searches have been conducted at every new accelerator.

If magnetic charges ρ_m and magnetic currents $\mathbf{j}_m$ were to exist, Faraday's law resulting from taking the curl of $\boldsymbol{E}_{\text{int}}$ as given in (13b) while recalling that curl grad vanishes and then replacing the curl in $\mathbf{A}$ by $\boldsymbol{B}_{\text{int}}$ as given in (13c), would read as

$$-\nabla\times\boldsymbol{E}_{\text{int}} = \alpha\left(4\pi\mathbf{j}_m + \frac{\partial\boldsymbol{B}_{\text{int}}}{\partial t}\right) \tag{24a}$$

and the Ampère-Maxwell law would read as

$$\nabla\times\boldsymbol{B}_{\text{int}} = \alpha\left(4\pi\mathbf{j} + \frac{\partial\boldsymbol{E}_{\text{int}}}{\partial t}\right), \tag{24b}$$

and the two would look more alike. The curl of $\boldsymbol{E}_{\text{int}}$ suggests that its solenoidal part would be generated by the time-varying $\boldsymbol{B}_{\text{int}}$ and moving magnetic charges $\mathbf{j}_m$ while the curl of $\boldsymbol{B}_{\text{int}}$ would imply that its solenoidal part would be generated by the time-varying $\boldsymbol{E}_{\text{int}}$ and moving electric charges $\mathbf{j}$. In both cases it is the movement of charge, whether magnetic or electric, that causes current flow while the time-varying fields are mutually generative. Additionally, the analogs of (1a) and (13d) are

$$\frac{\partial\rho_m}{\partial t} + \nabla\cdot\mathbf{j}_m = 0\,, \tag{25a}$$

and

$$F_m = \rho_m\boldsymbol{B}_{\text{int}} - \mathbf{j}_m\times\boldsymbol{E}_{\text{int}}\,, \tag{25b}$$

respectively, while the coupled wave equations in (16a) and (16b) have the electric and magnetic fields and their sources interchanged to give

$$\Box\,\boldsymbol{B}_{\text{int}} = -4\pi\left(\nabla\rho_m + \frac{\partial\mathbf{j}_m}{\partial t}\right) \tag{25c}$$

and

$$\Box\,\boldsymbol{E}_{\text{int}} = -4\pi\nabla\times\mathbf{j}_m\,, \tag{25d}$$

respectively.

Dirac [266]'s seminal paper makes specific reference to Weyl [388]'s gauge phase $U(1)$ and thereafter [266, 387] alludes to the vector potential of an external electromagnetic field without recourse to the adiabatic theorem [389]. The addition of the action $4\pi g_{\text{D}}k$ to the local phase ϕ makes no difference to its relative phase $\nabla\phi$ so that as a gauge fix this inclusion of the Dirac magnetic monopole does not ensure its detection.

However, in contrast to the polar vector $\mathbf{j}$ which is T even, the axial vector $\mathbf{j}_m$ is T odd so that the magnetic monopole's analog $\partial\mathbf{j}_m/\partial t$ of the Lorentz-Faraday force given in (8a) is even in time, a circumstance that would not only cause it to decelerate magnetic charge via (25c) but more importantly cause $\Delta S(t)$ to be symmetric in time at finite T in violation of the SLT as was argued earlier. This violation, perhaps, is why Nature has found no recent use for the elusive magnetic monopole [390–394], there being only a couple of reports [395, 396] of its detection neither of which were ever replicated. Were one to exist, a magnetic monopole would rank as a new elementary particle for which $\nabla\cdot\boldsymbol{B}_{\text{int}} = 4\pi\rho_m$ is finite and would exhibit a PT violation so as to change sign under C [397, cf. Sec. 8]. Driven by $T > 0$, the integrability of $\theta = \phi - Et$ conveyed in (4) does not require the presence of a nodal line emanating from a magnetic monopole to cause ϕ to jump in value upon each complete cycle it makes around ∂V. Currently there is no explanation for the quantization of electric charge and it is taken to be an empirical fact.

