# Computational Foundation of Thermodynamics

Johan Hoffman, Claes Johnson and Murtazo Nazarov

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### Abstract

We present a deterministic foundation of thermodynamics for slightly viscous fluids or gases based on a 1st Law in the form of the Euler equations expressing conservation of mass, momentum and energy, and a 2nd Law formulated in terms of kinetic energy, internal (heat) energy, work and shock/turbulent dissipation, without reference to entropy. The Euler equations are regularized in computational solution by a least-squares stabilized finite element method referred to as EG2. The 2nd Law expresses an irreversible transfer of kinetic energy to heat energy in shock/turbulent dissipation arising because the Euler equations lack pointwise solutions. The 2nd Law explains the occurence of irreversibility in formally reversible systems as an effect of instability with blow-up of Euler residuals combined with finite precision computation, without resort to statistical mechanics or ad hoc viscous regularization. EG2 includes a duality-based posteriori error control showing that mean-value outputs are computable to tolerances of interest (while point values are not).

## 1 The 1st and 2nd Laws of Thermodynamics

> Heat, a quantity which functions to animate, derives from an internal fire located in the left ventricle. (Hippocrates, 460 B.C.)

*Thermodynamics* is fundamental in a wide range of phenomena from macroscopic to microscopic scales. Thermodynamics essentially concerns the interplay between *heat energy* and *kinetic energy* in a *gas* or *fluid*. Kinetic energy, or *mechanical energy*, may generate heat energy by *compression* or *turbulent dissipation*. Heat energy may generate kinetic energy by *expansion*, but not through a *reverse* process of turbulent dissipation. The industrial society of the 19th century was built on the use of *steam engines*, and the initial motivation to understand thermodynamics came from a need to increase the efficiency of steam engines for conversion of heat energy to useful mechanical energy. Thermodynamics is closely connected to the dynamics of *slightly viscous* and *compressible* gases, since substantial compression and expansion can occur in a gas, but less in fluids (and solids).

The development of classical thermodynamics as a rational science based on logical deduction from a set of axioms, was initiated in the 19th century by Carnot [4], Clausius [3] and Lord Kelvin [21], who formulated the basic axioms in the form of the *1st Law* and the *2nd Law* of thermodynamics. The 1st Law states (for an isolated system) that the *total energy*, the sum of kinetic and heat energy, is conserved. The 1st Law is naturally generalized to include also conservation of mass and Newton's law of conservation of momentum and then can be expressed as the *Euler equations* for a gas/fluid with *vanishing viscosity*.

The 2nd Law has the form of an inequality $dS \geq 0$ for a quantity named *entropy* denoted by $S$, with $dS$ denoting change thereof, supposedly expressing a basic feature of real thermodynamic processes. The classical 2nd Law states that the entropy cannot decrease; it may stay constant or it may increase, but it can never decrease (for an isolated system).

The role of the 2nd Law is to give a scientific basis to the many observations of *irreversible* processes, that is, processes which cannot be reversed in time, like running a movie backwards. Time reversal of a process with strictly increasing entropy, would correspond to a process with strictly decreasing entropy, which would violate the 2nd Law and therefore could not occur. A perpetum mobile would represent a reversible process and so the role of the 2nd Law is in particular to explain *why* it is imposssible to construct a perpetum mobile, and *why* time is moving forward in the direction an *arrow of time*, as expressed by Max Planck [27, 28, 29]: *Were it not for the existence of irreversible processes, the entire edifice of the 2nd Law would crumble*.

While the 1st Law in the form of the Euler equations expressing conservation of mass, momentum and total energy can be understood and motivated on rational grounds, the nature of the 2nd Law is mysterious. It does not seem to be a consequence of the 1st Law, since the Euler equations seem to be time reversible, and the role of the 2nd Law is to explain irreversibility. Thus questions are lining up:

- If the 2nd Law is a new independent law of Nature, how can it be justified?
- What is the physical significance of that quantity named entropy, which Nature can only get more of and never can get rid of, like a steadily accumulating heap of waste? What mechanism prevents Nature from recycling entropy?
- How can irreversiblity arise in a reversible system?
- How can viscous dissipation arise in a system with vanishing viscosity?
- Why is there no *Maxwell demon* [25]?
- Why can a gas by itself expand into a larger volume, but not by itself contract back again, if the motion of the gas molecules is governed by the reversible Newton's laws of motion?
- Why is there an arrow of time?

# 2 The Enigma

> Those who have talked of “chance” are the inheritors of antique superstition and ignorance...whose minds have never been illuminated by a ray of scientific thought.
> (T. H. Huxley)

These were the questions which confronted scientists in the late 19th century, after the introduction of the concept of entropy by Clausius in 1865, and these showed to be tough questions to answer. After much struggle, agony and debate, the agreement of the physics community has become to view *statistical mechanics* based on an assumption of *molecular chaos* as developed by Boltzmann [1], to offer a rationalization of the classical 2nd Law in the form of a tendency of (isolated) physical processes to move from improbable towards more probable states, or from ordered to less ordered states. Boltzmann’s assumption of molecular chaos in a dilute gas of colliding molecules, is that two molecules about to collide have independent velocities, which led to the *H-theorem* for *Boltzmann’s equations* stating that a certain quantity denoted by $H$ could not decrease and thus could serve as an entropy defining an arrow of time. Increasing disorder would thus represent increasing entropy, and the classical 2nd Law would reflect the eternal pessimistists idea that things always get more messy, and that there is really no limit to this, except when everything is as messy as it can ever get. Of course, experience could give (some) support this idea, but the trouble is that it prevents things from ever becoming less messy or more structured, and thus may seem a bit too pessimistic. No doubt, it would seem to contradict the many observations of *emergence* of ordered non-organic structures (like crystals or waves and cyclons) and organic structures (like DNA and human beings), seemingly out of disordered chaos, as evidenced by the physics Nobel Laureate Robert Laughlin [22].

