From invariant variation problems to ideal translations for transitions: Symmetry conservation in thermodynamics, mechanics and quantum mechanics

Dedicated on the occasion of the 100. annual International Women´s Day, in great admiration, Emmy Noether, the first female extraordinary professor in Göttingen and Germany. Göttingen, the 8th of March 2021.

Elaboration of my talk with the title „Space and time in chemistry and physics: The continuous Noetherian symmetries from a statistical mechanics perspective“, Mathematische Gesellschaft Göttingen, given on the 11th of February 2021.

I. Thermodynamics

Integral time and space symmetry of energy conservation and conversion

Energy conservation in an isolated system.

Perspective Noether-Gauß, inside: Inner Euler-Lagrange fluctuations in time neither generate nor consume energy (Noether-Theorem). The integration law of Gauß implies: No energy flow through the wall.

Perspective wall/interface: No energy flow through the wall implies constant energy of the system.

Perspective outside: No flow to and from the wall implies constant energy of the system.

The dynamic perspective of the Euler-Lagrange equation belonging to the Noether-Theorem demands energy conservation for microscopic fluctuations in time. These temporal energy fluctuations are naturally described by Lagrangian motion with implicit energy and the mechanical state variables space and velocity. Hamiltonian motion is the natural description for equilibrium motion with homogeneous microscopic space with the mechanical state variables space and momentum.

Differential space-like and time-like symmetries of energy conversion

The most effective path of energy conversion minimizes entropy formation (perspective state function entropy S), maximizes work (spacial perspective of the path, volume work) and minimizes heat release (temporal perspective of the path).

Slow paths are more effective with regard to work output. Conflict of aims with maximum power!

The most ineffective path maximizes heat release and entropy gain and is without work output. (immersion heater). An efficient coupling of paths enables heat pump and air conditioner.

Phase Diagrams

Addition the Gibb´s phase rule: The sum of free intensive and extensive state variables is invariant.

(Very) Hypothetical conclusion:

The three equivalent formulations of and perspectives on energy conservation in an isolated system show similarities with prime ideals in ring theory, representing a subset of irreducible axioms with high multiplicity, a high “symmetry density”. Such multiple and irreducible elements seem to be important for building up a well-balanced axiomatic system. Energy conservation is in this sense the most fundamental and general conservation law. This reminds one of fundamental quadratic reciprocity, discovered among others by Legendre and proofed in many variants by Gauß.

II. Mechanics

Ideal Newtonian-Einsteinian-Motion

Bodies in equilibrium with gravity are weightless; their trajectories are relaxed and free of constraint force.

Inert mass and weight are generated by constraint forces: Weight as a counterforce to gravity, kinematic inertia by de- and accelerating forces (friction, engine thrust, etc.), algebraic inertia by implicit (and often global) constraints, which explicitly restrict the local kinematic space of motion.

Force is in relation to ideal equilibrium motion always a constraining force, a differential constant of forced motion generating inert mass. Heavy mass is a general differential constant of motion generating gravity. This seems to be the essential difference between inert and heavy mass.

For idealized motion without force and gravity momentum is conserved without feed-back. In the real case actio = reactio conserves momentum because gravity acts everywhere attractive.

Natural constraining forces generate local lines and circles, the equilibrium trajectories of gravity displaying local momentum and angular momentum conservation.

A natural calculation of non-equlibrium paths can be achieved *via* temporal relaxation of paths between two fixed points in time. Gravitational and kinematic forces add and are projected for each point in time and space of the path on the velocity vectors (defining the local heading) and on the turning vectors (defining the local direction of rotation, they are elements of local hyperplanes orthogonal to the velocity vectors). Vector projection, addition and rotation as well as force multiplication (based on analytical force laws) interact in an orthogonal and balanced manner; the only differential operation is the iterative shortening of the width of the time steps. The addition of the step-wise increased number of shortened velocity vectors ultimately relaxes to a stationary path. These operations feature the natural differential quantities force/acceleration (local line) and rate of direction change (local circle).

Hypothesis 1: Gravitational time dilatation belongs to a second, relativistic rotation axis. The superposition of the two rotations generates local space time curvature, defining the natural path of maximum time dilatation.