Dirac's synthesis [266] implies that magnetic monopoles may exist. Their dismissal here applies equally to alternative proposals for their production. Grand unification theories [398–400, for e.g.] (GUTs) predict that shortly after the Big Bang magnetic monopoles were created whose conservation of magnetic charge stabilized them against decay as relics of the past. Indeed, the original impetus for inflationary theories [401, 402, for e.g.] of the Universe [403–407] was the so-called "monopole problem". If the early Universe underwent a phase transition because the symmetry of GUT accruing from the supposed coupling of electromagnetic interactions with the electroweak and strong forces into a single force was broken then, in principle, magnetic monopoles should have been produced in abundance. As yet, there is no empirical evidence for any such primordial monopoles. Inflation supposedly diluted their density in the Universe so that it is unlikely in Borel's sense that one will ever be detected. An alternative to the dilution explanation is simply that there are none. Forty years after his provocative paper, Dirac is quoted [408, loc. cit., p. vii] in a letter written to Abdus Salam at Trieste that "I am inclined now to believe that monopoles do not exist. Too many years have gone without any encouragement from the experimental side." Thermodynamics requires that electric charge be a scalar and magnetic charge be a pseudoscalar under T reversal. Since both charges are alike and cannot independently flip signs only one of them exists and it is not the magnetic monopole. This has not led to any curb in the enthusiastic pursuit of monopoles wherever they hide. However, the MoEDAL Collaboration at the LHC* failed [409, et passim] to detect magnetic monopoles with $g_{\text{D}} = 1, 2, 3$ and masses up to 75 GeV/c^2 at the 95 % confidence level via the magnetic dual of the Sauter-Schwinger [410, 411] proposal†.

4.4 The scarcity of antimatter

The known Universe is primarily filled with matter, not antimatter [30, cf. Ch. 7]. There are no natural forms of antiparticles on Earth. Yet, antiprotons and positrons, the antiparticles of protons and electrons, respectively, can be produced in particle accelerators to serve vital roles in medical

*Large Hadron Collider

†This proposal of a mechanism for pair production is not a demonstrable "effect" in the ranks of the photoelectron, Zeeman, Stark, etc., each of which has been experimentally confirmed while to date the Sauter-Schwinger proposal has not.

physics [412]. The production of light antinuclei ($\overline{\mathrm{d}}$,$^3\overline{\mathrm{He}}$, and $^4\overline{\mathrm{He}}$, for e.g.) composed of antiprotons and antineutrons in high-energy cosmic-ray collisions with the ISM or from their annihilation of unknown dark-matter particles are under scrutiny within the AMS Collaboration on the ISS [413] and the ALICE Collaboration at CERN [414]. It has been intimated [415,416] that the observation of antihelium is the existence of antimatter-dominated regions containing anticlouds or antistars, it being estimated that there are ~ 2.5 ppb antistars within several hundred light years from our Sun.

If the C symmetry of the Lorentz-Faraday force $F_{\mathrm{int}} = \partial\mathbf{j}/\partial t$ were possible it would amount to its T reversal (equivalently, a CP-violation) which is prohibited by the SLT. The baryon number is conserved in all interactions of the SM with the exception of chiral anomalies involving sphalerons – saddle points of the electroweak potential – for which there is no experimental evidence. Both GUT and SUSY allow violations of the conservation of baryon and lepton numbers through proton decay, but this too has never been observed.

The oppositely-charged proton and electron are the primary representatives of the baryonic and leptonic particles and their antiproton and positron particles are of opposite sign. In their electromagnetic interactions, C symmetry on the proton would result in a T reversal since the Lorentz-Faraday force will go from being odd to even in t. For the electron, however, no such T reversal occurs since the Lorentz-Faraday force remains odd in t for the positron. In short, the SLT rules out the copious presence of antiprotons in the Universe for the same reason as the nonobservance there of magnetic monopoles: they are both in violation of the SLT. In contrast, the production of positrons in the Universe is in compliance with the SLT.

