Entropy is not maximum in the equilibrium state of complex systems

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Applied physical science theory has accrued through distilling empirical observations into "laws of nature" on which new findings are secured. Each field has its own empirical laws and language. All presumably should derive from physics. The only unifying principle currently is the Second Law of thermodynamics, postulated as the bridge between physics and macroscopic diffusion evident in all complex systems. I show that the Second Law is not valid because entropy is generally not maximum in equilibrium. Deviation from the Second Law widens with system complexity. This flaw is fatal to the entire theory of entropy because the state of a system cannot be determined without the Second Law. I reveal the flaw through a comprehensive new theory of thermodynamics deriving from quantum mechanics without entropy or additional postulates. This new "modal thermodynamics" theory provides a common, transparent framework for analyzing real systems of any size and complexity. Empirical laws are thereby grounded directly on physics, which should facilitate future research and development, particularly in interdisciplinary fields.

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Diffusion is the distinguishing feature of thermodynamics, compared to mechanics. It is the source of the traditional notion of dissipation. Diffusion is essential in transport equations, which form the basis of applied physical science theories. The Second Law, which states that entropy of an isolated system does not decrease in time on average, is postulated as the reason why diffusion is irreversible, systems equilibrate, and time progresses forward [1]. But, over the past 170 years, standard entropy theory of Classical Thermodynamics and Statistical Mechanics has not developed into a seamless rationale bridging microscopic physics and our world. Intractable issues stemming from the Second Law itself and its application [1, 2] have prevented forming such a bridge. These issues persist in the development of Quantum Thermodynamics [3, 4] and Relativistic Thermodynamics [5].

Standard theory explicitly avoids speculating about internal activity and instead aims to discern the overall state of a system through aggregate exchange with the outside. Yet diffusion can only be understood as the motion of individual particles. Diffusion is continual, balancing in equilibrium to produce zero net flow. Analyzing the change in state functions, such as entropy, with respect to global parameters cannot capture this activity.

Kinetic methods have been used for developing thermodynamics since the foundation of the field. Work investigating dynamics of many microscopic particles through the 1840s to 1870s provided insight on the origins of pressure, heat, equilibrium, the Law of Mass Action, and the Second Law. These methods employ Lagrangian mechanics and results are limited to approximately ideal gases, due to their computational difficulty.

The entropy theories of Rudolf Clausius [6] and Josiah Willard Gibbs [7] seem to provide a more universal understanding of complex processes. An identical form of the Law of Mass Action, derived from the postulated Laws of thermodynamics and the Fundamental Equation, apparently supersedes the proportional reaction rate proposed by Guldberg and Waage [8]. The Boltzmann and Gibbs postulates associating entropy with probability suggest that this entropic result is equivalent to kinetic balance. But this conclusion is subtly, yet fatally, wrong.

Identifying where the error occurs requires developing an alternative theory of thermodynamics based solely on kinetic arguments within quantum theory. Furthermore, because Lagrangian mechanics neglects the microscopic forces that drive diffusion [9], the evolution of any system of particles should be evaluated in a more fundamental way, by the mode of motion each particle occupies and the modes with which they may interact and to which they may transition.

Spontaneous events throughout a system and its environment cause nonunitary reduction of individual particles to single-particle modes [10]. As the number of degrees of freedom increases in a system, particle correlation time shrinks, macroscopic and microscopic energy become distinct, and properties stabilize. Analyzing system behavior for periods shorter than the correlation time requires unitary time propagation interspersed with spontaneous events. The following discussion assumes that measurements take much longer than the correlation time. Persistently correlated particles are treated as a distinct species of composite quasiparticle existing in a set of independent modes with short correlation time.

The current system state is the configuration of occupied modes. Quantum mechanical mode transition rates determine the overall net energy, momentum and particle flow rates. This approach naturally distinguishes all stable particle species with distinct characteristics, which represent different material phases of the same substance (e.g. water vapor, liquid and ice) as well as different chemical forms. The inherently probabilistic nature of resonant interaction implies that the likelihood for a system to recover its prior state becomes practically impossible in the thermodynamic limit of many degrees of freedom.