Most trained thermodynamicists would here say that emergence of order out of chaos, in fact does not contradict the classical 2nd Law, because it concerns “non-isolated systems”. But they would probably insist that the Universe as a whole (isolated system) would steadily evolve towards a “heat-death” with maximal entropy/disorder (and no life), thus fulfilling the pessimists expectation. The question from where the initial order came from, would however be left open.

The standard presentation of thermodynamics based on the 1st and 2nd Laws, thus involves a mixture of deterministic models (Boltzmann’s equations with the H-theorem) based on statistical assumptions (molecular chaos) making the subject admittedly difficult to both learn, teach and apply, despite its strong importance. This is primarily because the question *why* necessarily $dS \geq 0$ and never $dS < 0$, is not given a convincing understandable answer. In fact, statistical mechanics allows $dS < 0$, although it is claimed to be very unlikely. The basic objective of statistical mechanics as the basis of classical thermodynamics, thus is to (i) give the entropy a physical meaning, and (ii) to motivate its tendency to (usually) increase. Before statistical mechanics, the 2nd Law was viewed as an experimental fact, which could not be rationalized theoretically. The classical view on the 2nd Law is thus either as a statistical law of large numbers or as a an experimental fact, both without a rational deterministic mechanistic theoretical foundation. The problem with thermodynamics in this form is that it is understood by very few, if any:

- *Every mathematician knows it is impossible to understand an elementary course in thermodynamics.* (V. Arnold)
- *...no one knows what entropy is, so if you in a debate use this concept, you will always have an advantage.* (von Neumann to Shannon)
- *As anyone who has taken a course in thermodynamics is well aware, the mathematics used in proving Clausius' theorem (the 2nd Law) is of a very special kind, having only the most tenous relation to that known to mathematicians.* (S. Brush [2])
- *Where does irreversibility come from? It does not come form Newton's laws. Obviously there must be some law, some obscure but fundamental equation. perhaps in electricty, maybe in neutrino physics, in which it does matter which way time goes.* (Feynman [10])
- *For three hundred years science has been dominated by a Newtonian paradigm presenting the World either as a sterile mechanical clock or in a state of degeneration and increasing disorder...It has always seemed paradoxical that a theory based on Newtonian mechanics can lead to chaos just because the number of particles is large, and it is subjectivly decided that their precise motion cannot be observed by humans... In the Newtonian world of necessity, there is no arrow of time. Boltzmann found an arrow hidden in Nature's molecular game of roulette.* (Paul Davies [5])
- *The goal of deriving the law of entropy increase from statistical mechanics has so far eluded the deepest thinkers.* (Lieb [23])
- *There are great physicists who have not understood it.* (Einstein about Boltzmann's statistical mechanics)

# 3 Computational Foundation

In this note we present a foundation of thermodynmaics, further elaborated in [14, 18], where the basic assumption of statistical mechanics of molecular chaos, is replaced by *deterministic finite precision computation*, more precisely by a *least squares stabilized finite element method* for the Euler equations, referred to as *Euler General Galerkin* or *EG2*. In the spirit of Dijkstra [6], we thus view EG2 as the physical model of thermodynamics, that is the Euler equations together with a computational solution procedure, and not just the Euler equations without constructive solution procedure as in a classical non-computational approach.

Using EG2 as a model of thermodynamics changes the questions and answers and opens new possibilities of progress together with new challenges to mathematical analysis and computation. The basic new feature is that EG2 solutions are computed and thus are available to inspection. This means that the analysis of solutions shifts from *a priori* to *a posteriori*; after the solution has been computed it can be inspected.

Inspecting computed EG2 solutions we find that they are *turbulent* and have *shocks*, which is identified by pointwise large Euler residuals, reflecting that pointwise solutions to the Euler equations are lacking. The enigma of thermodynamics is thus the enigma of turbulence (since the basic nature of shocks is understood). Computational thermodynamics thus essentially concerns computational turbulence. In this note and [18] we present evidence that EG2 opens to a resolution of the enigma of turbulence and thus of thermodynamics.

The fundamental question concerns *wellposedness* in the sense of Hadamard, that is what aspects or *outputs* of turbulent/shock solutions are stable under perturbations in the sense that small perturbations have small effects. We show that wellposedness of EG2 solutions can be tested a posteriori by computationally solving a *dual linearized problem*, through which the output sensitivity of non-zero Euler residuals can be estimated. We find that mean-value outputs such as drag and lift and total turbulent dissipation are wellposed, while point-values of turbulent flow are not. We can thus a posteriori in a case by case manner, assess the quality of EG2 solutions as solutions of the Euler equations.

We formulate a *2nd Law* for EG2 without the concept of entropy, in terms of the basic physical quantities of kinetic energy $K$, heat energy $E$, rate of *work* $W$ and shock/turbulent dissipation $D > 0$. The new 2nd Law reads

$$\dot{K} = W - D, \quad \dot{E} = -W + D, \tag{1}$$

where the dot indicates time differentiation. Slightly viscous flow always develops turbulence/shocks with $D > 0$, and the 2nd Law thus expresses an irreversible transfer of kinetic energy into heat energy, while the total energy $E + K$ remains constant.