Neutrinos have many sources: supernovae, the Sun, the Earth and its atmosphere, nuclear reactors, particle accelerators, etc.; they have no charge; they interact via the electroweak force and, perhaps, gravity; they are observed indirectly via the particles that emerge when a neutrino hits a detector; they have left-handed helicities (spin antiparallel to momentum). Nobody knows if neutrinos ($\nu_{\mathrm{e}}, \nu_\mu, \nu_\tau$) are their own antiparticles ($\overline{\nu}_{\mathrm{e}}, \overline{\nu}_\mu, \overline{\nu}_\tau$) but all six leptons are regarded as distinct elementary particles in the SM. Neutrinos are the most abundant matter particles in the Universe and are candidates for dark matter. Hypothetical sterile neutrinos (which are believed to be right-handed and to interact only by gravity) have not been found in either the MicroBooNE [417] or the STEREO [418] experiments. The primary international experiments for neutrino science are NOvA, T2K, and DUNE. Due in large to their small but finite masses [419], neutrinos change flavor (e, μ, τ) in flight, a transformation known as neutrino oscillation [420, 421], behavior that lies beyond the purview of the SM. If the oscillations of neutrinos are different from that of their antineutrinos – a result which is currently not known within the $5\,\sigma$ standard of the SM – CP is broken with which neutrinos violate T-symmetry. This would relegate neutrinos to the same league of CP violators as quarks [422, cf. Sec. 13]. Cosmic leptogenesis [423, 424, for e.g.] and baryogenesis [425, 426, for e.g] are related if for no other arguable reason than that they both occur under the same conditions of thermal disequilibrium to which statistical mechanics is inapplicable.

If B and L are the baryon and lepton numbers, at thermal equilibrium both $\langle B\rangle_T$ and $\langle L\rangle_T$ vanish so there is no net generation of either number. This justifies our prior application of Clausius' inequality for the time-dependent change in the entropy to show that baryons are in violation of the T-asymmetry of the SLT. This equally applies to leptons (neutrino oscillations, regardless) and is consistent with Sakharov [427, 428]'s departure from thermal equilibrium criterion for particle asymmetry, be it a baryon or a lepton.

Leptons and baryons are in violation of the SLT through their disregard for the T-asymmetry of entropy that accrues from the subharmonicity of the local phase ϕ whose gradient $\nabla\phi$ is the velocity of the wave packet of the lepton or baryon resulting in their mutual observed asymmetry. In short, the SLT is the reason why the cosmos is free of antimatter whether it be leptonic or baryonic.

4.5 The strong CP problem

Probe images [429] of the light outside the Milky Way (the cosmic optical background, COB) have implicated axions, hypothetical finite mass, neutral, spin zero, long-lived bosons, as candidate sources [430, 431] of dark matter to explain why through their decay into photons the light seen in the COB is brighter than expected. The original reason [432, 433] for proposing the existence of axions was to explain why CP violations present in weak interactions are absent in strong interactions [14, 15, et passim] as evidenced by the nonobservance [434] of an EDM of a neutron. Prompted by Peccei-Quinn axion theory [432, 433] for the strong CP problem, Wilczek and coworkers [435, 436] were among the first to identify axions as possible progenitors of wave-like dark matter. Because low-mass axions are thought to emanate from the interiors of hot stars as possible cold Bose-Einstein condensates [437] and to couple to two photons in a magnetic field, the CAST Collaboration at CERN [438] directs a strong magnetic field at our Sun to detect the X-ray photons from axions but has yet to report any findings. The search continues [439–441] but has so far failed to report their presence. Regardless, elusive axions could serve a purpose different from being suggestive of an equally elusive dark matter.

Wilczek [442] showed that the electrodynamics of axions can be described if one adds a term of the form $a\boldsymbol{B}_{\mathrm{int}} \cdot \boldsymbol{E}_{\mathrm{int}}$ to the Maxwell Lagrangian for an electromagnetic field $(\boldsymbol{E}_{\mathrm{int}}, \boldsymbol{B}_{\mathrm{int}})$, where a describes the strength of the axion field. This adds further charge density $-\nabla a \cdot \boldsymbol{B}_{\mathrm{int}}$ to Gauss' law and current density $\nabla a \times \boldsymbol{E}_{\mathrm{int}} + \dot{a}\boldsymbol{B}_{\mathrm{int}}$ to Maxwell-Ampre's law, reflecting the fact that $a(\mathbf{x}, t)$ is both P and T odd. Recall-