Hypothesis 2: When heavy mass is transformed into energy according to $E=mc^2$, gravity itself may be a constant of motion, meaning that the gravitational pull belonging to m must be conserved. This may be realized in form of standing gravitational waves with rotational gravitational field components (similar to H atom orbits with angular momentum). The conservation of the degrees of freedom of electromagnetic coupling in the Maxwell equations for electric and magnetic components (two field line types, 1 coupling in the Faraday law for electricity, one field line type, two couplings in the Maxwell-Ampere law for magnetism) may be the paramount conservation law also applying to the more fundamental force field of gravity, featuring waves propagating at the same speed c as electromagnetic waves. This hypothesis is inspired by the Noetherian principle of searching for so far hidden invariants of motion. A putative mechanism for generating standing gravitational waves is described in the next section. In this picture dark matter and dark energy may be the result of an increased number of degrees of freedom for gravitational motion.

III. Mechanical kinetics and quantum mechanics

An isolated gas-phase system with constant volume can be separated in a quasi-stationary Hamilton flight space and a transient Lagrange collision space with the Hamiltonian and Lagrangian energy functions coupled by a Legendre transformation between the mechanical state variables velocity and momentum. The same separation can be achieved for each molecule, collision complex and cluster being either in an often quasi-stationary Hamilton state or in a transient Lagrange state. The transient Lagrange states describe the interchange of kinetic and potential energy in time along an ideal coordinate of motion. Under collision this is the Lennard-Jones (L-J) potential, under transition this is in chemistry the reaction coordinate. The Hamilton states describe the inner structure of energy storage of quasi-stationary, neither colliding nor reacting states.

The Lagrange function $L(t) = E_{kin}(t) - E_{pot}(t)$ describes for transitions and collisions the free kinetic energy in relation to the barrier height/depth of the potential energy well. This relation depends on the kinetic energy of the center of mass motion when entering at $t=t_0$ the coordinate of transient motion. $(L(t_0) - L(t))_{max} \geq 2\ E_{Barrier}$ is the criterion for a successful transition, at the moment it is not clear whether a similar criterion for net energy storage exists or not, like $L(t) < -2\ E_{pot}$ (L-J) in the turning point t. In certain cases the transition states can be stabilized in time. The general time dependence of L(t) can be evaluated with the time-step based linear vector algebra described in II.

The characteristic feature of the Legendre transformation between L and H is the differential and multiplicative coupling of the mechanical state variables velocity v and momentum p. They are transformed into each other (omitting for a moment the factor 2 from the derivative) by multiplication and derivation. This symmetry yields several differential constants of motion: Inert mass m and kinetic Energy $m/2v^2$ as velocity derivative and integral of momentum, as well as heavy mass m and the energy mv^2 as quotient and product of v and p. The symmetric coupling suggests for relativistic conditions that the multiplicative constant of motion mv^2 and the differential constant of motion $m/2v^2$ ultimately unite in the limiting case in $E=mc^2$. This can be conjectured as the result of the Legendre transformation of a harmonic Lagrange oscillation between slow classical motion (spring energy high, kinetic energy low) and fast relativistic motion (spring energy low, kinetic energy high) relaxing under release of gravitational field energy into a stationary harmonic Hamilton oscillator.

For quantum mechanics we postulate an orthogonalization of Hamiltonian and Lagrangian motion:

In the stationary Hilbert space with imaginary phase/time and real amplitudes holds Heisenberg´s uncertainty principle (limitation of coupled space-momentum resolution). The solutions of the Schrödinger equation provide the fine structure of energy storage (taking into account relativistic effects like spin, the Dirac-equation, leading to the coupled cluster method in quantum chemistry).

The quantum mechanical transition motion resembles the macroscopic case and proceeds *via* the transient dynamical Lagrange space, in the quantum limit with imaginary amplitude and real phase. In this picture there are two separable components of motion:

A Legendre projection of the starting and the target state into the transition state (TS) provides *via* suitable (scalar) products a geometric mean, a transition probability. The multiplicative projection is enabled by the Legendre symmetry between inner energy U (belonging to stable Hamilton states) and Gibbs energy $G = U + pV - TS$ (belonging to transient Lagrange states).

The multiplicative projections are in the statistical mechanical case of Eyring´s transition state theory the partition functions of reactants and the TS itself („no return" assumption, variational TST) and the Boltzmann factor (reflecting the difference in zero point energy of reactants and TS) giving together the (pre-)equilibrium constant of the activated complex K*. In spectroscopy, these are the overlap integrals of the wave functions of the starting and the target state. The (scalar) products provide in each case a symmetry comparison, the more similar and energetically close the geometry/symmetry the more likely, with less resistance, occurs the transition between the two states.