With the 2nd Law in the form (1), we avoid the (difficult) main task of statistical mechanics of specifying the physical significance of entropy and motivating its tendency to increase by probabilistic considerations based on (tricky) combinatorics. Thus using *Ockham's razor* [26], we rationalize a scientific theory of major importance making it both more understandable and more useful. The new 2nd Law is closer to classical Newtonian mechanics than the 2nd Law of statistical mechanics, and thus can be viewed to be more fundamental.

The new 2nd Law is a consequence of the 1st Law in the form of the Euler equations combined with EG2 finite precision computation effectively introducing viscosity and viscous dissipation. These effects appear as a consequence of the non-existence of pointwise solutions to the Euler equations reflecting instablities leading to the development shocks and turbulence in which large scale kinetic energy is transferred to small scale kinetic energy in the form of heat energy. The viscous dissipation can be interpreted as a penalty on pointwise large Euler residuals arising in shocks/turbulence, with the penalty being directly coupled to the violation following a principle of criminal law exposed in [12]. EG2 thus explains the 2nd Law as a consequence of the non-existence of pointwise solutions with small Euler residuals. This offers an understanding to the emergence of irreversible solutions of the formally reversible Euler equations. If pointwise solutions had existed, they would have been reversible without dissipation, but they don't exist, and the existing computational solutions have dissipation and thus are irreversible.

# 4 Viscosity Solutions

An EG2 solution can be viewed as particular *viscosity solution* of the Euler equations, which is a solution of *regularized Euler equations* augmented by additive terms modeling viscosity effects with small viscosity coefficients. The effective viscosity in an EG2 solution typically may be comparable to the mesh size.

For incompressible flow the existence of viscosity solutions, with suitable solution dependent viscosity coefficients, can be proved a priori using standard techniques of analytical mathematics. Viscosity solutions are pointwise solutions of the regularized equations. But already the most basic problem with constant viscosity, the incompressible Navier-Stokes equations for a Newtonian fluid, presents technical difficulties, and is one of the open Clay Millennium Problems.

For compressible flow the technical complications are even more severe, and it is not clear which viscosities would be required for an analytical proof of the existence of viscosity solutions [9] to the Euler equations. Furthermore, the question of wellposedness is typically left out, as in the formulation of the Navier-Stokes Millennium Problem, with the motivation that first the existence problem has to be settled. Altogether, analytical mathematics seems to have little to offer a priori concerning the existence and wellposedness of solutions of the compressible Euler equations. In contrast, EG2 computational solutions of the Euler equations seem to offer a wealth of information a posteriori, in particular concerning wellposedness by duality.

An EG2 solution thus can be viewed as a specific viscosity solution with a specific regularization from the least squares stabilization, in particular of the momentum equation, which is necessary because pointwise momentum balance is impossible to achieve in the presence of shocks/turbulence. The EG2 viscosity can be viewed to be the minimal viscosity required to handle the contradiction behind the non-existence of pointwise solutions. For a shock EG2 could then be directly interpreted as a certain physical mechanism preventing a shock wave from turning over, and for turbulence as a form of automatic computational turbulence model.

EG2 thermodynamics can be viewed as form of deterministic chaos, where the mechanism is open to inspection and can be used for prediction. On the other hand, the mechanism of statistical mechanics is not open to inspection and can only be based on ad hoc assumption, as noted by e.g. Einstein [8]. If Boltzmann's assumption of molecular chaos cannot be justified, and is not needed, why consider it at all, [24]?

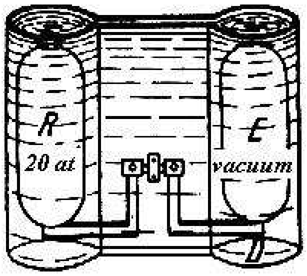

**Fig. 358 Concerning overflowing experiment of Joule (Scientific Papers). *R* contains at first air compressed to 20 atm, *E* is initially a vacuum, *D* the tube**

Figure 1: Joule's 1845 experiment

# 5 Joule’s 1845 Experiment

To illustrate basic aspects of thermodynamics, we recall Joule’s experiment from 1845 with a gas initially at rest with temperature $T = 1$ at a certain pressure in a certain volume immersed into a container of water, see Fig. 1. At initial time a valve was opened and the gas was allowed to expand into the double volume while the temperature change in the water was carefully measured by Joule. To the great surprise of both Joule and the scientific community, no change of the temperature of the water could be detected, in contradiction with the expectation that the gas would cool off under expansion. Moreover, the expansion was impossible to reverse; the gas had no inclination to contract back to the original volume. Simulating Joule’s experiment using EG2, we discover the following as displayed in Fig. 2-7