ing [145] that under T reversal, $\boldsymbol{E}_{\rm int}$ is even while $\boldsymbol{B}_{\rm int}$ is odd, the inclusion of axions as sources of $(\boldsymbol{E}_{\rm int}, \boldsymbol{B}_{\rm int})$ in (16a,16b) does not reverse the arrow of time in violation of the SLT so that CPT invariance holds for axion-mediated strong interactions. This contrasts to both magnetic monopoles and antimatter discussed previously where the opposite is true and neither are observed in accord with the reality of the SLT.

A recent study [443] of a single gravitationally-lensed quasar found its Einstein rings [444] to exhibit anomalies suggesting the presence of wave-like behavior consistent with ultralight axions as a more viable dark matter candidate than WIMPs.

SM predicted EDMs are many orders of magnitude below current experimental limits. The aforesaid SLT restoration of CPT invariance for strong CP interactions via axions does not bode well for measurement of the EDMs of subatomic particles which have never been found [445–447, for e.g.] below what is effectively naught for a bona fide dipole moment regardless of significant instrumental and Bayesian data processing advances. Neither the SM nor the SMC provides an explanation for leptonic or baryonic asymmetry.

4.6 Heaviside dark energy and the expansion of the Universe

Imagine replacing the nuclei and electrons of a molecule with uncharged point particles of arbitrary masses such that their Coulomb potential is replaced by the gravitational potential and ρ, ϕ, $\mathbf{j}$, and $\boldsymbol{F}_{\rm int}$ go over into $\rho_{\rm g}$, $\phi_{\rm g}$, $\mathbf{j}_{\rm g}$, and $\boldsymbol{F}_{\rm int,g}$, respectively, as the electromagnetic molecule analogizes to a self-gravitating body, which will proxy here as the Universe. Unlike the molecule in a heat bath catered to by the zeroth law of thermodynamics at finite temperature T, the Universe is alone in a CMB mean temperature [448] of ~ 2.725 K.

Gravitoelectromagnetism (GEM) connects the mass density $\rho_{\rm g}$ and the mass current density $\mathbf{j}_{\rm g} = \rho_{\rm g}\nabla\phi_{\rm g}$ in a gravitational field as Maxwell-like equations, an analogy (with $\epsilon_0 \to -1/4\pi G$) first pointed out by the late-nineteenth century physicist and electrical engineer Oliver Heaviside [449, 450]. As a linear approximation to GTR [451, 452] in the weak-field limit without being Lorentz invariant, GEM is the field theory for the hypothesized graviton, a neutral and massless boson thought to propagate transversely on the null geodesics of the metric tensor at the speed of light, just as photons do in geometric optics.

On 11 February 2016 the Laser Interferometer Gravitational Wave Observatory (LIGO) announced [453] it had detected gravitational waves produced by the merger of two black holes more than a billion light years from Earth. The Universe is filled with massive objects which undergo rapid accelerations that generate detectable gravitational waves of four LIGO-defined categories, viz. Continuous, Compact Binary Inspiral, Stochastic, and Burst. Through their specific interactions these massive objects cause $\partial\mathbf{j}_{\rm g}/\partial t$ to accelerate a test particle of velocity $\nabla\phi_{\rm g}$ with attendant gravitational waves: just like $\boldsymbol{F}_{\rm int}$, this source $\boldsymbol{F}_{\rm int,g}$ is odd in time and is fueled by the gradient in $\rho_{\rm g}$. Gravitational waves do not travel backwards despite the indifference of electrodynamics and quantum mechanics to the direction of time. Consequently, within the range of validity of GEM, the Universe is T-asymmetric in compliance with the SLT and harbors neither gravitomagnetic monopoles nor antimatter contrary to the earlier findings of Sakharov [427, 428] who restored CPT invariance by invoking an anti-Universe that proceeded in reverse time since the Big Bang and where antimatter dominates. Paradoxically, Sakharov's anti-Universe was rediscovered recently by Turok and coworkers [454, 455] in a new cosmological model that *inter alia* includes a sterile neutrino-based dark matter hypothesis. Like Sakharov's, it too violates the T-asymmetry of the SLT as does their mutual anti-Universe.