All particle dynamics are unified in this theory [11]. Chemical reactions are particle transformations between species of different substances. Pure first order phase transitions are transformations between species of the same substance. Transport is due to transformations between spatially separated modes. All terms in this theory are derived from first principles.

Quasi-equilibrium exists when all macroscopic net flows averaged over a measurement are sufficiently small. This is a steady state condition, not a maximal condition, as in entropy theory. Also note that this definition applies to any environment, including measurement apparatus. Flow occurs as local conditions change, driving the region toward a new equilibrium state.

An example of a single chemical reaction will suffice as a counter-example to the Second Law; all other types of transformation produce similar conclusions. A generic chemical reaction may involve some number of "reactant" species $\{Y_1, \cdots Y_r\}$ producing a number of "product" species $\{Y_{r+1}, \cdots Y_{r+p}\}$ obeying a stoichiometric equation $(-x_1)\,Y_1 + \cdots + (-x_r)\,Y_r \leftrightarrow x_{r+1}Y_{r+1} + \cdots + x_{r+p}Y_{r+p}$. The choice of sign for the stoichiometric coefficients ($\{x_1, \cdots x_r\} < 0$ and $\{x_{r+1}, \cdots x_{r+p}\} > 0$) simplifies (9).

First derive the opposing flow rates. The mode spectrum is discrete because a system must be confined to achieve equilibrium. Let $N_{j,m}$ be number of particles of species j in mode m with energy $\epsilon_{j,m}$. When particles are uncorrelated over a measurement, forward reaction rate is the sum of rates of all combinations of particle transitions producing the products from reactants. Reactant particles occupying a configuration of modes i transition to a configuration k of product species at a certain mean rate Γ_{ik}. A non-zero rate implies that energy and momentum is conserved within quantum uncertainty. The forward rate from each configuration i is proportional to the mode occupation number for each reactant. The total forward reaction rate is the sum over all reactant and product configurations:

$$\text{Forward rate} = \sum_{i}^{\substack{\text{Reactant}\\ \text{config.}}} \; \sum_{k}^{\substack{\text{Product}\\ \text{config.}}} \Gamma_{ik} \prod_{j=1}^{r} \prod_{l=1}^{-x_j} N_{j,m_{ijl}} \, . \tag{1}$$

This expression is general, though the particle mode distribution can be expressed succinctly only in equilibrium. The reverse reaction rate is similar, with Reactant and Product exchanged, because coupling is bidirectional.

Deduce the steady mode distribution following arguments in [10]. The number of possible particle configurations Ω that a system may achieve is a sensitive indicator of the flows within the system. The equilibrium distribution holds when this number is steady in time under the physical constraints imposed on the system. Consider the set of all particles of a specific species, identified by subscript j, within some defined boundary. (The following argument applies to every species within that boundary and all interaction. The quantum regime may be analyzed similarly [11].) In the classical regime, when particles rarely inhabit the same mode, the mean over the duration of a measurement, indicated by $\langle \cdots \rangle_t$, is

$$\begin{aligned} \left\langle \frac{\dot{\Omega}}{\Omega} \right\rangle_t \approx \sum_{m}^{\substack{\text{Mode}\\ \text{energy}}} \Big[\ln \langle N_j \rangle_t + \ln g_{j,m} - \ln \langle N_{j,m} \rangle_t \\ - \beta\epsilon_{j,m} - \eta \Big] \langle \dot{N}_{j,m} \rangle_t + \eta \langle \dot{N}_j \rangle_t + \beta \langle \dot{E}_j \rangle_t \end{aligned} \tag{2}$$

after imposing total number $N_j = \sum_m N_{j,m}$ and energy $E_j = \sum_m N_{j,m}\epsilon_{j,m}$ constraints on the set, and using Newton's accent notation for time derivatives. The Lagrange multipliers associated with these constraints are interpreted as a normalization factor η and inverse energy scale $\beta \equiv 1/k_B T$ defined as temperature with the Boltzmann constant k_B. It is assumed in (2) that the measurement takes longer than the correlation time and that the number of particles with the same mode energy is much greater than one and less than the mode degeneracy, $1 \ll N_{j,m} < g_{j,m}$, which is valid for all modes except the lowest few that are occupied by an insignificant number.