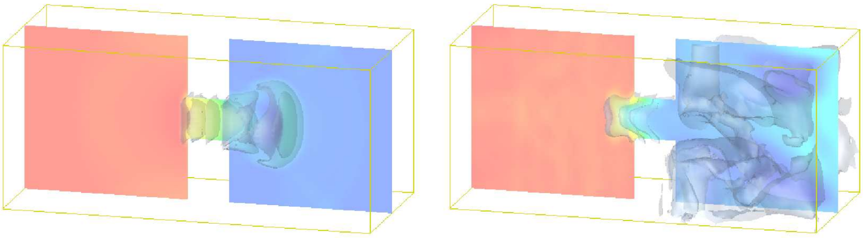

Figure 2: Density at two time instants

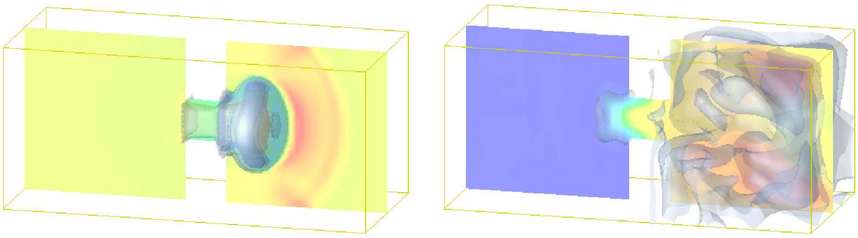

Figure 3: Temperature at two time instants

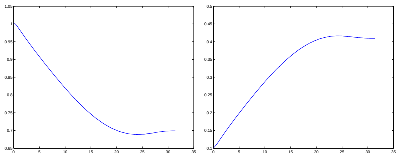

Figure 4: Average density in left and right chamber

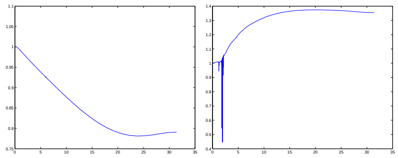

Figure 5: Average temperature in left and right chamber

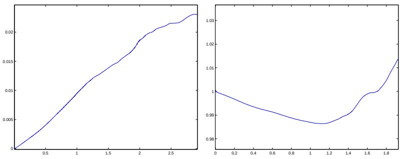

Figure 6: Average kinetic energy and temperature: short time

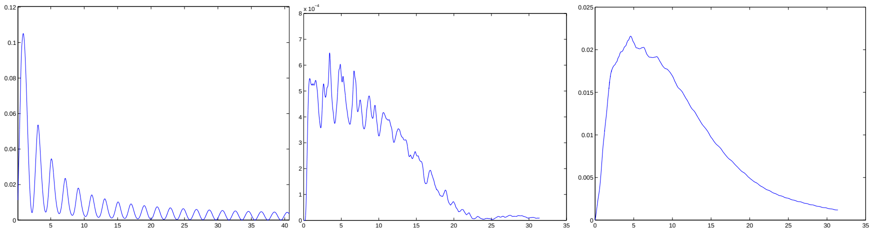

Figure 7: Average kinetic energy in both, left and right chamber(s): long time

In a first phase the temperature drops below 1 as the gas expands with increasing velocity, and in a second phase shocks/turbulence appear and heat the gas towards a final state with the gas at rest in the double volume and the temperature back to $T = 1$. The total (heat) energy is, of course, conserved since the density is reduced by a factor 2 after expansion to double volume. We can also understand that the rapidity of the expansion process makes it difficult to detect any temperature drop in the water in the inital phase. Altogether, using EG2 we can first simulate and then understand Joule's experiment, and we thus see no reason to be surprised. We shall see below as a consequence of the 2nd Law that reversal of the process with the gas contracting back to the original small volume, is impossible because the only way the gas can be put into motion is by expansion, and thus contraction is impossible.

In statistical mechanics the dynamics of the process would be dismissed and only the initial and final state would be subject to analysis. The final state would then be viewed as being "less ordered" or "more probable" or having "higher entropy", because the gas would occupy a larger volume, and the reverse process with the gas contracting back to the initial small volume, if not completely impossible, would be "improbable". But to say that a probable state is is more probable than an improbable state is more mystifying than informative. Taking the true dynamics of the process into account including in particular the second phase with heat generation from shocks or turbulence, we can understand the observation of constant temperature and irreversibility in a deterministic fashion without using any mystics of entropy based on mystics of statistics. In [13] we develop a variety of aspects of the arrow of time enforced by the new 2nd Law.

# 6 The Euler Equations

We consider the Euler equations for an inviscid perfect gas enclosed in a volume $\Omega$ in $\mathbb{R}^3$ with boundary $\Gamma$ over a time interval $I = (0, 1]$ expressing conservation of *mass density* $\rho$, *momentum* $m = (m_1, m_2, m_3)$ and *internal energy* $e$: Find $\hat{u} = (\rho, m, e)$ depending on $(x, t) \in Q \equiv \Omega \times I$ such that

$$\begin{array}{rcll} R_\rho(\hat{u}) \equiv \dot{\rho} + \nabla \cdot (\rho u) & = & 0 & \text{in } Q, \\ R_m(\hat{u}) \equiv \dot{m} + \nabla \cdot (mu + p) & = & f & \text{in } Q, \\ R_e(\hat{u}) \equiv \dot{e} + \nabla \cdot (eu) + p\nabla \cdot u & = & g & \text{in } Q, \\ u \cdot n & = & 0 & \text{on } \Gamma \times I \\ \hat{u}(\cdot, 0) & = & \hat{u}^0 & \text{in } \Omega, \end{array} \tag{2}$$

where $u = \frac{m}{\rho}$ is the velocity, $p = (\gamma - 1)e$ with $\gamma > 1$ a *gas constant*, $f$ is a given volume force, $g$ a heat source/sink and $\hat{u}^0$ a given initial state. We here express energy conservation in terms of the internal energy $e = \rho T$, with $T$ the temperature, and not as conservation of the *total energy* $\epsilon = e + k$ with $k = \frac{\rho v^2}{2}$ the *kinetic energy*, in the form $\dot{\epsilon} + \nabla \cdot (\epsilon u) = 0$. Because of the appearance of shocks/turbulence, the Euler equations lack pointwise solutions, except possible for short time, and regularization is therefore necessary. For a mono-atomic gas $\gamma = 5/3$ and (2) then is a *parameter-free model*, the ideal form of mathematical model according to Einstein...