Recall that the Maxwell stress tensor $\boldsymbol{\sigma}_{\rm int,g}$ has units of negative pressure*, with the diagonal elements providing the tension and the off-diagonal elements the shear, and represents the contribution of electromagnetism to the source of the gravitational field (curvature of spacetime) in GTR. The Poynting vector $\boldsymbol{S}_{\rm int,g} = \boldsymbol{E}_{\rm int,g} \times \boldsymbol{B}_{\rm int,g}$ provides the energy density of the gravitational waves emanating from the self-gravitating object as it expands at a rate that is accelerating just like the known Universe [457, et passim] due to the repulsive effect of $\boldsymbol{F}_{\rm int,g}$ on the gravitational field. Dark energy is the work done by the Heaviside analog $\boldsymbol{F}_{\rm int,g} = \nabla\cdot\boldsymbol{\sigma}_{\rm int,g} - \dot{\boldsymbol{S}}_{\rm int,g}$ of the Lorentz-Faraday force in causing this accelerating expansion, such energy being dark because gravitons are likely undetectable [458, 459].

The recently launched European Euclid telescope plans to investigate dark energy and dark matter in a Universe wherein $\sim 95\%$ of its inventory is unknown. Dark energy is quantified by an equation of state parameter [460, for e.g.] w, the ratio of pressure to density. All indications are that w is close to -1 suggesting that the pressure is both outward (sic negative) and constant.

Alternatively,

$$w(t) \propto \boldsymbol{F}_{\rm int,g}/\rho_{\rm g} = \nabla\phi_{\rm g} \ln\dot{\rho}_{\rm g} \,. \tag{26}$$

For the known Universe, $w(t)$ affects both its geometry, via $\nabla\phi_{\rm g}$, and the growth rate of its structures, via $\ln\dot{\rho}_{\rm g}$, so that $w(t) \leq 0$. The dark energy induced expansion is irreversible provided $\nabla\phi_{\rm g}$ is finite in conjunction with $\ln\dot{\rho}_{\rm g}$ serving as a time-varying sensitivity measure for $w(t)$; otherwise the Universe is in steady-state or is imploding, neither of which is believed to be true.

No one knows how the world will end but Katie Mack provides a guide [181] to some of the possibilities. Since

*Botanists [456, for e.g.] use the negative pressure ρhg of sap to explain how in the absence of an internal pump, ρ-density water ascends a height h through the xylem and phloem tissue against the acceleration due to gravity g for the tallest of trees.

the guide first appeared, several other speculative hypotheses have come along. For example, new early dark energy [461] with the potential to resolve the tension between recent local measurements of the expansion rate of the Universe using supernovae data and the expansion rate inferred from the early Universe via the CMB; dark matter particles with an extra force [462] proportional to the velocity squared mimics the temporal evolution of the effect of a cosmological constant; a mechanism [463] by which a dynamical form (quintessence) of dark energy could cause the acceleration of the Universe to cease and then transition from expansion to a phase of slow contraction of yet-another cyclic universe.