This rather static component belongs to the orientation space orthogonal to the transient coordinate and can be interpreted as free potential energy or phase space volume of the TS (Difficult: treatment of rotations, RRKM-theory). The static component describes an activation probability of the transient coordinate and is in the microscopic limit a Legendre projection with imaginary amplitude, it cannot be directly measured.

The dynamic phase component of L(t) provides for mechanical or chemical transitions the Eyring theory and for spectroscopic transitions the Planck-Einstein relation, it is in each case E/h with $E=k_BT$ for a thermal system. The phase speed (cycles per second) is a real and measurable quantity, and couples therefore to relativistic time dilatation. This mechanism synchronizes the relative speed of local relativistic clocks. This hypothesis is based on symmetry implications of the Legendre transformation between the Lagrange and the Hamilton function.

In this picture the thermodynamic Legendre transformation from U to G provides the average path length, width and slope, the mechanical from H to L the average speed and together they yield the effective flow. The Legendre symmetry allows for multiplicative calculation of the flow from suitable, characteristic quasi-stationary Hamilton states (starting state, TS, and target state).

The (measurable) chance of reaction or transition in a given time interval leads in quantum mechanics to quasi-stationary amplitudes of thus meta-stable Hamilton states. Their real phase $(E=k_BT)/h$ is an observable but in this case statistical property of the system wave function. Individual reaction times can be detected but they are no integral constants of motion, while energy and angular momentum eigenstates are. This is the characteristic difference between Hamiltonian and Lagrangian motion on the quantum level.

The rate law of transition state theory

$$dE/dt = \Delta_{R,element}E \cdot d[\text{reactant}]/dt = -[\text{reactant}] \cdot E/h \cdot K^*(=p(\text{activation per phase cycle}))$$

applies in general and yields *via* integration the exponential function as the universal, fully symmetric temporal path of transition with the half-life ln2 / (E/h)·K* as characteristic differential constant of motion:

$$\Psi(t)(\text{system}) = [\text{Reactant}] \cdot \Psi(t)(\text{element}) = \Psi(t=0)(\text{system, normalized})\cdot\exp(-t\cdot(E/h)\cdot K^*)$$

This continuous formulation belongs to the limit of very high numbers of molecules/particles.

Postulating for the chemical-mechanical system the temporal phase synchronization as the effect of a force carrier (graviton), in analogy to the photon for the electromagnetic and the gluon for the strong interaction, a universal mechanism can explain the exponential time profiles observed for unimolecular reactions, fluorescence and phosphorescence as well as radioactive decays. The synchronization of quantum entangled motion and its decay is understandable within this mechanism. The maximum phase speed results from the Planck time: $\sqrt{\frac{c^5}{G\hbar}}$

When this model applies for quantum entangled states with coupled information, the result is instantaneous relaxation even for cosmic distances. On the molecular scale photosynthesis becomes in this picture a process enabled by a concerted coupling of photon and graviton phases/clocks.

Observation: Energies oscillate during one period in the Lagrange phase cycle of a harmonic oscillator four times between E_{total} and – E_{total} for L (=E_{kin} – E_{pot}) and four times between 0 and E_{kin} for E_{kin}, two times in forward and two times in backward direction.

This Lagrange energy cycle may explain that one half of the gained field energy is converted to kinetic energy when the H atom is formed *via* the Legendre transition of a Lagrange electron into its stationary orbit of the H atom moving in the Coulomb potential being shared with the proton. Similar to the differential path symmetry in thermodynamics: When half of the gain in field energy is converted to kinetic energy in each cycle, the final stationary state must reflect this ratio. One may postulate that only this ratio shows constructive interference (seems to be phenomenologically similar to Feynman´s path integral approach to quantum mechanics).

This mechanism may also provide an alternative explanation for the selection rules for rotational and vibrational excitations as a property of the transition motion. Higher excitation may be forbidden because of destructive interference. For an anharmonic oscillator this extinction is incomplete. For electronic transitions the radial and spherical motions are decoupled allowing for Δl=1 cascades that can be measured in form of outgoing (p or f) electron waves. However, the mechanism can be very complicated as for some cases the interaction of the electronic, mechanical, and nuclear wave functions of a molecule have to be taken into account.