The sum in (2) need only include modes occupied on average, not necessarily every possible state. Furthermore, note that this average is not reliant on particle trajectories in phase space, which avoids associating probability with mean sojourn time and the ergodic hypothesis. Neither does this average represent an ensemble nor our lack of knowledge nor subjective belief, avoiding all ambiguity in interpreting probability [2, 12, 13].

Out of equilibrium, the total particle number and energy of the set varies, and the mode spectrum is continuously shifting, due to the transitions of interacting particles. When the system settles sufficiently such that the rates of change in mode spectrum and total particle number and total energy are small, then the sum in (2) dominates, yet the rate of change in mode occupation remains non-zero and uncorrelated. Therefore, a steady state requires that each coefficient in square brackets is zero, producing a mean distribution dependent only on the current steady mode energy spectrum. All mode transition rate information is contained in $\langle \dot{N}_{j,m} \rangle_t$. The mean number of particles of species j occupying each mode m in the classical regime is

$$\langle N_{j,m} \rangle_t = \langle N_j \rangle_t \; e^{-(\epsilon_{j,m}/k_B T) - \eta_j} \, . \tag{3}$$

Hereafter, all thermodynamic properties are understood to be mean values and the time brackets are omitted.

This result may be expressed as statistical distribution over system states with energy $E_s = \sum_j \sum_m N_{j,m}\epsilon_{j,m}$. The normalization factor is related to the system partition function,

$$Z(T,\{N_k\},V,..) = \sum_{s}^{\text{States}} e^{-E_s/k_BT} \,, \tag{4}$$

by

$$\begin{aligned}\eta_j(T,\{N_k\},V,..) &= \ln Z(T,\{N_1,..,N_j,..\},V,..)\\ &\quad - \ln Z(T,\{N_1,..,N_j-1,..\},V,..)\\ &= \partial \ln Z/\partial N_j|_V \,. \end{aligned}\tag{5}$$

The ellipsis represents all other independent parameters. Equation (5) equals the change in partition function when one particle of species j is added to the system in equilibrium and so is named the particle partition logarithm (PPL). Neither partition function nor PPL are physical quantities and so need not be extensive or intensive.

The mean forward reaction rate (1) in equilibrium in the classical regime may then be written as

$$\text{Forward rate} = \Psi_{\text{forward}} \prod_{j=1}^{r} \left(N_j e^{-\eta_j}\right)^{-x_j} \,, \tag{6}$$

defining the forward effective rate factor as

$$\Psi_{\text{forward}} \equiv \sum_{i}^{\substack{\text{Reactant}\\ \text{config.}}} \Gamma_i \prod_{j=1}^{r} \prod_{l=1}^{-x_j} \exp\left[\frac{-\epsilon_{j,m_{ijl}}}{k_{\text{B}}T}\right] \,. \tag{7}$$

with $\Gamma_i = \sum_k \Gamma_{ik}$. In virial particle models, describing most, if not all, microscopic particles, the PPL includes a logarithm of the volume, so that reaction rate is a function of particle number densities.

The mean reverse reaction rate likewise may be written

$$\text{Reverse rate} = \Psi_{\text{reverse}} \prod_{j=r+1}^{r+p} \left(N_j e^{-\eta_j}\right)^{x_j} \,, \tag{8}$$

with the reverse effective rate factor summed over product mode configurations. Equilibrium holds when these mean rates balance so that their ratio is unity, implying

$$\prod_{j=1}^{r+p} \left(N_j e^{-\eta_j}\right)^{x_j} = K \,. \tag{9}$$

This result matches Eq. (13) in [11]. Here the new "rate quotient" is defined as

$$K \equiv \Psi_{\text{forward}}/\Psi_{\text{reverse}} \,, \tag{10}$$

not to be confused with "reaction quotient." Transition rates tend to weight the effective rate factors around an activation energy specific to each reaction. This activation energy is shared in both forward and backward directions and so cancels in the rate quotient. The rate quotient then tends to be a slowly varying function of temperature, stress and number density.