In contrast to such prevailing dogma, the preceding identification via (26) herein of dark energy as the work done by the Heaviside analog of the Lorentz-Faraday force in causing this accelerating expansion makes no reference to a cosmological constant Λ [464, 465] and its relation to the accelerating expansion of the cosmos [466]. There is no known experiment that can distinguish between Λ and a vacuum energy density. This ambiguity results in dark energy [467] and vacuum energy [468] being pursued as the leading candidates of finite Λ. Unruh and coworkers [469] tackled this beguiling problem in favor of the gravitational property of the quantum vacuum (assuming it gravitates in compliance with the equivalence principle of GTR) to suggest that there is no necessity for a finite Λ to explain the observed slowly accelerating expansion of the Universe as opposed to its catastrophic explosion*. Were T to approach zero, the self-gravitating object would no longer expand but could conceivably fragment or implode before dying as it ceases to emit further gravitons in assuring that its enthalpy U vanishes in compliance with the first law of thermodynamics†. If the Universe is stable, dark energy can maintain its current value, the laws of physics prevail into the future, and its fate will be an eventual heat death. However, if as is popularly believed, it is unstable or metastable because the mass of the Higgs boson is appreciably less than that of the top quark [471], the quantum vacuum may spontaneously decay to a lower-energy state whereupon black holes consume galaxies and each other before eventually evaporating via Hawking radiation [472] emissions. At that point, all that remains in the Universe are photons and gravitons and wayward masses so remote from each other that they do not interact with anything, gravitationally or otherwise. Frautschi [473, loc. cit. p. 599] failed to identify a scheme for the immortality of life: his hope that radiant energy production would continue without limit so that life capable of using it forever can be created is not likely to transpire.

As the only survivors of that *fin de cosmos*, photon and graviton fields resort interminably to Gertsenshtein [474] exchange in which one field produces the other under the aegis of their respective $\boldsymbol{B}_{\text{int,g}}$. The process is irreversible in accord with the quantum Clausius inequality given in (11b) provided the respective ϕ_{g} for the photon and graviton field is subharmonic. At this juncture time stops and is superfluous since in the absence of mass it lacks measure.

With possibly one provocative exception [475–477], all indications [478] are that the known Universe is flat or, if it has any curvature, it is small. Since the boundary ∂V is embedded in $V(t)$, the Willmore functional [479] of $V(t)$ given by

$$\mathcal{W}(V(t)) = \oint_{\partial V} da\, \hat{\mathbf{n}} \cdot (H(\mathbf{x})^2 - K(\mathbf{x})) \geq 0\,, \qquad (27)$$

serves as a measure of how much $V(t)$ deviates from a hypersphere on which $H^2 = K$ everywhere, where H is the local mean curvature (average trace of $\mathbf{S}$, the shape operator) and K is the local Gaussian curvature (determinant of $\mathbf{S}$) of $V(t)$. Finite $\mathcal{W}(V(t))$ provides a route to monitor local changes under Willmore flow [480] and provides an alternative to the pursuit of a cosmological constant based on the Weyl curvature of the Maxwell stress tensor $\boldsymbol{\sigma}_{\text{int,g}}$ [74, 481].

Once the Willmore flow of $V(t)$ is established, the phase $\phi_{\text{int,g}}$ is provided via the Perron-Wiener-Brelot solutions to a Dirichlet problem [482, cf. Ch. 4] on the boundary ∂V whereon it is maximized and within which it is subharmonic. The phase is furthermore relatable to its hyperspherical harmonic expansions [483, 484] available in principle for many-body systems beyond banal one- and two-particle approaches. With $\mathcal{W}(V(t))$ and $\phi_{\text{int,g}}$ so determined, the de Broglie-Sommerfeld condition in (4) comes into its own in providing the distribution of mass $\rho_{\text{int,g}}$ in the system as a function of energy and its sidekick, entropy.

4.7 Recirculation

Under extreme mechanical loading or shearing conditions, materials are driven so far from equilibrium that they and their molecules change shape irreversibly. Cell membranes tend to position themselves so as to minimize their Willmore energy [485], a finding consistent with the long-standing importance for both biologic [486, cf. Ch. 9], [487], [488] and nonbiologic [489] specificity disregarded in the fog of one upmanship [490].

A neutral atom of atomic number Z has a boundary $\partial V \subseteq R^N$ with $N = Z$. A lone atom in V at $T > 0$ is orientationally spherical and its V is of finite mean curvature $1/r_Z$ and Gaussian curvature $1/r_Z^2$, where r_Z is the atomic radius. For a molecule at $T > 0$ within $\partial V \subseteq R^n$ with $n = M + N$, the stabilizing Lorentz-Faraday $\mathcal{V}_{\text{int}}(\mathbf{x})$ and Coulomb $\mathcal{V}_{\text{C}}(\mathbf{x})$ potentials are noncentral and V is unlikely to be spherical. There is

*After a brief ($<< 1$ s) period of inflationary expansion (sic stretching), the Universe ostensibly contracted for ~ 9 billion years before it started to expand again at an accelerating rate fueled by dark energy or, equivalently, an energy density homogeneously distributed in the vacuum that is many orders of magnitude larger than the value Einstein thought it ought to have.