# 7 Energy Estimates for Viscosity Solutions

For the discussion we consider the following regularized version of (2) assuming for simplicity that $f = 0$ and $g = 0$: Find $\hat{u}_{\nu,\mu} \equiv \hat{u} = (\rho, m, e)$ such that

$$\begin{array}{rcl} R_\rho(\hat{u}) & = & 0 \quad \text{in } Q, \\ R_m(\hat{u}) & = & -\nabla \cdot (\nu \nabla u) + \nabla(\mu p \nabla \cdot u) \quad \text{in } Q, \\ R_e(\hat{u}) & = & \nu |\nabla u|^2 \quad \text{in } Q, \\ u & = & 0 \qquad \text{on } \Gamma \times I, \\ \hat{u}(\cdot, 0) & = & \hat{u}^0 \quad \text{in } \Omega, \end{array} \tag{3}$$

where $\nu > 0$ is a *shear viscocity* $\mu >> \nu \geq 0$ if $\nabla \cdot u > 0$ in expansion (with $\mu = 0$ if $\nabla \cdot u \leq 0$ in compression), is a small *bulk viscosity*, and we use the notation $|\nabla u|^2 = \sum_i |\nabla u_i|^2$. We shall see that the bulk viscosity is a safety feature putting a limit to the work $p\nabla \cdot u$ in expansion appearing in the energy balance.

We note that only the momentum equation is subject to viscous regulariztion. Further, we note that the shear viscosity term in the momentum equation multiplied by the velocity $u$ (and formally integrated by parts) appears as a positive right hand side in the equation for the internal energy, reflecting that the dissipation from shear viscosity is transformed into internal heat energy. In contrast, the dissipation from the bulk viscosity represents another form of internal energy not accounted for as heat energy, acting only as a safety feature in the sense that its contribution to the energy balance in general will be small, while that from the shear viscosity in general will be substantial reflecting shock/turbulent dissipation.

Below we will consider instead regularization by EG2 with the advantage that the EG2 solution is computed and thus is available to inspection, while $\hat{u}_{\nu,\mu}$ is not. We shall see that EG2 regularization can be interpreted as a (mesh-dependent) combination of bulk and shear viscosity and thus (3) can be viewed as an analytical model of EG2 open to simple form of analysis in the form of energy estimates.

As indicated, the existence of a pointwise solution $\hat{u} = \hat{u}_{\nu,\mu}$ to the regularized equations (3) is an open problem of analytical mathematics, although with suitable additional regularization it could be possible to settle [9]. Fortunately, we can leave this problem aside, since EG2 solutions will be shown to exist a posteriori by computation. We thus formally assume that (3) admits a pointwise solution, and derive basic energy estimates which will be paralleled below for EG2. We thus use the regularized problem (3) to illustrate basic features of EG2, including the 2nd Law.

We shall prove now that a regularized solution $\hat{u}$ is an approximate solution of the Euler equations in the sense that $R_\rho(\hat{u}) = 0$ and $R_e(\hat{u}) \geq 0$ pointwise, $R_m(\hat{u})$ is weakly small in the sense that

$$\|R_m(\hat{u})\|_{-1} \leq \frac{\sqrt{\nu}}{\sqrt{\mu}} + \sqrt{\mu} << 1, \tag{4}$$

where $\|\cdot\|_{-1}$ denotes the $L_2(I; H^{-1}(\Omega))$-norm, and the following 2nd Law holds:

$$\dot{K} \leq W - D, \quad \dot{E} = -W + D, \tag{5}$$

where

$$K=\int_\Omega k\,dx,\quad E=\int_\Omega e\,dx,\quad W=\int_\Omega p\nabla\cdot u\,dx,\quad D=\int_\Omega \nu|\nabla u|^2\,dx.$$

Choosing $\nu << \mu$ we can assure that $\|R_m(\hat{u}_{\nu,\mu})\|_{-1}$ is small. We can view the 2nd Law as a compensation for the fact that the momentum equation is only satisfied in a weak sense, and the equation for internal energy with inequality.

The 2nd Law (5) states an irreversible transfer of kinetic energy to heat energy in the presence of shocks/turbulence with $D>0$, which is the generic case. On the other hand, the sign of $W$ is variable and thus the corresponding energy transfer may go in either direction.

The basic technical step is to multiply the momentum equation by $u$, and use the mass balance equation in the form $\frac{|u|^2}{2}(\dot{\rho}+\nabla\cdot(\rho u))=0$, to get

$$\dot{k}+\nabla\cdot(ku)+p\nabla\cdot u-\nabla(\mu p\nabla\cdot u)\cdot u-\nabla\cdot(\nu\nabla u)\cdot u=0. \tag{6}$$

By integration in space it follows that $\dot{K}\leq W-D$, and similarly it follows that $\dot{E}=-W+D$ from the equation for $e$, which proves the 2nd Law. Adding next (6) to the equation for the internal energy $e$ and integrating in space, gives

$$\dot{K}+\dot{E}+\int_\Omega \mu p(\nabla\cdot u)^2\,dx=0,$$

and thus after integration in time

$$K(1)+E(1)+\int_Q \mu p(\nabla\cdot u)^2\,dxdt=K(0)+E(0). \tag{7}$$

We now need to show that $E(1)\geq 0$ (or more generally that $E(t)>0$ for $t\in I$), and to this end we rewrite the equation for the internal energy as follows:

$$D_ue+\gamma e\nabla\cdot u=\nu|\nabla u|^2,$$

where $D_ue=\dot{e}+u\cdot\nabla e$ is the material derivative of $e$ following the fluid particles with velocity $u$. Assuming that $e(x,0)>0$ for $x\in\Omega$, it follows that $e(x,1)>0$ for $x\in\Omega$, and thus $E(1)>0$. Assuming $K(0)+E(0)=1$ the energy estimate (7) thus shows that