The maximum microscopic orthogonality and parallelism of Hilbert-Hamilton and Lagrange motion can be distinguished in characteristic experiments that elaborate the statistical character of spacial momentum resolution limitation and temporal energy flow limitation.

In a slit experiment with perfectly prepared momenta of electrons there is infinite time to generate and measure the diffraction pattern. The points in time of single events do not play any role. The spacial resolution of the experiment must be high enough to display the diffraction pattern. The landing position is unpredictable for single electrons. The sharpness of the diffraction pattern is a function of the ensemble size, the number of prepared and landed electrons. Measured minimum (Euler-Lagrange) integral constant of motion: Planck´s action quantum, *via* Heisenberg´s uncertainty principle.

In a kinetic experiment there is a single starting point in time, to be prepared as sharp as possible, e.g. with laser technique. The result is an ensemble of molecules, simultaneously prepared in an activated state. The time resolution of the experiment must be high enough to display the characteristic time profile. The time of the reactive events is unpredictable for a single molecule. The sharpness of the measured time profile is a function of the ensemble size, the number of simultaneously activated molecules. Measured differential constant of motion: half-life, *via* the exponential concentration profile.

In this picture of coupled Lagrangian and Hamiltonian motion the superposition state is a Lagrange wave, a long-lived transition state with imaginary amplitude; it cannot be directly measured. In the measurement process the Lagrange wave relaxes to a Hamilton eigenstate. This state is visible and measurable. The phase speed of the transition is limited by the kinetic energy of the electron. The chemical analogue is the transition state of a multichannel reaction. In this picture it is paradox to expect to see the whole product spectrum in a single measurement event.

Final remarks:

In this compact elaboration the author has tried to provide a consistent axiomatic model for motion in space and time within thermodynamics, mechanics, and quantum mechanics. It is based on the synthesis of the chemical perspective of thermodynamics and kinetics with the physical Lagrange/Hamilton/Schrödinger perspective of mechanics and quantum mechanics. The result displays the methodological spectrum of research of our group and our cooperation partners [1-5]. It is a condensation of more the twenty years thinking about the foundations of and connections between these fields in teaching and research. The interlink is the Legendre transformation between energy functions in thermodynamics and mechanics and the associated differential constants of motions. This paper is a short summary without elaboration of all important details. A more comprehensive presentation is planned.

Key and starting point for the elaborated axiomatic system in this paper is the observation in experiment and molecular simulation that in the microscopic phase equilibrium 2 nm sized water droplets/crystals can oscillate in time between the liquid and solid crystalline state, while water and ice seem to rest in space and time in the macroscopic case [3]. Seemingly space and time can change their role in discriminating the phase state. Starting from this observation, and here is the connection to Emmy Noether´s theorem, one can identify Heisenberg´s uncertainty principle as microscopic version of space homogeneity and momentum conservation, giving rise to the question of the microscopic pendant to homogeneous time and energy conservation? As a trained chemical kineticist one can identify the frequency factor in Eyring´s transition state theory as a microscopic limitation of energy flow, which, being trained in mathematics, can be identified as the missing link or symmetry element. In my view the theory of R. Steven Berry on microscopic liquid-solid oscillations in clusters is based on the path symmetry when repeatedly cutting into half a volume in phase equilibrium, meaning that in each step the symmetry constraint, the fixed intensive state variable of the special macrostate must be conserved as a consequence of Boltzmann statistics. At the microscopic bottom this is only possible in Lagrangian motion with implicit energetic structure and temporal transient dynamics. In my view the Berry theory has anticipated most of the important points in this paper except for the much more fundamental symmetry implications of Legendre transformations and their connection to differential constants of motion. This connection is based on the differential coupling of extensive/explicit state variables with the intensive/implicit ones and can be used to extrapolate and analyze optimum paths between e.g. systems described by Lagrangian and Hamiltonian motion in a multiplicative manner (by calculating equilibrium constants).