†If ever $0 < T \ll 1$, Q and W vanish via (12e) and (23b), respectively, so that $U = 0$ and $F = 0$ whereat nothing further happens since no more work can be done at which time ΔS vanishes, a view first proposed by Thomson (sic Kelvin) [470] and commonly known as the Heat Death (aka Big Freeze) of the Universe.

no *a priori* reason why any but the simplest of molecules cannot take on knotted configurations in their chemical graphs. The volume of a molecule is not necessarily a simply connected surface whose boundary is free of holes. Pursuit of the protean development of V for a molecule under Willmore flow might provide an algorithmic basis for those notions of molecular volume and shape in use since pioneered by Einstein and Perrin but found wanting by some [362, et passim].

5 Conclusion

By simplifying the system of interest to that of a single entity – a molecule or any other particle or structure in its known Universe – whose only descriptor is its wave function from which the Lorentz-Faraday force emerges without appeal to the equipartition theorem [491, for e.g.] but rather from the gradient of its phase when the system connects to a thermal field, whence it relays both the direction of time and entropy increases to the observable macroscopic world of thermodynamics from the microscopic worlds of quantum mechanics and electrodynamics.

Both the SLT and Faraday's law of electrodynamics are of similar vintage and status. Surprisingly, they share a hitherto unrecognized connection at the microscopic level. Whereas the former receives unrelenting challenges and suggested modifications, the latter presents just a few conceptual difficulties and paradoxes for some but without offers to replace it for any technological benefit over that which it has long wielded. Here it was shown that both laws are easily understood by standard quantum mechanics that does not dismiss the local phase of a system's state as being as physically unimportant as is widely promulgated.

The relationship between the thermodynamic arrow of time and time-reversal symmetry in nonrelativistic quantum mechanics was shown to lie in the continuity equation for the probability density and its connection to the probability current through the local phase of the charge amplitude. The change in the entropy of an autonomous molecule in contact with a heat bath was shown to be asymmetric in time and increases (irreversible process) or remains unchanged (reversible process) according as the relative change in its wave function's local phase is finite or vanishes, respectively. Thermal equilibrium is attained though weak neutral currents caused by internal electric and magnetic fields originating with the conservative Lorentz-Faraday forces acting on the nuclei and electrons of a molecule as affected by its hotter environment.

The evolution of $\mathbf{j}$ as identified in (8b) is driven by the feedback $\nabla \cdot \mathbf{j}$ as modulated by the finite time-independent gradient of ϕ, the phase of the wave function ψ. This feedback is integral to a system in a thermal field and however it determines the dynamics of the system, in no way does it control that dynamics. If the feedback is negative it tends to produce stability as evidenced by the fulfillment of the virial theorem. The SLT determines that the feedback loop evolution is negative, consistent with Sommerfeld [144, cf. §28]'s radiation condition on ψ as was previously noted (*vide supra*). If, however, the feedback is positive as identified in (8c), it gives rise to instabilities as manifested by violations of the virial theorem, exemplified by dark energy acceleration of the Universe in the weak field limit, for instance.

Processes between the system and its surroundings driven by nonthermal gradients are similarly accompanied by an increase in the total entropy whose T-asymmetry prevails through its ongoing relation to the rate of change in the probability current, an operator that is even in time. While the wave function's local phase was shown not to influence the system's necessary fulfillment of the first law of thermodynamics, its subharmonicity was shown to be a necessary and sufficient condition for it to comply with the SLT as first formulated by Clausius. The time asymmetry of $\Delta S(t)$ additionally implies that the detection of permanent EDMs of subatomic particles (electron, proton, neutron, muon) – a consequence of CP violations and T-asymmetry in particle physics, with or without the assumptions of CPT symmetry [28, 29] – may never succeed. Indeed, the latest high-precision measurement [492] of the EDM of an electron drew a blank. The spectroscopic technique used by Roussy et al. [492] has an estimated mass reach of 40 TeV, an order of magnitude higher than at the LHC.