$$\int_Q \mu p(\nabla\cdot u)^2\,dxdt\leq 1, \tag{8}$$

and also that $E(t)\leq 1$ for $t\in I$. Next, integrating (6) in space and time gives, assuming for simplicity that $K(0)=0$,

$$K(1)+\int_Q \nu(\Delta u)^2dxdt=\int_Q p\nabla\cdot udxdt-\int_Q \mu p(\nabla\cdot u)^2dxdt\leq\frac{1}{\mu}\int_Q pdxdt\leq\frac{1}{\mu},$$

where we used that $\int_Q pdxdt=(\gamma-1)\int_Q edxdt\leq\int_I E(t)dt\leq 1$. It follows that

$$\int_Q \nu|\nabla u|^2dxdt\leq\frac{1}{\mu}. \tag{9}$$

By standard estimation (assuming that $p$ is bounded), it follows from (8) and (9) that

$$\|R_m(\hat{u})\|_{-1} \leq C(\sqrt{\mu} + \frac{\sqrt{\nu}}{\sqrt{\mu}}),$$

with $C$ a constant of moderate size, which completes the proof. As indicated, $\|R_m(\hat{u})\|_{-1}$ is estimated by computation, as shown below. The role of the analysis is thus to rationalize computational experience, not to replace it.

## 8 Compression and Expansion

The 2nd Law (5) states that there is a transfer of kinetic energy to heat energy if $W < 0$, that is under compression with $\nabla \cdot u < 0$, and a transfer from heat to kinetic energy if $W > 0$, that is under expansion with $\nabla \cdot u > 0$. Returning to Joule's experiment, we see by the 2nd Law that contraction back to the original volume from the final rest state in the double volume, is impossible, because the only way the gas can be set into motion is by expansion. To see this no reference to entropy is needed.

## 9 A 2nd Law witout Entropy

We note that the 2nd Law (5) is expressed in terms of the physical quantities of kinetic energy $K$, heat energy $E$, work $W$, and dissipation $D$ and does not involve any concept of entropy. This relieves us from the task of finding a physical significance of entropy and justification of a classical 2nd Law stating that entropy cannot decrease. We thus circumvent the main difficulty of classical thermodynamics based on statistical mechanics, while we reach the same goal as statistical mechanics of explaining irreversibility in formally reversible Newtonian mechanics.

We thus resolve *Loschmidt's paradox* [24] asking how irreversibility can occur in a formally reversible system, which Boltzmann attempted to solve. But Loschmidt pointed out that Boltzmann's equations are not formally reversible, because of the assumption of molecular chaos that velocities are independent before collision, and thus Boltzmann effectively assumes what is to be proved. Boltzmann and Loschmidt's met in heated debates without conclusion, but after Boltzmann's tragic death followed by the experimental verification of the molecular nature of gases, Loschmidt's paradox evaporated as if it had been resolved, while it had not. Postulating molecular chaos still amounts to assume what is to be proved.

## 10 Comparison with Classical Thermodynamics

Classical thermodynamics is based on the relation

$$Tds = dT + pdv, \tag{10}$$

where $ds$ represents change of entropy $s$ per unit mass, $dv$ change of volume and $dT$ denotes the change of temperature $T$ per unit mass, combined with a 2nd Law in the form $ds \geq 0$. On the other hand, the new 2nd Law takes the symbolic form

$$dT + pdv \geq 0, \tag{11}$$

effectively expressing that $Tds \geq 0$, which is the same as $ds \geq 0$ since $T > 0$. In symbolic form the new 2nd Law thus expresses the same as the classical 2nd Law, without referring to entropy.

Integrating the classical 2nd Law (10) for a perfect gas with $p = (\gamma - 1)\rho T$ and $dv = d(\frac{1}{\rho}) = -\frac{d\rho}{\rho^2}$, we get

$$ds = \frac{dT}{T} + \frac{p}{T}d(\frac{1}{\rho}) = \frac{dT}{T} + (1-\gamma)\frac{d\rho}{\rho},$$

and we conclude that with $e = \rho T$,

$$s = \log(T\rho^{1-\gamma}) = \log(\frac{e}{\rho^\gamma}) = \log(e) - \gamma\log(\rho) \tag{12}$$

up to a constant. Thus, the entropy $s = s(\rho, e)$ for a perfect gas is a function of the physical quantities $\rho$ and $e = \rho T$, thus a *state function*, suggesting that $s$ might have a physical significance, because $\rho$ and $e$ have. We thus may decide to introduce a quantity $s$ defined this way, but the basic questions remains: (i) What is the physical significance of $s$? (ii) Why is $ds \geq 0$? What is the entropy non-perfect gas in which case $s$ may not be a state function?

To further exhibit the connection between the classical and new forms of the 2nd Law, we observe that by the chain rule,

$$\rho D_u s = \frac{\rho}{e}D_u e - \gamma D_u \rho = \frac{1}{T}(D_u e + \gamma\rho T\nabla\cdot u) = \frac{1}{T}(D_u e + e\nabla\cdot u + (\gamma-1)\rho T\nabla\cdot u)$$

since by mass conservation $D_u\rho = -\rho\nabla\cdot u$. It follows that the entropy $S = \rho s$ satisfies

$$\dot{S} + \nabla\cdot(Su) = \rho D_u s = \frac{1}{T}(\dot{e} + \nabla\cdot(eu) + p\nabla\cdot u) = \frac{1}{T}R_e(\hat{u}). \tag{13}$$

A solution $\hat{u}$ of the regularized Euler equations (3) thus satisfies

$$\dot{S} + \nabla\cdot(Su) = \frac{\nu}{T}|\nabla u|^2 \geq 0 \quad \text{in } Q, \tag{14}$$

where $S = \rho\log(e\rho^{-\gamma})$. In particular, in the case of the Joule experiment with $T$ the same in the initial and final states, we have $s = \gamma\log(V)$ showing an increase of entropy in the final state with larger volume.