Flow cannot be derived in standard theory. Instead, maximum entropy is stipulated as the equilibrium condition. Equation (9), absent the rate quotient, is precisely the result found in standard thermodynamics for chemical equilibrium under constant temperature and volume or pressure conditions. Gibbs entropy in equilibrium may be expressed as

$$S = k_B \frac{\partial}{\partial T}\left(T \ln\left[Z\Big/\prod_j N_j!\right]\right)\Big|_V \,. \tag{11}$$

The factorial terms are added to address the Gibbs Paradox and make entropy an extensive quantity.

Equilibrium chemical potential is related to Helmholtz free energy ($F = U - TS = -k_BT\ln[Z/\prod_j N_j!]$) by

$$\mu_j = \partial F/\partial N_j|_V = -k_BT\left(\eta_j - \ln N_j\right) \,, \tag{12}$$

given that the formation energy of elemental particles is set to zero by Gibbs's convention. This same relation follows from Gibbs free energy at constant temperature and pressure. Equation (9) may then be written

$$e^{\Delta F/k_BT} = K \,, \tag{13}$$

where the free energy of reaction at constant volume or pressure is identified as $\Delta F = \sum_j \mu_j x_j$.

Josiah Gibbs derived his theory from the assumptions that entropy of an isolated system exists out of equilibrium and is maximum in equilibrium [14]. Consequently, the free energy of a system in contact with an ideal heat reservoir is minimum in equilibrium, implying $\Delta F = 0$ [15]. But this conclusion can be true in the above modal result only if the rate quotient always equals one.

The rate quotient is not identically equal to one for two primary reasons. First, by definition, Ψ_{forward} equals Ψ_{reverse} only for symmetric transformations when the mode distribution is the same for reactants and products. The rate quotient equals one for spatial transport transformations in a stationary, homogenous and chemically inert system, implying uniform temperature, stress and number density in equilibrium. Ideal gas systems by definition obey $K = 1$ in equilibrium. Otherwise, $K \approx 1$ may be feasible for inhomogeneous systems under very limited conditions such as for extremely dilute reactive solutes whose interaction is dominated by a solvent.

A second argument is that while the derivation of (3) involves mode transition rates to achieve detailed balance, they factor out of the condition for the equilibrium mode population in (2). The Boltzmann distribution would not be so robust and the world would be a much different place otherwise. The rate quotient, therefore, contains all of the mode transition rate information and ΔF contains none. A general equilibrium condition, for a dynamic process such as reactions, logically must include rate information from non-equilibrium states. In other words, the Boltzmann distribution is sufficient only to define equilibrium of a stationary, single material phase. Each possible particle transformation requires an additional independent rate condition to determine the balanced populations of substances and phases.

The entropy condition, (13) assuming $K = 1$, is often construed as detailed balance of kinetic probabilities by assuming the Gibbs postulate relating entropy difference between two states to the ratio of their probabilities to occur. But such probability must depend on transition rates which, again, this condition lacks. Non-equilibrium probability and entropy cannot be extrapolated from (11).

The Law of Mass Action as derived by Gibbs is (13), with $K = 1$, expressed in terms of activity $e^{\mu_j / k_\mathrm{B}T}$. Activity is evaluated in practice as two empirical factors: The value in an arbitrarily chosen standard state and the relative change from this standard to the current state. The product of relative activity factors is called the reaction quotient, equal to the exponential of free energy change in the standard state. The relative factor is further split into an activity coefficient and mole fraction. The activity coefficient approaches unity under ideal conditions and simply appears to account for our lack of knowledge of the actual chemical potential. But in light of (13), it mistakenly absorbs the rate quotient as well, if $\Delta F = 0$ is assumed. This is a likely reason why the role of the rate quotient has not been appreciated to date.

Free energy, therefore, is not minimum and entropy is not maximum in equilibrium, except in simple cases when $K = 1$. The Second Law cannot be valid if quantum mechanics is true.