A second line of reasoning, which could only be integrated in the final stages, starts with the observation that for the brachistochrone, the fastest connection of two points within the earth gravity field *via* a slide without friction, the Euler-Lagrange equation becomes a runtime minimization problem. „Can this be achieved in general, e.g. with a suitable time-stepping scheme?“, was my question at this point. This can indeed be achieved when the equilibrium criterion for extremes under constraints in the Lagrange multiplier procedure is interpreted with focus on the path geometry. A necessary precondition for an extreme under constraints is fulfilled, when the gradient of the (Lagrange) function is element of the “orientation space” being orthogonal to the restricted space of motion under constraint, and thus to the given path. The pseudo gradients can be calculated from the implicit algebraic constraints for each point of the path and the explicit constraint is to move orthogonal to these pseudo gradients. In this way the effective and allowed accelerations can be calculated for each point of the path. This yields an equation of motion in which the term $v(t) + a(t)\cdot\Delta t/2$ for the velocity change in a time step reflects the dynamics of charge current (mass-like motion, $v(t)$) and displacement current (field-like motion, $a(t)\cdot\Delta t/2$) in the Maxwell equations of electrodynamics, which makes directly plausible the generation of gravitational waves propagating at the speed of light c for relativistic conditions. (elaborated in more detail in the presentation for the Mathematische Gesellschaft Göttingen on February 11 2021).

The synopsis of these observations has lead to identifying the Noether theorem as the integral law on global constants of motion and to identifying the connection between Legendre transformations with the local differential constants of motion by which optimum, ideal paths for transitions can be described. These differential constants of motion have been, however, for quite a long time in the focus of our research [2]. On the basis of these findings the consolidation of the results has been tackled and is presented here.

In the view of the author the results of this elaboration provide a new basis for a straight forward synthesis of the standard model and relativistic gravitation. The microscopic coupling of energy and time is enabled by force carriers for field interactions, which are extended by the already proposed graviton for the mechanical phase or clock. The Higgs field belongs in this picture to gravity as the original and most fundamental force whose spacial excitation provides mass and whose temporal excitation provides the synchronization of energy and information exchange processes. Quantum mechanics work so well because Legendre projections allow for calculating transition probabilities from (quasi) stationary Hamilton states *via* (scalar) products. The statistical nature of reaction kinetics and temporal cluster oscillations are in contradiction to a symmetric time in quantum mechanics. This problem is fixed by the force carriers lending microscopic phase synchronization.

This presentation provides new interpretations which clearly go well beyond the scope of our research. Therefore there is no prerogative claim, this is just a looking ahead based on new insights.

Finally, I must confess that I have unconsciously followed Emmy Noether´s ingenious approach to systemically look for invariants, but I did not understand the mathematical systematic. But this seems to be a more general phenomenon. However, in this paper I have tried to catch up.

Perhaps it is time in this globalized science world, which drives differentiation in sub-fields and sub-disciplines further and further, to refocus on Emmy Noether, to look for connecting and irreducible structure elements. Each single, new invariant property allows to understand many phenomena as a variant of an underlying irreducible pattern. This lends orientation and calls for more scientific reasoning in terms of epistemology as the paramount philosophical discipline of all scientific research. Actually, each data reduced mp4 or mp3 video and audio reflects this idea.

[1] N. Giemelshein, S. Giemelshein, C. C. Pradzysnki, T. Zeuch, U. Buck: “The temperature and size distribution of large water clusters from a non-equilibrium model”, *J. Chem. Phys.* **132** (2015) 244305.
[2] K. Hoyermann, F. Mauß, M. Olzmann, O. Welz, T. Zeuch: “Exploring the chemical kinetics of partially oxidized intermediates by combining experiments, theory, and kinetic modeling “, *Phys. Chem. Chem. Phys.* **19** (2017) 18128-18146.
[3] D. Moberg, D. Becker, C. W. Dierking, F. Zurheide, B. Bandow, U. Buck, A. Hudait, V. Molinero, F. Paesani, T. Zeuch: “The end of ice I “, *Proc. National Academy Sci. USA*. **116** (2019) 24413-24419.
[4] P. T. M. Carlsson, S. Celik, D. Becker, T. Olenius, J. Elm, T. Zeuch: “Neutral Sulfuric Acid−Water Clustering Rates: Bridging the Gap between Molecular Simulation and Experiment“, *J. Phys. Chem. Lett.* **19** (2020) 4239-4244.
[5] D. Becker, C. W. Dierking, J. Suchan, F. Zurheide, J. Lengyel, M. Fárník, P. Slavíček, U. Buck, T. Zeuch: “Temperature evolution in IR action spectroscopy experiments with sodium doped water clusters“, *Phys. Chem. Chem. Phys.* ***23*** (2021) DOI: 10.1039/d0cp05390b.