We sum up by noting that the classical and new form of the second law effectively express the same inequality $ds \geq 0$ or $Tds \geq 0$. The new 2nd law is expressed in terms of the fundamental concepts of of kinetic energy, heat energy and work without resort to any form of entropy and statistical mechanics with all its complications. Of course, the new 2nd Law readily extends to the case of a general gas.

# 11 EG2

EG2 in cG(1)cG(1)-form for the Euler equations (2), reads: Find $\hat{u} = (\rho, m, \epsilon) \in V_h$ such that for all $(\bar{\rho}, \bar{u}, \bar{\epsilon}) \in W_h$

$$\begin{aligned} ((R_\rho(\hat{u}), \bar{\rho})) + ((hu \cdot \nabla \rho, u \cdot \nabla \bar{\rho})) &= 0, \\ ((R_m(\hat{u}), \bar{u})) + ((hu \cdot \nabla m, u \cdot \nabla \bar{u})) + (\nu_{sc} \nabla u, \nabla \bar{u})) &= 0, \\ ((R_\epsilon(\hat{u}), \bar{e})) + ((hu \cdot \nabla \epsilon, u \cdot \nabla \bar{\epsilon})) &= 0, \end{aligned} \tag{15}$$

where $V_h$ is a trial space of continuous piecewise linear functions on a space-time mesh of size $h$ satisfying the initial condition $\hat{u}(0) = \hat{u}^0$ with $u \in V_h$ defined by nodal interpolation of $\frac{m}{\rho}$, and $W_h$ is a corresponding test space of function which are continuous piecewise linear in space and piecewise constant in time, all functions satisfying the boundary condition $u \cdot n = 0$ at the nodes on $\Gamma$. Further, $((\cdot, \cdot))$ denotes relevant $L_2(Q)$ scalar products, and $\nu_{sc} = h^2 |R_m(\hat{u})|$ is a residual dependent *shock-capturing viscosity*, see [18]. We here use the conservation equation for the total energy $\epsilon$ rather than for the internal energy $e$.

EG2 combines a weak satisfaction of the Euler equations with a weighted least squares control of the residual $R(\hat{u}) \equiv (R_\rho(\hat{u}), R_m(\hat{u}), R_e(\hat{u}))$ and thus represents a midway between the Scylla of weak solution and Carybdis of least squares strong solution.

# 12 The 2nd Law for EG2

Subtracting the mass equation with $\bar{\rho}$ a nodal interpolant of $\frac{|u|^2}{2}$ from the momentum equation with $\bar{u} = u$ and using the heat energy equation with $\bar{e} = 1$, we obtain the following 2nd Law for EG2 (up to a $\sqrt{h}$-correction controled by the shockcapturing viscosity [20]):

$$\dot{K} = W - D_h, \quad \dot{E} = -W + D_h, \tag{16}$$

where

$$D_h = ((h\rho u \cdot \nabla u, u \cdot \nabla u)). \tag{17}$$

For solutions with turbulence/shocks, $D_h > 0$ expressing an irreversible transfer of kinetic energy into heat energy, just as above for regularized solutions. We note that in EG2 only the momentum equation is subject to viscous regularization, since $D_h$ expresses a penalty on $u \cdot \nabla u$ appearing in the momentum residual.

# 13 The Stabilization in EG2

The stabilization in EG2 is expressed by the dissipative term $D_h$ which can be viewed as a weighted least squares control of the term $\rho u \cdot \nabla u$ in the momentum residual. The rationale is that least squares control of a part of a residual which is large, effectively may give control of the entire residual, and thus EG2 gives a least squares control of the momentum residual. But the EG2 stabilization does not correspond to an ad hoc viscosity, as in classical regularization, but to a form of penalty arsing because

Euler residuals of turbulent/shock solutions are not pointwise small. In particular the dissipative mecahnism of EG2 does not correspond to a simple shear viscosity, but rather to a form of "streamline viscosity" preventing fluid particles from colliding while allowing strong shear.

## 14 Output Uniqueness and Stability

Defining a mean-value output in the form of a space-time integral $((\hat{u},\psi))$ defined by a smooth weight function $\psi$, we obtain by duality-based error estimation as in [17] an a posteriori error estimate of the form

$$|((\hat{u},\psi))-((\hat{w},\psi))|\leq S(\|R(\hat{u})\|_{-1}+(\|R(\hat{w})\|_{-1})\leq S(\|hR(\hat{u})\|_0+(\|hR(\hat{w})\|_0),$$

where $\hat{u}$ and $\hat{w}$ are two EG2 solutions on meshes of meshsize $h$, $S=S(\hat{u},\hat{w})$ is a stablity factor defined as the $H^1(Q)$-norm of a solution to a linearized dual problem with coedd with the data $\psi$ and $\|\cdot\|_0$ is the $L_2(Q)$-norm. An output $((\hat{u},\hat{\psi}))$ is *wellposed* if $S\|hR(\hat{u})\|_0\leq TOL$ with $S=S(\hat{u},\hat{u}))$ and $TOL$ a small tolerance $TOL$ of interest.