What evidence supports the Second Law? It is a statement about non-equilibrium entropy, because an isolated system in equilibrium does not evolve. Stating that the universe evolves toward higher probability presumes that a universal probability function exists. The Boltzmann and Gibbs postulates then define non-equilibrium entropy in terms of this universal probability. Yet no consistent definition for entropy has been found out of equilibrium [16]. Equations of motion for these functions are not known. “Notwithstanding its fundamental character, a unifying theory of entropy production valid for general processes, both classical and quantum, has not yet been formulated” [4]. Boltzmann’s H-theorem suggests kinetic support for the Second Law in an ideal gas only after artificially invoking molecular chaos, and no general proof of the H-Theorem has been found [1]. Entropy is said to be produced internally, beyond our perception, in order to account for dissipation and latent heat on change of phase. But these phenomena are accounted for explicitly, and entropy is a proper state function invariant under all cyclic processes, when total system energy is conserved, not just internal energy [17].

Dynamic quantities, namely chemical activity, latent heat and phenomenological transport coefficients, cannot be derived from (11), again due to the lack of rate information. Instead, these parameters are measured empirically or sometimes estimated by kinetic arguments. It is inconsistent, however, to employ kinetic theory when necessary and ignore its logic otherwise. This is true for Quantum Thermodynamics applying standard principles to systems requiring quantum description [4]. The above reasoning shows that, when employed universally, kinetic theory invalidates entropy theory. Gibbs well understood this hazard: “On the other hand, a method involving the notion of entropy, *the very existence of which depends upon the second law of thermodynamics*, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension” [18]. (Entropy, free energy and the Fundamental and Gibbs-Duhem equations become superfluous statistical identities without the constraint of the Second Law.) The choice between “modal thermodynamics” theory, derived from first principles as demonstrated above, or semi-empirical entropy theory, based on postulates, is mutually exclusive.

In modal thermodynamics, all energy, momentum and particle flows are due to a difference in forward and reverse rates akin to (1) and include macroscopic and microscopic parts [11]. The latter represents degrees of freedom that are too obscure to be tracked individually and must be estimated statistically. Quantum fluctuations in mode transitions disrupt correlated mode populations, nudging a system toward stable equilibrium in a spontaneous process that we call diffusion. We observe the macroscopic motion of a body as being acted on by a local “thermodynamic force” that includes the diffusive part of momentum flow. From our macroscopic perspective, we naturally associate diffusion with forward time progression even though particle interactions are symmetric in time. Local diffusion assures evolution toward a global steady state, implying by our logic that time progresses in the same direction universally. There is no need for the Second Law to justify an “arrow of time” and the tendency to evolve toward equilibrium.

This theory reveals the original seeds of confusion. Entropy of an ideal gas is maximum in equilibrium because transformation among species does not occur. Clausius derived Classical Thermodynamics largely from ideal gas analysis. Gibbs mistakenly extrapolated Clausius’ conclusion to describe multi-species systems. His equilibrium condition of equal chemical potentials is an assumed form of kinetic balance between species that neglects the statistical mechanics of particle interaction.

Equation (13) does not contradict the premise by which Clausius deduced his condition on equivalence value, later named entropy, for simple spontaneous processes. Heat transport derived by fundamental kinetic arguments produces flow from hotter to colder regions “by itself,” so long as no other stronger thermodynamic gradient exists that may cause energy to diffuse against a temperature gradient. Similarly derived particle and energy transport and stress equations also match empirical transport laws, exhibiting compound sensitivities and reciprocal flow relations [11]. The statement "energy, momentum and particles diffuse toward a steady state" captures these conclusions, describing all thermodynamics of any system in any state.

Entropy has captivated attention since Clausius proposed it in 1865 [19] because the Second Law appears to explain evolution in simple and elegant terms by an intriguing universal condition. It has proven difficult to probe beneath this facade with confidence, instead revealing a host of persistent issues stemming from several crucial assumptions. The contradiction identified here suggests why: Macroscopic behavior we perceive is inherently quantum mechanical. Diffusion can only be understood as discrete, probabilistic transitions and cannot be determined by any function of population distribution alone. The practical advantage of this insight is that a theory based solely on fundamental particle interactions is open to inspection and may be applied rigorously to systems of any degree of complexity.

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