It is worth noting that the Hamiltonian operator of the system has played no explicit role in this exposition other than through the ubiquitous self-adjointness of the Laplacian, confined or free. Entropy production is greater when the local phase is subharmonic on the boundary rather than within the molecular volume. Faraday's law of induction was shown to hold for a single molecule provided the gradient of its local phase is finite, a necessary and sufficient condition for it not to present with its well-known paradoxes.

The primary contribution of this paper is the identification of internal conservative Lorentz-Faraday forces acting on the nuclei and electrons of a molecule in a thermal field and their decomposition into coupled internal electric and magnetic fields. This highlights the role of the dynamic probability current in causing entropy changes to be T-asymmetric contrary to the received word [98, 493–495, for e.g] that the direction of the arrow of time in macroscopic systems ought to originate from dominant (sic fundamental) time-reversal symmetric classical and microscopic dynamics or quantum fluctuation relations when in reality the opposite applies due to fact that the world is observed macroscopically even if perceived microscopically. Additionally, it brings out the role of the local phase of the state in distinguishing reversible from irreversible thermodynamic processes in accord with Clausius' formulation of the SLT and in providing a microscopic basis for Faraday's law of induction through the presence of electrically neutral currents mediated by photon exchange in all intramolecular interactions involving the nuclei and elec-

trons of the molecule and so revealing the greater importance of electrodynamics over electrostatics as long ago asserted by Earnshaw in accounting for the stability of molecules.

Due to its failure to fully live up to its marquee standing, the SMC has spurred many explorations beyond its domain for "new physics" but without first addressing what is its most fundamental oversight: its failure to comply with the SLT and its corollary, that entropy increases in irreversible processes to punctuate the evolution of the known Universe.

By going back to Clausius' inequality and interpreting it quantum mechanically, what has been done here is to refute the claim that time is reversible in showing that the entropy gain is T-asymmetric for a molecule – or any other particle or structure in its Universe – from their initial appearance in a thermal field to their final destiny. This paper makes only one prediction: travel to the past is impossible either quantum mechanically or electromagnetically, not because it is as highly improbable as it is found to be, but because it would cause entropy changes to decrease contrary to the SLT. The GTR has played no role in this finding*.

The asymmetry in entropy invalidates several falsifiable predictions of the SMC attributable to its disregard for the SLT – including, the cosmic facts that magnetic monopoles do not exist, that antimatter is scarce to none, that hypothetical axions explain the strong CP paradox without necessarily accounting for dark matter, and that dark energy is the basis for the accelerated expansion of the known Universe.

In the practice of reductionism, macroscopic physics supervenes upon the microscopic, the SLT being the most conspicuous exception to that superfluous tenet. The supersedence of classical thermodynamics over quantum mechanics and electrodynamics across spatio-temporal scales ranging from an individual quantized system to its known Universe has been shown herein. Additionally, in showing that reversible (irreversibility) processes are affiliated with the particle $\nabla\phi = 0$ (wave $\nabla\phi > 0$) behavior of matter, attention has been drawn to a heretofore overlooked connection between the different roles of classical thermodynamics and time-invariant quantum mechanics and electrodynamics in respect to arrow-of-time asymmetry and wave-particle duality.

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To Katyg Behesnilian (1950-2022) my long-time partner and muse, shine on bubrig until the end of time.

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*Solutions to the GTR field equations exist that purport to provide for time travel via closed time-like curves [496, et passim]. These speculative universes accommodate an Orwellian endless present where history pauses, just as in the case of reversible processes where $\Delta S(t) = 0$ and distinguishing later from earlier (and vice versa) events does not matter. With irreversible processes, however, $\Delta S(t) > 0$ and discerning current from past events counts as it does in the known Universe in harmony with the SLT; attempting to know past from present events implies that $\Delta S(t) < 0$ whereby evolution reverses, a physical impossibility that historians and allied scholars adroitly avoid.

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