In the case shocks/turbulence $\|R(\hat{u})\|_0$ will be large $\sim h^{-1/2}$, while $\|hR(\hat{u})\|_0$ may be small $\sim h^{1/2}$, and an output thus is wellposed if $S<<h^{-1/2}$. In [18] we present computed stability factors for different weights $\hat{\psi}$, with global support corresponding to global mean-value outputs and local support to pointwise outputs. We find that global mean-values of turbulent flow are wellposed, but local not.

## 15 Reactive Flow

We now generalize the Euler equations (18) to a *mixture* of $N$ gas species, undergoing $M$ chemical reactions: We seek the *species densities* $\rho_1,...,\rho_N$, the *mixture momentum* $m=\rho u$ with $u=(u_1,u_2,u_3)$ the *mixture velocity* and $\rho=\sum_i\rho_i$ the *mixture density*, and the *mixture internal energy* $e$ satisfying

$$\begin{array}{rcll}\dot{\rho}_i+\nabla\cdot(\rho_i u)&=&s_i, & \text{in } Q,\quad i=1,...,N,\\ \dot{m}+\nabla\cdot(mu)+\nabla p&=&f & \text{in } Q,\\ \dot{e}+\nabla\cdot(eu)+p\nabla\cdot u&=&\sum_i s_i r_i & \text{in } Q,\\ u\cdot n&=&0 & \text{on } \Gamma\times I,\\ \hat{u}(\cdot,0)&=&\hat{u}^0 & \text{in } \Omega,\end{array}\tag{18}$$

where $s_i$ is the net reaction rate of species $i$ from all the reactions, and we assume the following constitutive relations

$$e=\sum_{i=1}^N\rho_i r_i+\rho T$$

with $T$ the *mixture temperature* and $r_i$ the *heat of formation* of species $i$, together with a *mixture pressure* $p$ given as the sum of the partial pressures from the different species:

$$p=CT\sum_i\frac{\rho_i}{W_i}.$$

where $W_i$ is the molecular weight of species $i$ and $C$ a positive constant. Evidently, we assume here that the species velocities are all equal to the mixture velocity and that all species take on the mixture temperature. We assume that the reaction rate $s_i$ of species $i$ is given by an *Arrhenius law*. The new 2nd Law takes the follwoing form in the present case:

$$\dot{K} = W - D, \tag{19}$$

$$\dot{E} = -W + D + \sum_i s_i r_i, \tag{20}$$

where $D > 0$ is the turbulent dissipation, and The 2nd Law shows irreversibility of turbulent mixing and heating, while the chemical reactions as such, are reversible.

## 16 Dual Linearized Problem

The Euler equations in the variables $\hat{u} = (\rho, u, e)$ take the following form, using that $p = (\gamma - 1)e$,

$$\begin{array}{rcl} \dot{\rho} + \nabla \cdot (\rho u) &=& 0 \quad \text{in } Q, \\ \dot{\rho} u + \rho \dot{u} + \nabla \cdot (\rho u u) + (\gamma - 1)\nabla e &=& f \quad \text{in } Q, \\ \dot{e} + \nabla \cdot (e u) + (\gamma - 1) e \nabla \cdot u &=& g \quad \text{in } Q, \\ u \cdot n &=& 0 \quad \text{on } \Gamma \times I \\ \hat{u}(\cdot, 0) &=& \hat{u}^0 \quad \text{in } \Omega. \end{array} \tag{21}$$

The corresponding dual linearized problem in the variables $\hat{\varphi} = (\rho_d, \varphi, e_d)$ with $\varphi = (\varphi_1, \varphi_2, \varphi_3)$, takes the form

$$\begin{array}{rcl} -\dot{\rho}_d - u \cdot \nabla \rho_d - u \cdot \dot{\varphi} - \sum_i u_i u \cdot \nabla \varphi_i &=& -\psi_\rho, \\ -\rho \dot{\varphi} - \rho u \cdot \nabla \varphi - \rho \nabla \rho_d - e \nabla e_d - (\gamma - 1)\nabla(e e_d) - \rho \sum_i u_i \nabla \varphi_i &=& -\rho \psi, \\ -\dot{e}_d - u \cdot \nabla e_d + (\gamma - 1)\nabla \cdot u e_d - (\gamma - 1)\nabla \cdot \varphi &=& -\psi_e, \end{array} \tag{22}$$

in $Q$, with data $\hat{\psi} = (\psi_\rho, \psi, \psi_e)$ depending on the output. Eliminating $\dot{\varphi}$ from the first equation using the second we obtain the following dual linear convection-reaction initial value problem linearized at $\hat{u}$: Find $\hat{\varphi}$ such that in $Q$

$$\begin{array}{rcl} \dot{\rho}_d + \sum_j u \cdot \nabla \varphi_j u_j + \frac{e}{\rho} u \cdot \nabla e_d + \frac{\gamma - 1}{\rho} u \cdot \nabla(e e_d) &=& \psi_\rho + u \cdot \psi, \\ \dot{\varphi} + u \cdot \nabla \varphi + \sum_i u_i \nabla \varphi_i + \nabla \rho_d + \frac{e}{\rho} \nabla e_d + \frac{\gamma - 1}{\rho} \nabla(e e_d) &=& \psi, \\ \dot{e}_d + u \cdot \nabla e_d - (\gamma - 1)\nabla \cdot u e_d + (\gamma - 1)\nabla \cdot \varphi &=& \psi_e, \end{array} \tag{23}$$

with $\hat{\varphi}(\cdot, 0) = 0 \quad \text{in } \Omega$. Note that since $u \cdot n = 0$, no boundary conditions on $\hat{\varphi}$ are needed.

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